EFFECTS OF ALLOYING ELEMENTS ON TWINNING IN ALPHA-TITANIUM ALLOYS

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DECLARATION

Part of the work has been submitted previously as final reports of undergraduate projects in the University of Manchester, in the Faculty of Engineering & Physical Science. Parts of the metallographic preparations and material characterization, such as grain size and texture determination, was accomplished under my supervision and constant assistance within the following undergraduate projects:

- "Effect of Aluminium on Quasi Static Compression Behaviour of Cross-rolled A Titanium" by Liyi Zhang
- "Effect of tin and zirconium on Twinning in A Titanium" by Yinze Ji,
- "Effect of Zirconium on deformation behaviour in α Titanium" by Luqmaan Fazal
- "Effect of Tin on Deformation Behaviour in α Titanium" by Yinze Ji.
- "Strain Localisation in Titanium Aluminium Binary Alloys" by Albert Duncan Smith
- "Nanoindentation: A Tool For Studying Plasticity" by Ben Gardener
- "The effect of AI on the strength and anisotropy of α -Ti" by Jack Palmer

It should be emphasized that all work undertaken in the named projects was carried out with the intention to contribute to the present dissertation. My supervision ensured high quality and comparability of the data and also a good experience for the undergraduate students. Work of other authors has been referenced accordingly.

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Abstract

Effects of Alloying Elements on twinning in α-titanium alloys

Abstract of a thesis submitted by Arnas Gerald Fitzner to the School of Materials in the University of Manchester for the Degree of Doctor of Philosophy on the 31st December 2014.

It has been found that commercially pure (CP) Titanium (Ti) undergoes substantial amount of deformation twinning during plastic forming in a wide range of temperatures and strain rates giving CP-Ti good ductility and allowing up to 90% thickness reduction by cold rolling. Aluminium (AI) rich α Ti-alloys lack this superior ductility but exhibit therefore up to five times higher yield strength, which was connected experimentally to reduced activity of deformation twinning with addition of AI to Ti. Ultimately this is also valid in the α phase of two-phase alloys such as Ti6Al4V and thought to be key to the reduced ductility in AI rich alloys. It is to date unclear if ordering of AI in the Ti matrix, a change in the stacking fault energy (SFE) with alloying or a transition of the cellular dislocation structures in CP-Ti to planar slip patterns at high Al contents reduces twin activity. The focus of this dissertation project is therefore the transition of microstructural details and the deformation structures in the α phase with increasing AI concentration. For simplified investigations binary Ti-AI alloys containing 3.5, 7, 10 and 13at.% Al have been created with comparable grain morphology and texture within this study. For a better understanding of the role of Al also binary Ti-Sn (Tin) alloys (1 & 3.4at.% Sn) and Ti-Zr (Zirconium) alloys (3.6 & 10at.%) as well as an Oxygen (O) rich Ti-10at.%Al and the industrial compositions of Ti6Al4V were produced on the same route and investigated by the same methods. This alloy range allows evaluation of the effects of the c/a ratio, ordering phenomena and the SFE on the twin activity. The knowledge was finally transferred to industrially forged CP-Ti and Ti5Al2.5Sn. TEM and neutron diffraction confirmed the onset of Ti₃Al formation from AI concentrations above 7at.% (4wt%), but no ordering of Zr or Sn atoms was found after solution treatments. The evolution of lattice strain and lattice reorientation due to twinning with increasing compressive strain was captured by in-situ experiments under neutron diffraction at Engin-X, ISIS. Post-mortem EBSD micro and macro texture mappings revealed that the twin fraction in Al reduces above a critical concentration of 7at.% (4wt%), which was enhanced with increasing ordering towards Ti₃Al. Sn and Zr addition showed no significant effect on the overall twin fraction, but increased twin numbers with facilitated nucleation and impeded twin growth, which may be related to the SFE. Increasing slip planarity and a transition from prismatic slip towards basal slip with addition of AI was found with means of Digital image correlation (DIC). DIC also revealed intense prismatic slip in grains undergoing $\{10\overline{1}2\}$ tension twinning and virtually barely any strain accumulation within a twin below 9% plastic strain, rationalised by much increased nanohardness in the twin in comparison to the parent. Nanoindentation also revealed that alloying with Al reduces the crystal anisotropy. Finally it is believed that ordering and the closely related transition of slip patterns lead to the reduction in twin activity, while c/a ratio, crystal anisotropy and SFE seem less important.

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THANK YOU ALL!!

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Dedication

This work is dedicated to my daughter Emilia Fitzner Camean.

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1. Introduction

For more than 50 years titanium alloys have been an integral feature of high performance engineering applications. During this time a variety of methods for processing titanium alloys has been developed as well as an understanding of the mechanical response to a wide range of operating conditions [Bache 2001, Leyens 2003]. Motivaton is the growing areospace sector with the highest global energy consumption. Saving weight in a rotated or translated construction directly saves energy, emissions of for instance CO₂ and natural resources in general [Helms 2006]. Titanium has an outstanding strength to weight ratio, good corrosion resistance and good temperature resistance, which makes it ideal for a wide range of high-end applications in the aerospace sector but also for chemical applications [Levens 2003, Taylor 2008]. Titanium's biocompatibility also makes it useful for medical applications. Further applications are placed in the leisure industry. Apart from the good mechanical and chemical properties, the recyclability to nearly 100% is an additional reason for the commercial success of Titanium. Furthermore Titanium is the fourth most common metal and the ninth most common element on earth, with reserves of approximately 650 billion tonnes of Titanium oxide [Leyens 2003]. Rutile (TiO₂) and Ilmenite (FeTiO₃) are the main oxides used for Titanium production. After pre-cleaning and enrichment, the ores are reduced during the extended Kroll process into a metallic Ti-sponge. This Ti-sponge can be used for alloying other materials or as a base for Ti-alloys. Together with other alloying elements, recycled material or pre-alloys, the compacted sponge is welded to electrodes and subsequently melted in a vacuum arc furnace to form an ingot. The chemical composition of the alloy greatly influences the formability of the ingot and its properties. The most widely used alloy nowadays is the α - β alloy Ti-64 (Ti-6AI-4V), but the service temperature is limited to 315°C [Leyens 2003]. Recent developments extend the applications of Ti-alloys, such as Ti-834 (Ti-5.8AI-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C), Ti6242 (Ti-6Al-2Sn-4Zr-2Mo) or Ti6246 (Ti-6Al-2Sn-4Zr-6Mo) are used for the compressor section of a jet engine up to temperatures of 540°C [Leyens 2003, Heckel 2006, Cernik 2010]. Ti 685 (Ti-6AI-5Zr-0.5Mo-0.2Si) shows only moderate strength but excellent creep and fatigue properties up to 550°C and is therefore used in critical aerospace components like discs or shafts [Krishna 1997]. Near α alloys like Ti5Al2.5Sn are also used for cryogenic applications [Nagai 1986]. All these alloys exhibit different α - β phase fractions and microstructures and require specific forming routes on the way to the final product shape. The shape of the final product is limited by the formability, while its properties are dictated by the composition, but also by microstructure and texture, as described in the literature review (chapter 3). Strong textures develop during thermo-mechanical treatments and introduce a mechanical anisotropy in the material, which needs to be considered in optimised lightweight constructions [Leyens 2003, Gebhardt 2003]. One key parameter for the development of textures and anisotropy is deformation twinning. Especially during forming of pure Titanium, twinning alters the texture and work hardening behaviour dramatically until intermediate thickness reductions of ~40% [Chun 2005, Salem 2006, Zherebtsov 2011]. The grain refinement due to twin boundaries and the Arnas Fitzner, PhD Thesis, 2014

crystal reorientation by tension twinning generally hardens the material, while compression twinning results in texture softening of the material [Salem 2006]. The formation of primary as well as secondary and tertiary twins accommodates substantial plastic strain during forming of CP-Ti until deformation by slip dominates the work hardening behaviour at thickness reductions above ~40%, up to 90% [Philippe 1988, Chun 2005]. Furthermore twins induced by surface treatments like shot peening or machining can be thought as an initator for cracks in fatigue load and accelerate oxygen absorption at elevated temperatures [Thomas 2009].

In order to design lightweight products with most appropriate composition for a particular application and suitable mechanical anisotropy, it is important to understand how twinning and slip change the properties during forming. The literature review does not focus on previous attempts to establish dependencies of the mechanical behaviour on parameters like temperature, strain rate and grain size but focuses on the chemistry and discovered changes in the relative activity of different deformation modes [Okazaki 1973, Sakai 1974, Lederich 1978, Nemat-Nasser 1999, Williams 2002, Li 2013]. For instance, the most widely used commercial alloy Ti6Al4V shows significantly less twin activity than CP-Ti [Yapici 2006, Prakash 2010]. It was shown on single crystals that Aluminium addition to CP-Ti changes the relative activity of basal and prismatic slip and supresses twinning [Sakai 1974, Williams 2002], which can be connected to ductility loss in polycrystalline material [Truax 1974]. To date, it remains unclear how the different twin types are formed and why twinning becomes supressed in Ti alloys like Ti-64, even though multiple theories on twin nucleation, propagation and thickening have been developed on hexagonal materials [Yoo 1981, Christian 1995, Beyerlein 2010]. The lack of understanding of twin formation makes it difficult to comprehend why twinning is supressed at AI concentrations of around 10at.% (6wt%) in present high strength Ti alloys. Understanding mechanisms, which impede twin formation, may be one of the keys to the improvement of ductility and formability of high strength Ti-alloys containing Al.

Therefore, binary model α-alloys with comparable microstructures and textures have been manufactured to investigate effects of alloying elements on twin formation and activity, as described in chapter 4. Chapter 5 gives a general overview of the approached alloys and summarises possibilities of direct comparisons, mostly independent from the grain size and texture. Al, as most efficient substitutional strengthening element, is the focus of the study (chapter 6, 7 and 8), but also the commonly used substitutionals Tin (Sn) and Zirconium (Zr) are considered for a better understanding of the role of Al in the chapters 9 and 10. Also, the effect of the interstitial element oxygen on twinning in a Ti-Al alloy is captured in chapter 11. Chapter 4 explains experimental procedures, like the use of Electron backscattered diffraction (EBSD) and energy dispersive spectroscopy (EDS) to characterise microstructure and texture of annealed alloys and after deformation in detail. Selected area transmission electron diffraction and neutron powder diffraction were used to characterise the nature of ordering and precipitation in the material. The activity of the dominant tensile twinning mode during compression and the

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related lattice strain evolution are studied in-situ using neutron diffraction. Ex-situ EBSD analysis supports these data qualitatively and allows quantification of different twin types. All those characterisation techniques were applied to the binary alloying systems Ti-Al (chapter 6), Ti-Sn (chapter 9) and Ti-Zr (chapter 10) as well as to the ternary Ti-Al-O system (chapter 11) to allow direct evaluation of alloying on twin activity. Next to the overall lattice strain development measured with neutron diffraction, local strain patterns within grains have been visualised using digital image correlation (DIC). Slip trace analysis of these DIC strain maps allows insight into the interactions between deformation slip and twinning, as captured in chapter 7. The mechanical anisotropy is described in chapter 8, using polycrystalline compression samples with varying starting textures and with means of nanoindentation to elucidate the anisotropy of the hcp-unit cell.

Further work was carried out to prove the suppressive effect of ageing on twin activity in the Ti-Sn system, the industrial composition Ti6Al4V, and industrially forged Ti5Al2.5Sn. Additionally, all model alloys were tested in uniaxial tension to characterise tensile strength and ductility. Metallographic characterisation of the effect of ageing and the tensile samples was not completed entirely and stopped at different stages due to time constrictions. The completed parts of the work are briefly described in short communications in chapter 14 to motivate further research and outline the results.

The summary, chapter 13, focuses on the effect of alloying on twin formation, in dependence of parameters like the alloying element itself but also the c/a ratio, the state of ordering and strain localisation, the stacking fault energy and the crystal anisotropy. Finally, future work on the topic is explained briefly in chapter 14

2. Aim and Objectives

The main purpose of this PhD is to develop mechanistic understanding of why the addition of Aluminium to pure Titanium supresses deformation twinning. To further explore the role of the α stabilising Al on deformation patterns in the α phase, also binary α -alloys containing Sn or Zr and more complex Al rich alloys are characterised and their deformation behaviour is observed.

It is assumed that the elements AI, Sn and Zr have different effects on the deformation mechanisms of Ti. By changing the active deformation systems the anisotropic behaviour of the material can be changed. The degree of deformation twinning in different α -Titanium alloys will be established. It is not entirely understood yet how twins are nucleating and which are the criteria ruling the growth behaviour. For modelling approaches of the mechanical behaviour and the development of microstructure and texture it is desirable to establish criteria for twin nucleation and growth. CRSS values for slip systems exist for different Ti alloys gained mostly on single crystal experiments. This work extends past investigations of single crystals to polycrystalline material and contributes to understanding of specific deformation systems as function of the chemistry. In order to avoid grain size and texture effects great care was taken to create situations in which microstructures, textures and loading conditions are comparable. Rotation of the global starting texture during compression gives insight into the strength anisotropy as function of alloying and can establish compositional effects independent of the starting texture. In order to observe the material during mechanical deformation, ex-situ and insitu analysis was accomplished. EBSD texture measurements indicate activated twin typed and were used for a quantification of twin activity. In-situ neutron diffraction shows the texture and lattice strain development during deformation. Therewith a detailed analysis of material properties and active deformation systems was accomplished.

Therefore the aim is to describe the complexity how substitutional AI, Sn and Zr atoms affect deformation systems and strengthen the material and to which extend conclusions can be translated into industrial alloys. Suggestions are made how twinning gets affected by alloying and impacts the ductility.

3. Literature review

3.1. Crystal structure and microstructure

At room temperature, commercially pure Titanium (CP-Ti) has a hexagonal closed packed (hcp) crystal structure as shown in Fig. 3-1 a). The hcp unit cell for CP-Ti has a length of 0.468nm in the *c*-axis and of 0.295nm in the *a*-axis, resulting in a c/a ratio of 1.59. The most important planes are the basal {0001}-planes, the prismatic $\{10\overline{1}0\}$ planes and the pyramidal $\{\overline{1}011\}$ -planes as marked in Fig. 3-1 a) [Leyens 2003]. The coefficient of thermal expansion in the *c*-axis is smaller than the coefficient in the *a*-axis in a temperature range between room temperature and 200°C, which results in an increasing c/a ratio with decreasing temperature [Pawar 1968]. Anisotropy is also found in the Young's modulus, which is 145 GPa in the *c*-direction and much higher than in the *a*-direction (100 GPa) [Leyens 2003]. Results from Britton et al. using nanoindentation on polycrystalline CP-Ti, as plotted in Fig. 3-2, show the same trend but a smaller absolute anisotropy. Bonds between neighbouring atoms in the basal plane are weaker than in other planes, resulting in easier atomic displacements along the a-axis than along the c-axis [Pawar 1968] and anisotropic diffusion rates [Perez 2003].



Fig. 3-1: Crystal structure of a) hcp α -phase and b) bcc β -phase [Leyens 2003]



Fig. 3-2: Anisotropy of the hcp-unit cell of CP-Ti. The grey circles are the unloading modulus and the black triangles the unloading nanohardness as function of the declination angle [Britton 2010]

The hcp- α phase shows an allotropic phase transforms above a certain transus temperature to the β phase as shown in Fig. 3-1 b). The β -phase has a body centred cubic crystal (bcc) structure with a lattice parameter of 0.332nm. The β -phase is not as densely packed as α -Ti and exhibits higher diffusion rates. Most material properties change their behaviour with the phase transformation. The more isotropic and ductile mechanical behaviour of the β phase is used for instance during hot forming of Ti products. Alloying elements can alter the β -transus temperature and stabilise the β phase or the α phase. The compositions range from pure α alloys over near- α alloys with less than 5% β -phase and α - β alloys with high ductility up to pure β alloys. An increased β fraction leads to higher strength and cold formability but degrades the weldability. The α phase has benefits in terms of fracture toughness, creep strength and chemical resistance, what makes it so interesting for applications in jet engines. Apart from the phase fractions, the microstructure influences the mechanical properties like in common metals: smaller grains increase strength, ductility and crack propagation but lower the likelihood for crack initiation, fracture toughness and creep strength. Lamellar structures, as they are common after cooling from β phase, are beneficial in fracture toughness, creep strength and oxidation behaviour. Equiaxed microstructures, usually obtained after thermo mechanical treatments, have good strength and ductility but issues in fracture toughness, oxidation and creep. Their risk for initiation of fatigue cracks is lowered but the propagation is faster than in lamellar structure [Leyens 2003]. The present study focuses on equiaxed microstructures consisting dominantly of α -phase. Interesting for the investigated α -alloys is that AI and O stabilise the α phase to higher temperatures, while Sn and Zr have only little influence on the β -transus temperature. Only the element V in the investigated alloys stabilises the β -phase down to room temperature.

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3.2. Deformation mechanisms of the α phase

Hexagonal closed packed materials like Titanium deform mainly on slip- and twin-systems at low temperatures [Nemat-Nasser 1999]. After Frank-von-Mises-criterion five independent deformation systems are required to realize plastic deformation in a polycrystalline material but in hcp materials only a limited number of independent slip systems is offered under room temperature conditions [Salem 2003]. It is reported that the missing systems can be offered by twinning which allows for good ductility in for instance CP-Ti [Philippe 1988, Kalidini 2003]. However, recent work on CP-Ti and Ti5Al2.5Sn has shown that many grains exhibit only one or two slip system within one grain but virtually no twinning [Li 2013].

The ability of material to deform on only one single slip system questions the validity of the Frank-van-Mises-criterion. Ortiz and Repetto outlined the theory how plastic deformation can be realised with strongly limited slip systems in a polycrystal [Ortiz 1999]. The crystallography of commonly observed deformation systems in Ti and other hcp-metals is tabulated in Tab. 3-1 and described in the following.

Deformation	Glide	Shear	Rotation	Misorien	Shear	Total/	Refer-
system	shear	tion	axis	angle [°]	5[1]	dent	ence
	plane					variants	
Basal (a) glide	{0002}	<11 2 0>	<1 <u>1</u> 00>	Small	0.005-0.02	3/2	Zaefferer 2003, Chun 2010, Yang 2011
Prismatic 〈a〉 glide	{10 1 0}	<11 2 0>	(0001)	Small	0.05-0.07	3/2	Zaefferer 2003, Chun 2005, Yang 2011
Pyramidal (a) glide	{10 <u>1</u> 1}	<11 2 0>	⟨0 <u>1</u> 12⟩	Small		6/4	Zaefferer03, Chun 2005, Yang 2011
Pyramidal (1 st) ⟨c + a⟩ glide I	{10 <u>1</u> 1}	⟨11 <u>2</u> 3⟩	⟨13. 85 3⟩	Small	0.01	12/5	Zaefferer03, Chun 2010, Yang 2011
Pyramidal (2 nd) ⟨c + a⟩ glide	{11 <u>2</u> 2}	⟨11 <u>7</u> 3⟩	$\langle 1\overline{1}00 \rangle$	Small		6/4	Zaefferer03, Chun 2010
Pyramidal (2 nd) ⟨c + a⟩ glide	{11 <u>2</u> 1}	⟨11 <u>2</u> 3⟩	⟨6. <u>15</u> 3⟩	Small		12/5	Padilla 2007, Chun 2010
TT1	$\{10\overline{1}2\}$	$\langle 10\overline{1}1 \rangle$	$\langle 11\overline{2}0\rangle$	85	0.174	6/4	Chun 2005, Bozzolo 2010
TT2	$\{11\overline{2}1\}$	$\langle \overline{11}26 \rangle$	$\overline{\langle 1\overline{1}00\rangle}$	35	0.630	3/2	Chun 2005, Bozzolo 2010
СТ	{11 2 2}	<pre>(1123)</pre>	$\langle 1\overline{1}00\rangle$	65	0.219	-/8	Chun 2005, Bozzolo 2010
CT _{HT}	$\{\overline{10\overline{1}1}\}$	$\langle 10\overline{1}2 \rangle$	$\langle 11\overline{2}0\rangle$	57	0.099	12/6	Chun 2005, Padilla 2007

Tab. 3-1: Commonly observed slip and twin systems in Ti [Hasija 2003, Chun 2005, Zaefferer 2003, Bozzolo 2010, Padilla 2007, Yang 2011, Yoo 1981, Li 2013],



Fig. 3-3: Slip systems in hcp Ti, adapted from [Padilla 2007] without pyramidal $\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ slip 3.2.1.Slip

Crystallographic slip describes the movement of dislocation populations on slip planes in a particular direction. The most common slip systems in hcp-materials are the $\{10\overline{1}0\}$ -, $\{0001\}$ -planes in <a>-direction with burgers vector b=1/3($11\overline{2}0$) as shown in Fig. 3-3, indicated by the blue arrow on the blue planes. Also commonly observed is pyramidal a slip with the same burgers vector on the $\{10\overline{1}1\}$ -plane, indicated in red in Fig. 3-3 [Padilla 2007]. In pure Titanium, first-order prismatic slip $\{10\overline{1}0\}(11\overline{2}0)$ is the principal deformation mechanism (see Fig. 3-3) [Williams 2002] and slip on basal or pyramidal planes is less common [Aiyangar 2005]. These three glide planes with a-slip direction offer four independent slip systems. It has been shown in Zinc that basal slip causes a reorientation of c-axis into the normal direction during rolling and a rotation of the $\{11\overline{2}0\}$ -axis in the rolling direction causing small misorientation angles [Philippe 1988]. The activated deformation system is dependent on the chemistry of the alloy, the c/a ratio and furthermore factors like grain size, strain rate, temperature as well as the loading direction in respect to the crystal orientation, as described later on. [Christian 1995].

Two basic types of dislocations are commonly described: edge and screw dislocations. Both are line defects in a crystal lattice. Fig. 3-4 (a) shows an edge dislocation between points A and D. The area above ABCD moved in direction of the slip vector (left) in relation to the bottom about the shaded area. The amount of displacement equals the burgers vector b. The burgers vector of the edge dislocation is perpendicular to the dislocation line, therefore it moves only sidewise. Fig. 3-4 (b) shows the arrangement perpendicular to the dislocation line. The region around the dislocation experiences compressive stresses above and tensile stresses below the dislocation.

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Slip vector



Fig. 3-4: Edge dislocation in a cubic lattice, slip line AD perpendicular to slip vector (a) and view normal to the edge dislocation (b) [Dieter 1986]

This allows the dislocation to move with small displacements of surrounding atoms as the schematic Fig. 3-5 shows. If atom 1 in Fig. 3-5 a) is shifted slightly to the left, the extra half plane migrates from x to y (Fig. 3-5 b). After several of these incremental movements the dislocation moves to the other end of the crystal (Fig. 3-5 d). As only small displacements have to be accomplished to shear a crystal in this way, the required force is relatively small and can be qualified with the Peierls stress (Equation 3-2).



Fig. 3-5: Atom movement near dislocations in slip (a) and movement of an edge dislocation (b) [Hull 2001]

Under certain circumstances, like thermal activation or the presence of sufficient vacancies, the edge dislocation can move perpendicular to its burgers vector, known as dislocation climb. When the dislocation moves within the slip plane it is called a kink, moves it in another slip plane it is called a jog. Jogs have been considered to act as twin nucleus in fcc material by Venables [Venables 1961] and the ease of kink formation in fcc and hcp materials was connected to solid solution hardening previously [Butt 1981, Cahn 1996].

Screw dislocations (Fig. 3-6) move in a different way to edge dislocations. Just in the case of edge dislocations the volume above ABCD (in Fig. 3-6 a) is displaced. But unlike the edge dislocation having a burgers vector parallel to AB, it is parallel to AD in the screw. Screw

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dislocations are less restricted in movement than edge dislocations because they do not have a specific slip plane and climb of screw dislocations is not possible. To move the upper part in respect to the lower part of ABCD, a circuit around the dislocation line needs to be done to go from x to x'. Fig. 3-6 b) shows the relative displacement after one circuit. Open circles present already slipped atoms above the slip plane and solid circles present unslipped atoms under the slip plane. [Dieter 1986]



Fig. 3-6: Screw dislocation along AD, parallel to the slip vector (a) and atomic arrangement parallel to the slip plane (b) [Dieter 1986]

A slip system is activated when the externally applied stresses are sufficiently high on a slip system. Schmid's law resolves the acting force *P* on the cross section *A* on the slip system. The stress on a specific slip system depends on the angle Φ between the normal of the slip plane N and the loading direction *P* as well as the angle λ between the loading direction and the slip direction, as Equation 3-1 describes and depicted in Fig. 3-7. The ratio of the applied stress to the resolved shear stress is called Schmid factor *m*. The resolved shear stress is highest when $\Phi = \lambda = 45^{\circ}$ and the Schmid factor m becomes 0.5 and slip is most likely to occur on this slip system. If one of the angles is 90° m becomes 0 and no slip on this system will occur. The slip system is activated when the macroscopic stress overcomes the critical resolved shear stress (CRSS) for the considered slip system [Dieter 1986]. For illustration purposes Fig. 3-8 shows Schmid factor maps for the most important slip systems in the hcp lattice.

$$\tau_R \approx \frac{P}{A} \cos \lambda \cos \Phi = \sigma \cos \lambda \cos \Phi = \tau_{plane} m$$

Equation 3-1: Resolved stress on slip plane [Dieter 1986]



Fig. 3-7: Sketch for the RSS on specific planes after Schmid's law [Dieter 1986]



Figure 2.13 Unit triangle with iso-curves of Schmid's factor for (a) prismatic, (b) basal and (c) firstorder pyramidal gliding with in superposition experimental data. For prismatic (d), basal (e) and first-order pyramidal (f) slip systems, poles corresponding to experiments from literature are reported on the unit triangle mapped with Schmid's factor contour lines, compiled from Bridier et al (2005).

Fig. 3-8: Unit triangle with iso curves for prismatic (a,d) basal (b,e) and first order pyramidal slip (c,f) with superimposed experimental data [Thomas 2007]

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The shear stress on a slip system required to move a dislocation in a particular direction is called Peierls stress τ_P and estimated by Equation 3-2, with *G* being the shear modulus and ν the Poisson's ratio.

$$\tau_P \approx \frac{2G}{1-\nu} e^{-2\pi w/_b}$$

Equation 3-2: Peierls-Nabarro stress [Dieter 1986, Hull 2001]

The width of the dislocation *w* and the distance between atoms in slip direction *b* determine the ease of movements. The width of a dislocation core depends on interatomic potentials, the crystal structure as well as the stacking fault energy and can be expressed as function of the distance between slip planes *a*. The width *w* equals a'/(1 - v) for an edge dislocation and *a* for a screw dislocation. Slip preferably occurs on widely spaced planes with short interatomic distances in slip direction and when the fault is wide and planar. As a consequence a lower Peierls stress is expected for low SFE materials [Hull 2001]. Investigations on Ti single crystals showed that the Peierls mechanism is only active below 210 K but an undefined mechanism above this temperature is rate controlling [Evans 1968].

More recent developments consider the energy for slip activation by computer simulations with interatomic potentials [Girshick 1998-a&b, Yakovenkova 2007], embedded atom method (EAM) or density functional theory (DFT) [Pei 2013]. Fig. 3-9 shows the γ -surface for the basal and prismatic plane in Ti, describing the required energy to shear the crystal on the slip plane by a given displacement vector.

Minima in the γ -surface reveal metastable stacking faults. Fig. 3-9 a) shows the γ -surface of the basal plane, exhibiting an intrinsic stacking fault with the displacement 1/3 $\langle \overline{1}100 \rangle$ and Fig. 3-9 b) shows the γ -surface of the prismatic plane with the minimum at 1/6 $\langle \overline{1}2\overline{1}0 \rangle$ +0.18 $\langle 0001 \rangle$, both calculated with a Finnis-Sinclaire model by Girshick et al. [Girshick-a 1998]. Even though for instance lattice parameters, elastic properties and diffusivity can be reasonably predicted by these methods [Fernandez 1996, Girshick-a 1998, Sandloebes 2012], predictions from dislocation activities are predicted differently from different potentials as Girshick et al. describe. A bond order potential was shown to show no metastable stacking fault [Girshick 1998-b, Bacon 2002]. Nevertheless, results for different Mg-alloys, as presented by Pei et al. [Pei 2013], are promising.



Fig. 3-9: γ -surface for a) the basal plane and b) the prismatic plane calculated with a Finnis-Sinclaire-type potential for Ti [Girshick-b 1998]

3.2.2.Twinning

Different kinds of twins exist in crystals. Deformation twins accommodate plastic strain during deformation and will be the focus of this chapter. Annealing twins appear after a heat treatment and are a sign of prior deformation or stress relaxation. A martensitic phase transformation cannot be seen as twinning, because the lattice structure changes [Cahn 1996]. Unlike crystallographic slip, deformation twinning is characterised by significant rotations of the crystal lattice, realised by an organised movement of atoms by a fraction of the atomic spacing in an array [Song 1995]. The twins form within grains during deformation and introduce new graintwin boundaries, which refine the grain size and alter the texture of the material dramatically. Both, grain refinement and texture change, impact the mechanical properties [Salem 2002, Salem 2003, Salem 2005, Kalindini 2003]. The crystal structure in twin and matrix is identical but mirrored on the twin plane. The so called mirror-, habit- or shear-plane is listed in Tab. 3-1 for the most common twin types in Ti, which defines together with the shear direction, the rotation axis and the misorientation angle the twin type. Fig. 3-3 gives a schematic illustration of the characteristics for the four most common twin types. The $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tension twin (TT1) dominates at ambient temperatures in CP-Ti, Ti-alloys and many other hcp-metals, but also the $\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twin (TT2) and the $\{11\overline{2}2\}\langle11\overline{2}3\rangle$ compression twin (CT) are readily observed at ambient temperature and described in the following more detailed. The $\{10\overline{1}1\}$ (10 $\overline{1}2$) compression twin (CT_{HT}) is reported to occur only at high temperatures [Paton 1970] and was not observed in the present study.

Twinning generally becomes less likely with increasing temperature [Mc Cabe 2006, Nemat-Nasser 1999, Honniball 2012]. Moreover, the loading direction in respect to the texture has a dramatic effect on the activation of twin mechanisms. The polarity of twinning enables tension twins to form only when tensile stresses are imposed on the c-axis and compressive stresses on the a-axis, while compression twins form only when compressive stresses act on the c-axis. Furthermore it was found that the twin activity increases with increasing strain rate and strain or

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stress levels [Philippe 1988, Nemat-Nasser 1999, Salem 2006]. Even for varying strains, strain rates and temperatures Chichili et al. [Chichili 1998] report almost linear correlation between stress and twin density, as Fig. 3-10 shows before the twinning saturates at high plastic strains or high stresses. Twin activity generally decreases with decreasing grain size, rationalised by a higher Hall-Patch slope for twinning compared to slip without a detailed understanding of the underlying mechanism [Meyers 2001, Yu 2010, Yu-a 2012]. It was found during studies on Mg and Zr that the twin number is more affected by the grain size than the twin thickness [Capolungo-a 2009, Beyerlein 2010b].



Fig. 3-10: Evolution of twin density as linear function of the flow stress at different strain rates, strains and temperatures [Chichili 1998]

The total accommodated strain from twinning can be approximated with Equation 3-3, where *s* is the twin shear strain for a specific twinning systems and V_{Twin} the corresponding twinning volume fraction. This strain related to the applied plastic strain gives the maximum strain, which can be accommodated by a twinning system assuming an optimal orientation to the strain direction for all captured twins. The rest of the strain has to be accommodated by other deformation mechanisms.

$$\varepsilon_{max} = \sqrt{\frac{1}{2}s \cdot V_{Twin}}$$

Equation 3-3: Strain accommodation by twinning shear [Battaini 2007]

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Twin formation

The activation of deformation twinning is often rationalised with the associated twin shear and the shuffling requirements as calculated by Yoo as function of the c/a ratio [Yoo 1981]. In the case of Ti, the $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tension twin is by far the most frequently observed twin mode resulting in a shear strain of s = 0.17, which is slightly smaller than the shear strain of the less commonly observed $\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ compression twin (s = 0.22) and significantly smaller than the shear strain of the rarely reported $\{11\overline{2}1\}\langle \overline{1126}\rangle$ tension twin (s = 0.63) [Yoo 1981, Chun 2005]. However, the $\{10\overline{1}1\}\langle 10\overline{1}2\rangle$ compression twin generates by far the smallest shear strain of only s = 0.09 but has been reported to only occur at high temperature [Paton 1970]. Consideration of the required atomic shuffle for twin formation, next to the twin shear value itself, can explain why the $\{10\overline{1}1\}$ compression twin does not occur at ambient temperature [Yoo 1981, Chun 2005].

The twin boundary energy was reported to be higher for the $\{10\overline{1}1\}$ compression twin than for the common $\{11\overline{2}1\}$ compression twin and would explain why the former is more difficult [Yoo 1991]. However, the twin boundary energy seems not an appropriate measure to rank the probability of individual twin modes as ab-initio calculations and predictions from most atomic potentials summarised in Table 1 in the review of Yoo et al. [Yoo 2002] predict a much lower twin boundary energy for the $\{10\overline{1}1\}\langle10\overline{1}2\rangle$ compression twin compared to the $\{11\overline{2}2\}\langle11\overline{2}3\rangle$ compression twin which would suggest this high temperature twinning mode to be more active. Also, the $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twin shows higher twin boundary energy than the $\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twin, while the frequency of observations for the former one is higher. Problem for those calculations is that the core width varies significantly between the different potentials.

Solely geometrical and energetic approaches do not seem to explain twin formation. However, the requirement to include the atomic shuffling indicates the importance of formation dynamics to explain twin formation. Deformation twinning is explained with a step-wise nucleation, propagation and growth mechanism [Song 1995, Yoo 2002]. Most likely might be heterogeneous twin nucleation, where twins emerge by a dissociation of dislocation into two partial dislocations from an already existing stacking fault. Density functional theory (DFT) calculations support this zonal-twinning mechanism, as lower elastic energy is required to form $\{10\overline{1}2\}(10\overline{1}1\}$ tension twins when partial dislocation are involved than without [Wang-a 2009], even though the situation may be different for other twin types [Wang-b 2009].

More recent publications, based on experimental data and backed up with different modelling approaches, investigate stress concentrations on grain boundaries [Beyerlein a 2010, Beyerlein 2011, Yu b 2012, Abdolvand a&b 2012] or on precipitates (in Mg) [Robson 2010] and on slip transfer over grain boundaries [Wang 2010, Bieler 2014] to further understand twin formation. It is not clear if twin growth is dependent or independent of slip, as both mechanisms are theoretically possible [Serra 1996, Capolungo-b 2009]. The importance of slip in connection with

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twinning was already suggested by Paton and Backofen, who found <c+a>-slip bands prior to the formation of $\{11\overline{2}2\}$ -twins [Paton 1970].

Slip as prerequisite for twinning can be observed during in-situ measurements of Mg [Agnew 2003] and Zr [Xu 2008] and its importance was also recognised for Ti [Paton 1970, Preuss 2010]. However, the role of slip before twin formation has not been discussed based on the results of various in-situ experiments [Oliver 2004, Preuss 2010, Abdolvand 2011, Abdolvand c 2012, Warwick a & b 2012]. Brown et al. also support the idea that twinning might be assisted by slip with experimental and theoretical studies on Beryllium [Brown 2011]. They found that the $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ twin is strain rate insensitive, but prism slip becomes more difficult at higher strain rate and therefore interactions between $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ twins and prismatic slip become less frequent and twin activity appears reduced. Basal slip is reported to be comparably less sensitive to strain rate effects [Brown 2011].

3.2.3. Interaction between slip, twinning and grain boundaries

As explained earlier, in chapter 3.2.2, slip seems a necessary prerequisite for twinning. To date, it is not entirely understood how grain boundaries interact as barriers to dislocation motion or twin nucleation sites. Early work by Paton et al. showed constant <c> and <c+a> dislocation density in a $\{11\overline{2}2\}$ -compression twin in TEM dark field micrographs (Fig. 3-11), while it decreases with increasing distance from the interface in the matrix [Paton 1970]. Respectively c-type dislocations in the matrix (untwinned) are rare and when present then they are accompanied by a-type dislocations [Chichili 1998]. This suggests that <c+a> dislocations may be required to form a compression twin.



Fig. 3-11: TEM dark field: $\{11\overline{2}2\}$ -twin from compression parallel to c-axis with <c> or <c+a> dislocations in Ti [Paton 1970]

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Slip around $\{10\overline{1}1\}$ twins in α -Ti was furthermore observed during creep experiments by Aiyangar et al. [Aiyangar 2005]. Also, Meyers et al. give a key role to the pile up of dislocations caused by slip in the formation of twins in BCC metals [Meyers 2001].

Recent studies [Wang-a 2010, Guo 2014] have shown that dislocations can easily be transferred over a grain boundary when the strain from active slip system aligns well with the strain on a neighbouring slip system. However, slip transfer does not occur easily when the active slip systems is not well aligned with a soft slip system in the neighbouring grain and stress concentrations build up and act as dislocation source in the neighbouring grain. Guo et al. state that slip is blocked at a Luster-Morris parameter below 0.7, but transferred above 0.7 and with sufficiently high shear stress on the outgoing slip plane. Analogues to the Schmid factor, the Luster-Morris parameter estimates the likelihood of a passing dislocation from the angle ψ between the active slip system with plane normal n_d in a soft grain to the twinning plane normal n_t in the hard grain and the angle between slip direction b_d and shear direction b_t, as shown schematically in Fig. 3-12. A value of 1 indicates complete compatibility while a value of 0 indicates incompatibility.

 $m' = \cos \psi \cos \kappa$



Equation 3-4: Luster-Morris parameter [Wang-a 2010]

Fig. 3-12: Schematic of slip transfer at grain boundary [Wang-a 2010]

Wang et al. [Wang-a 2010] observed increased likelihood for tension twin nucleation in hard grains when prismatic slip in soft adjacent grains was active and a high Luster-Morris parameter between both systems.. Wang et al. describe that the parameter is not well appropriate to predict twin-twin interactions across grain boundaries [Wang-b 2010]

3.2.4. Detection of slip and twinning:

The $\{10\overline{1}2\}$ -tension twin normally traverses through the entire grain and is initially thin and straight but ends occasionally within the grain. After growth a pronounced lenticular morphology

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develops, with tapered ends [Chichili 1998, Paton 1970]. The other twin systems ($\{11\overline{2}1\}\langle\overline{11}26\rangle$ and $\{11\overline{2}2\}(11\overline{2}3)\}$ do not develop the pronounced lenticular shape and are rather needle shaped, like thin $\{10\overline{1}2\}$ ($10\overline{1}1$) tension twins. However in CP-Ti the $\{10\overline{1}2\}$ -tension twin and the $\{11\overline{2}2\}$ -compression twin can look similar. In-situ neutron diffraction measurements have been successfully used to monitor the activity of the $\{10\overline{1}2\}(10\overline{1}1)$ twin but not for other twin modes [Preuss 2010, Skippon 2013]. A unique detection of the different twin systems is possible with EBSD micro maps. Statistical determination from the misorientation distribution are appropriate to detect $\{11\overline{2}2\}(11\overline{2}3)$ and $\{10\overline{1}2\}(10\overline{1}1)$ twins, but not sensitive enough for the $\{11\overline{2}1\}(\overline{11}26)\}$ twin at usually little activated volumes [Bozzolo 2010]. Analysis of fine-scaled maps using the specific rotation axis with the according misorientation angle, as listed in Tab. 3-1, is required to identify and quantify twin systems. This approach also allows the determination of secondary and tertiary twins [Bozzolo 2010]. To a certain degree, slip activity can be evaluated from EBSD mappings of moderately to strongly deformed hcp-metals using the in grain misorientation axis, as described by Chun et al. [Chun 2010]. The active slip system can also be indicated after small to moderate strain levels by TEM analysis or by electron channelling contrast imaging (ECCI) [Crimp 2001, Crimp 2006, Gutierrez-Urrutia 2009, Zaefferer 2012]. Only TEM analysis can distinguish between dislocations with <c> and <a> component and show partial dislocations. Slip activity typically influences the texture and a gradual texture change can be seen.

3.2.5.Influence of deformation systems on hardening behaviour

The deformation behaviour is ruled by the interaction of softening by recovery or recrystallization, dislocation hardening and the reorientation of the lattice by twinning. Twinning not only leads to a the reduction of free slip distance (Hall-Patch hardening) but also to more favourable orientations for slip in case for compression twinning (texture softening) or less favourable orientations for slip in case of tension twinning (texture hardening). The transformation from glissle to sessile dislocations inside twins is also reported to strengthen the material when twinning is active (Basinski mechanism). [Kalidini 2003]

The relative activity of those deformation mechanism leads to specific work hardening rates, while each change of work hardening rate seems to need a critical strain related to the dislocation motions [Nema-Nasser 1999]. Fig. 3-13 shows four stages of the strain hardening for brass and pure titanium, which both show twinning during deformation. Stage A, B and C occur in CP-Ti at temperatures between 77K and 1120K and a quasi-static strain rate of about 10^{-4} /s [Nema-Nasser 1999].

Stage A is noticeable by a decreasing strain-hardening rate, caused by dynamic recovery during the deformation [Salem 2002] and deformation prior to onset of twinning [Wu X. 2008]. The strain-hardening rate increases with the grain size [Salem 2006]. In **stage B** twinning is active and reduces the free slip length, which leads to an substantial increase of work-Arnas Fitzner, PhD Thesis, 2014

hardening-rate [Nema-Nasser 1999]. The increasing hardening rate is seen as upward curvature in stress-strain curves [Chichili 1998]. The slope of stage B is directly connected to the amount of twinning. A high slope indicates more twin activity in relation to slip activity [Salem 2003, Wu. X. 2008]. Because of the increased hardness in twins in respect to the parent grains, an overall hardening follows. Stage B ranges from ε =-0.05 to -0.22 in CP-Ti [Salem 2002]. The initiation of **stage C** is connected to a decrease in the strain-hardening rate after the local maximum (see Fig. 3-13). After a certain degree of deformation twinning saturates. The production rate of deformation twins reduces and less hardening follows [Kalidindi 2003]. **Stage D** is only observed for fcc metals which are showing secondary twins, while hcp metals are showing twin intersections at early states of deformation [Kalidindi 2003].

By fitting parameters, like the initial slip or twin resistance, and hardening parameters for each deformation system as well as coupled slip-twin hardening parameters in crystal plasticity models reasonable reproduction of the stress-strain behaviour could be achieved for high purity Ti [Wu X. 2007]. This emphasises the fact that each deformation system has its role on the strain hardening response. Relative changes of the activity of the deformation systems affect therefore the work hardening behaviour and texture development, as it is the case in materials of different chemical compositions [Wu X. 2008].



Fig. 3-13: Typical strain hardening responses of polycrystalline metals which exhibit twinning as deformation mechanism during compression [Kalidini 2003]

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3.3. Effects of alloying

Alloying is most commonly used to strengthen metals but due to the complex nature of metals only specific elements are appropriate for alloying. For instance the low tensile strength of CP-Titanium (400MPa) can be increased up to 1400MPa with increasing impurity levels or addition of alloying elements [Van Thyne 1954, Higgins 2006]. Some atoms are soluble in a matrix lattice and form a solid solution until the solubility limit. At higher concentrations second phases ordering phenomena occur and precipitate form, which alter the properties. Alloying elements affect also the ease of deformation systems and lower the stacking fault energy of the pure metals. While research on Ti alloys in the past decades could already help to guide material processing and alloy development, many phenomena are not understood or have opposing effects on the mechanical properties. This chapter outlines crucial effects of the most common alloying elements in α -Ti: Al, Sn and Zr. Not considered are temperature effects or effects of other popular elements like V and Fe or Ta, Pd and Nb for bio-medical-applications [Okazaki 1993]. While the effect of α_2 formation is considered, the effect of β -phase is not.

Empirical testing has brought up the Al-equivalent equation given in Equation 3-5, ensuring an α -alloy as long the Al-equivalent does not exceed 9% [Donachi 2000, Leyens 2003, Luetjering 2007]. However, the effects of N or C on the phase stability are not factored in despite their relativey strong effects [Van Thyne 1954]. Rough values for the strength increase per wt% Al (55MPa), Sn (28MPa) and Zr (3.5MPa) are given by Donachi et al, but the assumption of linear behaviour does not necassirily match the hardening laws described later in this chapter [Donachi 2000].

Equation 3-5: Aluminium equivalent equation for α-phase stability [Donachi 2000]

$$Al_{eq} = 1Al + 1/3Sn + 1/6Zr + 100 < 9\%$$

In the following effects and observations of the elements in Equation 3-5 are reviewed and discussed in terms of their effect on plasticity at high stresses, rather than creep or diffusional flow at low stresses [Janghorban 1990, Janghorban 1991].

3.3.1. Solubility and phase formation

Aluminium (AI) is an α -stabilizer with significant solid solubility [Donachi 2000]. Al replaces atoms from the matrix substitutionally. The binary Ti-Al phase diagram by Schuster and Palm [Schuster 2006], as shown in Fig. 3-14, shows an increase in temperature of the solvus line between α and α + β from 882°C in CP-Ti up to more than 1100°C with 25at.% Al. However, at temperatures below 800°C, Al is fully soluble up to a concentration of about 15at.%. Higher concentrations lead to precipitation of Ti₃Al in DO₁₉ structure and the formation of Titanium-Aluminides from about 40at.% Al. Of special interest for the current project are the phase boundaries of the α phase only. The phase diagram by Schuster and Palm neglects earlier

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reports of short range ordering (SRO) towards Ti_3AI from concentrations of about 7at.%AI as detected by Namboodhiri et al. with electrical resistivity measurements and by TEM analysis [Namboodhiri 1973, Namboodhiri 1983]. Other investigations [Kornilov 1963, Kuraeva 1967, Chaze 1987] report of single α phase fields up to 10at.% AI. Possibly due to this contradictions Schuster did not include the SRO region in the phase diagram.

Tin has, like AI, a good solubility in α -titanium [Kornilov, 1963]. A further common ground of Sn and AI is that both retard the rates of transformation into the β phase and strengthen the alloy. The binary Ti-Sn phase diagram, presented in Fig. 3-15, shows solubility of Sn in Ti until about 7at.% at RT and is in good agreement with theoretical calculations [Wang 2011]. At higher Sn concentrations Ti₃Sn precipitates directly into DO₁₉ structure, apparently without the gradual change through SRO as in the binary Ti-AI system. The transus temperature decreases slightly with tin addition making it a neutral element for phase stabilisation. A review on the ternary Co-Ti-Sn system [Yin 2007] suggests Sn solubility of 8.5at.%Sn in the α phase or even 16at.% Sn in the β phase. Experimental work offers contradicting information on the existence of a two-phase field (α +Ti₃Sn) [Yin 2007]. Confusion may have occurred due to suppression of thermo dynamical reactions. The reaction from the two-phase field " β Ti + Ti₃Sn " to single-phase α Ti during cooling may not have been completed. Therefore metastable β Ti could be present [Liu 2005]. Ti₃Sn precipitates are incoherent [Liu 2005]. Together with AI, Sn behaves as α -stabilizer and Sn can replace AI in the Ti₃AI-phase [Luetjering 2007].



Fig. 3-14: Binary Ti-Al equilibrium phase diagram [Schuster 2006]

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Fig. 3-15: Sn-Ti Phase diagram [Okamoto 2010]

Zirconium (Zr) is like Sn classically considered as a neutral element in terms of phase stability [Leyens 2003]. However, addition of Zr to Ti decreases the transus temperature slightly [ASM Handbook 1992, Hari Kumar 1994]. Unlike Al and Sn, Zr is fully soluble in α - and β -phase (Fig. 3-16). The oxidation behaviour in air becomes dramatically worse with Zr addition and leads to rapid ZrO₂ formation at temperatures above 600°C [Halley-Demoulin 1994].



Fig. 3-16: Ti-Zr phase diagram [ASM handbook 1992]

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Oxygen (O) strongly stabilises the α phase field to more than 1800°C at about 20at.% before Ti₂O precipitates, as seen in binary Ti-O phase diagram (Fig. 3-17) [Wahlbeck 1966, Domalaga 1973]. The combined use of Al and O raises the β transus temperature but barely influences the α - β transus temperature and consequently widens the α - β two-phase region [Thyne 1954, Schofield 1957, Molchanova 1965, Ouchi 1998]. Fig. 3-18 shows binary sections of the ternary Ti-Al-O phase diagram.



Fig. 3-17: Binary Ti-O phase diagram [Domagala 1973]



Fig. 3-18: Vertical sections of the ternary Ti-Al-O system with O contents of a) 0.05%, b) 0.5%, c) 1.0%) [Molchanova 1965]

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3.3.2.Impact of alloying on lattice and c/a ratio development

An increase in c/a ratio leads to more closely packed basal planes and therefore facilitates slip on the basal plane [Rosi 1953]. In contrast the packing on pyramidal and prismatic planes becomes less dense and slip with <c+a>-direction more difficult [Li 2013]. Yoo et al. connected a change in c/a ratio to the shear value necessary to form deformation twins [Yoo 1981]. They show that increasing the c/a ratio decreases the shear strain value for tension twinning and increases the shear for compression twinning. Even though this theoretically favours twin formation for the former or impedes for the latter, the atomic shuffling seems to be the more dominant parameter to judge the ease for twinning [Yoo 1981].

Teer and Salem showed that the addition of Al or Sn increases the c/a ratio of Ti [Teer 1977], as shown in Fig. 3-19 and in agreement with other work on the Ti-Al system [Denney 1955, Ghosh 2008]. In the case of the Ti-Al system this is achieved due to a more rapid decrease in the *a*-parameter compared to the *c*-parameter. Addition of Zr to Ti increases the *c*- and the *a*-parameter without an effect on the c/a ratio [Sen 1998]. The c-axis parameter of α titanium is very sensitive to contaminations by nitrogen and oxygen [Pawar 1968] and elongates with increasing O concentration. Measurements on the lattice parameter development and the theory mentioned beforehand suggest that addition of Al or Sn to Ti should first favour basal slip and second favour tension twinning. Accordingly addition of Zr to Ti should have no effect on the likelihood of the slip or twin systems, if the c/a ratio dominates the properties.



Fig. 3-19: Development of c/a ratio as function of AI or Sn concentration [Teer 1977]

Approaches to quantify theoretically the elastic lattice distortion of binary alloys are not straightforward. Vegard's law (Equation 3-6) can be used as an approximation for some metals but better fits are achieved in ionic salts. It sets the lattice parameter a of titanium alloy a_{alloy} in linear relation to the atomic concentration of the alloying element at_B and the lattice parameter of the alloying element a_B just by simply considering the geometric difference of the lattice parameter to the matrix a_{Ti} . [Denton 1991, Lubarda 2003]. In hcp materials this should also be

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adapted to calculate the lattice parameter c of the titanium alloy c_{alloy} by considering the lattice parameter c of alloying element c_B instead of a_B , as shown by Ivermark [Ivermark 2009] and in Equation 3-6.

$$a_{alloy} = at_B a_B + (1 - at_B) a_{Ti}$$
$$c_{alloy} = at_B c_B + (1 - at_B) c_{Ti}$$

Equation 3-6: Adaptation to Vegard's law for hcp-materials [Ivermark 2009]

Tab. 3-2 gives values for the alloying elements of the present study to calculate the lattice distortion and some additional atomic details. It can be seen that Al has a bigger *a*-lattice parameter compared to Ti, suggesting increasing lattice spacing with Al addition. Contrary experiments have shown decreasing a and c parameter for addition of Al to Ti [Denney 1955]. The atomic diameter seems more promising as Al has a 1.1% smaller diameter than Ti. However the atomic diameter cannot be used either as contradicting results were found in the Ti-Sn system in the present work. Also other alloying systems like Cu-Zn, Al-Mg, Al-Ag and Au-Ag yield results, which cannot be predicted from Vegards law, while other systems (Cu-Au, Cu-Al) show better matches. A better understanding how lattice structures develop upon alloying may be achieved when also the electron concentration, electrochemical effects and static displacements are considered [Dieter 1986, Lubarda 2003].

Symbol	Ti	AI	Zr	Sn	V
Element	Titanium	Aluminium	Zirconium	Tin	Vanadium
Relative atomic mass	47.867	26.9815386	91.224	118.71	50.9415
Atomic number	22	13	40	50	23
Diameter [pm]	289.6	286.4	318	281	268
Lattice parameter a [nm]	0.295	0.405	0.323	0.582	0.303
Lattice parameter c [nm]	0.468	-	0.515	-	-
Delta diameter [%]	0	-1.1	9.8	-3	-7.5
Electron configuration	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ² 4s ²	1s ² 2s ² 2p ⁶ 3s ² 3p ¹	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ² 4p ⁶ 4d ²	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ² 4p ⁶ 4d ¹⁰ 5 s ² 5p ²	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ³ 4s ²

Tab. 3-2: Values for Vegards law and further details for the elements [Merck 2011]

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3.3.3.Diffusion rates and electric resistivity

The knowledge about diffusion rates is important for heat treatments, hot working and recrystallisation temperatures. The diffusion rates are higher in the β phase than in the α phase, as seen in Fig. 3-20 a). In the α phase Sn and Al have low diffusion rates, like V as well. Oxygen, as interstitial, diffuses faster than substitutionals. Fe, Ni and Co use an interstitial diffusion mechanism as well and exhibit high diffusion rates [Perez 2003].

The diffusion rates for substitutional elements (like AI) in Ti and self-diffusion rates decrease dramatically with decreasing impurity content, especially the Fe content, which is explained by a vacancy-controlled diffusion mechanism. Zr diffuses with the vacancy mechanism like AI does. [Perez 2003, Luetjering 2007]

Diffusion properties were previously linked to electronic structures of atoms [Cahn 1996, Perez 2003]. A more direct way of measuring electronic interactions are resistivity measurements. The resistivity depends on the amount of valence electrons and thermal vibration [Ames 1965]. Those measurements (see Fig. 3-20 b) show that Sn disturbs the electronic structure more than AI, and much more than Zr. The effect on deformation and strengthening from such disturbances is not entirely explored to date, but a suggestion based on electronic models already made by Collings and Gegel [Collings 1973].



Fig. 3-20: a) Arrhenius diagram of Titanium's self-diffusion and some alloying elements in α and β phase and b) electrical resistivity as function of solute concentration in Ti-alloys [Ames 1965, Luetjering 2007].

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3.3.4. Solid solution strengthening

A solid solution is a mixture between a metal and another element, forming one crystal during solidification. Depending on the size of the solute it can be in interstitial or substitution solution. When atoms of both alloying partners are similarly sized, within 15% of size difference, the alloying partner substitutes atoms in the matrix and a substitutional solution is formed (Fig. 3-21 a&b). A much smaller foreign atom will go in interstitial solution (Fig. 3-21 c). With concentrations beyond the solubility limit precipitation will form as discussed in the next chapter. [Dieter 1986, Higgins 2006]





Despite the wide practical applications of alloys based on solid solution strengthening, the strengthening mechanisms between solute atoms and matrix are not entirely understood [Higgins 2006]. It is known that solute atoms can affect for instance the elastic modulus, stacking fault energy (SFE), electrical properties, short-range order and long-range order. Solutes affect more the frictional forces of dislocation motion rather than only the static locking force of a dislocation as they affect the full work hardening behaviour [Dieter 1986].

Elastic interactions (locking force)

Lattice distortions (Parelastic interactions) of the solute interact with dislocations and generally impede their movement so that deformation becomes more difficult [Labusch 1970]. If the alloying partner is larger than the matrix, schematically shown in Fig. 3-21 a), the lattice surrounding the atom is expanded and compressive forces are introduced. When the alloyed atom is slightly smaller, Fig. 3-21 b), the lattice is contracted and tensile forces act on the matrix. This dilatation (expansion or compression) impedes the motion of edge dislocations. A much smaller element will go in interstitial solution and will cause expansion in the surrounding lattice Fig. 3-21 c). Interstitials introduce next to the dilatation also a shear component and also impede screw dislocations [Dieter 1986]. Screw dislocations are not impeded from simple dilatation, as they have no hydrostatic stress field. For some systems the strengthening effect is Arnas Fitzner, PhD Thesis, 2014

thought to be proportional to the misfit although this is not true for many alloying systems. The atomic size of the solute may also depend on parameters like matrix element, concentration and temperature and is therefore not easy to estimate. When the solute not only introduces elastic stresses but also alters the modulus locally (Dielastic interaction) edge and screw dislocations are impeded. [Berry 1962, Dieter 1986, Cahn 1996].

Chemical interaction

The stacking fault may exhibit a different solubility than the matrix, which can lead to segregation of solutes on the fault. Solute atoms usually lower the SFE, which leads to increased separation of partial dislocations. Increased solute concentration on the fault would lead to a locally reduced SFE and increased separation of partial dislocations. The motion of those partials with large spacing becomes consequently more difficult and strengthens the material. This effect is also called dislocation pinning. [Dieter 1986, Cahn 1996]

Electrostatic interactions

Electrical interactions, based on the relative valences of solute and matrix, have a much smaller effect than the previous described interactions. A solute atom has different valence electrons and will form a local charge centre and interact with the electrical dipole of a dislocation. [Dieter 1986, Cahn 1996]

Order interactions

Solute atoms reduce the equilibrium energy when they either find the equilibrium number of dissimilar neighbours or by clustering together. Solute atoms in a homogenous alloy can find such arrangement by dislocation motion, which can have quadratic strengthening effect [Cahn 1996]. On the other hand, an ordered arrangement can be achieved by appropriate heat treatments and the process of disordering requires additional energy. An additional energy to shear ordered domains is the anti-phase boundary energy in a long range ordered structure and the smaller diffuse anti-phase boundary energy in a short range ordered structure. [Dieter 1986]

Long-range order interactions lead to the assumption, that a dislocation line can move locally and does not require to move as a complete as described by common dislocation models. Such flexible dislocation line bends around regions of high local interaction energy from the described effects, which superimpose their effects on the dislocation.

Theoretical efforts to describe solid solution strengthening predict generally a square-root shaped curve with increasing concentration and happen to be complex differential equations [Labusch 1970, Labusch 1972]. This is based on the assumption that the alloying partner becomes less effective with increasing solute concentration.

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Such square root shaped curve compares reasonable with hardness measurements on the Ti-Zr system [Ho 2008] but not in any sense with experimental values on the Ti-Al system, showing rather quadratic strengthening until 10at.% (6wt%) Al [Truax 1974]. From empirical data it becomes obvious that Al is the most effective substitutional solid solution strengthener in Ti until about 13at.% (8wt%). Also, Sn strengthens Ti well in a range from 0.8-2.5at.% (2-6wt%) Sn whereas Zr shows moderate positive mechanical effects in a range from 1-4.4at.% (2-8wt%). Oxygen is a very effective interstitial solution strengthener [Donachie 2000, Williams 2007].

3.3.5. Precipitation Strengthening

Limited solubility in many alloying systems leads to a multiphase microstructures, with a second phase possibly being dispersed or aggregated [Dieter 1986]. A dispersed second phase is defined as particle and can vary in size from sub-micrometer scale to many µm. Precipitation strengthening is usually additive to solid solution strengthening. It results from the supersaturated solution and ensures maximal solid solution strengthening. The degree of strengthening depends for example on size, shape, volume fraction and distribution, the crystallographic fit and elastic as well as plastic properties of the particles. The properties of the particles in turn result in internal variation of the stress state in the surrounding matrix and alter the properties of the matrix. Optimal strength and ductility values are usually achieved from a fine and homogenous dispersed harder second phase in the soft matrix. [Dieter 1986]

Precipitation strengthening can be achieved by the addition of second phase particles in powder form (usually oxides, carbides, nitrides or borides) or by a decreasing solubility of the alloying partner during cooling. Precipitation strengthening in Ti6Al4V uses the situation of decreasing solubility of Al in Ti with decreasing temperature. Ti₃Al precipitates during ageing at about 500°C [Luetjering 2007] and is clearly harder than the α phase [Fu 1995]. Additionally, the cubic β phase aggregates between the α grains.

Particle shearing occurs in Ti6Al4V because of small elastic strains induced from the coherently bound α_2 particles and their nanometre size. Luetjering and Weissmann describe the shearing of Ti₃Al as cutting mechanism [Luetjering 1970] and this is associated to an increase in the CRSS for dislocation glide [Hornbogen 2006]. The cutting or shearing process destroys the perfect ordering within one crystallographic plane, which requires additional energy compared to a dislocation movement in disordered material. The additional energy equals the antiphase boundary energy γ_{APB} . The CRSS increase depends on γ_{APB} , the burgers vector *b*, the particle distance S_T and particle diameter d_T .

$$\Delta \tau_S = \frac{\pi \gamma d_T}{4bS_T}$$

Equation 3-7: Force to shear a particle

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However, determination of size and distances from Ti₃Al precipitates in non or lightly aged Ti6Al4V is extremely difficult experimentally due to phase dimensions on the nano scale [Wu 2012].

3.3.6.Ordering in Ti-Al and effects on mechanical behaviour

An ordered alloy can be understood as multiple lattice structures from two or more elements in one perfect arrangement of atoms. This ordering can extend over a full crystal and is therefore referred to as long-range order (LRO), as in Ti₃Al or TiAl with stoichiometric composition. In under stoichiometric compositions with dilute solute concentration the ordering is usually limited to small regions, known as precipitates. Another possibility is that only partially ordered structures form, so called short-range order (SRO). In any case, the ordering reduces the total energy of the system at a given temperature [Smallman 1999].

Differential thermal analysis (DTA) and electrical resistivity measurements are classic methods to detect phase transformations. As exhibited by Sircar et al. [Sircar 1986], the α - α_2 phase boundary can be found for high AI concentrations using DTA technique but cannot show α_2 formation in Ti-10at.%AI. Resistivity measurements are a more sensitive means and Namboodhiri et al. could show α_2 formation at a concentration of only 4wt% AI (7at.%) [Namboodhiri 1973]. However, neither technique gives information about the precipitating phase, neither about the primary phase unlike in diffraction techniques. If an ordered structure can be better identified using electron, X-ray or neutron diffraction depends on the scattering properties of each element. While AI and Ti have rather similar scattering amplitudes for X-rays and electrons they have very different scattering amplitudes for neutrons [Smallman 1999, Thirumalai 2000]. Therefore electron and x-ray diffraction yield little contrast of both elements while neutron diffraction is much more appropriate to show any signs of ordering. Shul and Siegel demonstrated that an order-disorder transformation is not detectable when the scattering factors are too similar [Shull 1949].

Previous researchers found weak reflections when using TEM diffraction from samples of Ti-15at.%Al (500ppm O) after ageing (80h@550°C) [Wood 1998], where precipitates appeared spherical. Further ageing grows ellipsoidal precipitates along the c-axis [Luetjiering 1970, Wood 1998,] and enhanced the Ti₃Al reflections. The existence of α_2 precipitates has been reported at Al concentration as low as 8.5at.% [Chaze and Coddet 1987, Lütjering and Williams 2007, Truax 1974], which was also found to decrease the work hardening capacity of the alloy. Fig. 3-22 a) gives an example for α_2 precipitates visualised via dark field imaging and Fig. 3-22 b) shows the corresponding super lattice diffraction spot from aged Ti6Al4V.

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Fig. 3-22: Example for Ti₃AI precipitations in Ti6Al4V aged 100h at 500°C. a) DF image using the Ti₃AI reflection as indicated in b) the diffraction pattern on the $\langle 10\overline{1}0 \rangle$ zone axis [Gysler 1981]



a)

b)



Williams et al. report a particle size of 6nm estimated from X-ray line broadening techniques on aged Ti6.6 wt%Al (1 week at 550°C), while TEM dark field micrographs (Fig. 3-23 a) show somewhat larger precipitates [Williams 2002]. No article presented trustful signs of ordering below 10at.%Al with electron or x-ray diffraction. Koike et al. show signs of ordering by X-ray diffraction, but the peaks appear over proportionally large and at the wrong diffraction angle, making one believe that they are artefacts of sample preparation [Koike 2006].

The group of Mills found a diffuse peak at the position of the $\{10\overline{1}1\}$ -plane of Ti₃Al in neutron diffraction patterns as indicated with DP in Fig. 3-24 a, which becomes more intense with different ageing treatments as shown for one example in Fig. 3-24 b) [Thirumalai 2000]. The diffuse nature of those peaks indicates existence of SRO instead of LRO.

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Fig. 3-24: a) Neutron diffraction pattern of Ti-10Al with indicated peak positions for the hcp systems and the DP indicates the super lattice reflection of α_2 (λ =2.357Å) as magnified in b). b) also plots an aged sample with increased intensity of the {1011} peak of α_2 [Thirumalai 2000]

Ordered domains introduced by ageing have been known to strengthen the material for many decades [Evans 1968]. However, Williams et al. ascribed the α_2 -phase a negligible influence on CRSS due to coherent precipitates with a small misfit and a small difference in modulus between α - and α_2 -phase [Williams 2002]. Fu et al. summarised that the modulus of Ti₃Al is nearly 50GPa above the modulus of α -Ti [Fu 1995]. This should lead to a strengthening effect due to the requirement of anti-phase boundary formation. The shearing of a fully ordered domain will form an anti-phase boundary (APB) while a diffuse anti-phase boundary (DAPB) is formed when a SRO domain is sheared. First principle calculations suggest that the formation of a DAPB requires less energy than the formation of an APB for Ti₃AI [Fu 1995, Van de Walle 2002]. Planar slip is theoretically favoured in the presence of such ordering, as the first passing dislocation disorders the structure and subsequent dislocations reorder the structure partially and require therefore less energy than the first dislocation (Fig. 3-25). Dislocation coupling and planar slip are expected and become more prominent with AI concentrations above 7at.% (4wt%) and lower temperature as calculated from first principles and confirmed from experiments [Blackburn 1969, Paton 1973, Truax 1974, Van de Wale 2002, Williams 2002]. Illustration is given in Fig. 3-26 with multiple slip bands on prismatic planes with rather diffuse secondary slip lines on other planes surrounding them in Ti1.4wt%AI, while Ti-5wt%AI exhibits much sharper slip band with a serrated secondary slip band. The slip appears even more localized in the industrial alloy Ti6Al4V exhibiting therefore much higher dislocation density within the active slip bands [Jones 1981]. It may be noted that different slip systems disorder the DO_{19} structure to varying extend: The basal <a>-slip {0002} (1120) induces four nearest neighbours, while prismatic <a>-slip creates either only two "wrong" second nearest neighbours or two "wrong" nearest and four second nearest neighbours leading to soft and hard prismatic <a>-slip. Also <c+a> slip and cross-slip are inhibited by DO₁₉, leading to highly planar deformation [Luetjering 2007].



Fig. 3-25: Calculated DAPB energies as function of AI concentration, with k being the multiple of the burgers vector. Concentrations are given in at.%. [Van de Wale 2002]



Fig. 3-26: Deformation slip on prismatic planes in a) Ti-1.4wt%AI, b) Ti-5wt%AI [Wililams 2002] and Ti6AI4V [Jones 1981], showing more localised slip towards higher AI concentrations.

Recent TEM investigations have indeed confirmed the formation of coupled dislocations with increasing degree of SRO. Neeraj and Mills undertook creep experiments with three different heat treatments for Ti6wt%Al (Ti10at.%) to observe the effect of SRO. They annealed for 24h at 900°C and either ice water quenched (IWQ) to reduce the formation of ordering or air cooled (AC) to room temperature to give little time for ordering effects. In order to introduce more prominent order they step aged the material at 600°C and for 24h and at 400°C for another 5h. The ice water quenched samples showed the lowest creep resistance and homogeneous deformation, as seen in Fig. 3-27. 'There was no glide plane softening effect to cause planar slip' whereas the air cooled sample and the step aged sample showed planar slip in basal, prismatic and pyramidal planes and higher creep resistance. Fig. 3-28 a) shows homogeneous dislocation distribution when little ordering is present and increasingly localised dislocations with increasing ordering (b and c). The pairing of the first few lead dislocations has been attributed to SRO, whereas dislocations become equally distanced further away from the leading dislocations. This indicated that the SRO-regions have been sheared and dislocations can move with fewer restrictions subsequently [Neerai 2001]. The group of Mills concluded: 'The presence of SRO leads to persistent, highly planar slip resulting in extended pile-ups at grain

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boundaries and interfaces' [Brandes 2004] and locally very low work hardening rates and minimises the interaction between slip systems during creep experiments [Neeraj 2000]. Planar slip leads macroscopically to little strain hardening in Ti alloys [Neeraj 2001].



Fig. 3-27: Creep strain as function of time for step aged, air cooled (AC) and ice water quenched (IWQ) samples [Neeraj 2001]



Fig. 3-28: Deformation in a) ice water quenched sample with homogeneous slip, b) air cooled sample with slip concentrated in screw pile-ups and c) step aged sample with planar slip in basal planes and [Neeraj 2001]

3.3.7.CRSS dependencies

CRSS values for all the deformation systems are sensitive to impurities and alloying elements [Philippe 1988]. Dieter and Bacon assume that solid solution atoms increase the CRSS more when the atomic size difference between solvent and solute atoms increases. Interactions between populations of dislocations and defects like vacancies, interstitial or substitutional atoms increase the CRSS. [Dieter 1986]

The major reason why it is so difficult for present literature to agree on CRSS values for particular deformation systems is their dependence on multiple factors like sample size, strain rate or temperature. For example a temperature increase lowers CRSS values for prism and basal <a>-slip as well as for <c>-component deformation [Williams 2002, Partridge 1967], as shown for Ti and Mg in Fig. 3-29. To represent those dependencies of CRSS values complex functions are required, backed up by experimental work.

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Fig. 3-29: CRSS values for prism and basal slip in Mg and Ti as function of Temperature [Partridge 1967]

Comparison of experiments at ambient temperature on single crystals [Sakai 1974] and micro cantilevers of Ti [Gong 2009, Gong 2010] have shown that smaller crystals with similar chemistry exhibit higher CRSS values, as summarised in Fig. 3-30. A reasonable power law fit can be applied even though different methods of testing are compared in Fig. 3-30.



Fig. 3-30: CRSS values for prismatic slip as function of the testes crystal size by various authors [Gong 2009, Gong 2010, Sakai 1974]

Of highest significance for the current work is the observation that CRSS values in Ti are dependent on the AI concentration [Sakai 1974, Williams 2002]. Fig. 3-31 plots literature data of single crystal work on Ti-AI binaries for ambient temperature as function of the AI concentration and shows that the CRSS for basal and prismatic <a> slip become approximately equal at 12-14at.% AI. CRSS values for prismatic <a>-slip from Sakai and Fine agree roughly with data from Williams et al. for prismatic slip at room temperature, summarised in Fig. 3-31, but the Arnas Fitzner, PhD Thesis, 2014

scavenging effect between interstitials and AI as described by Sakai and Fine is not captured. Apart from minor differences in the used crystal sizes, differences in interstitial and impurity concentrations for the datasets may explain this discrepancy. Sakai's crystals had very low O and N concentrations (below 500ppm and 150ppm), and C levels of 100-300ppm but no values are given from Williams et al.

Next to comparably easier basal slip with AI addition also pyramidal slip becomes comparably easier. Care has to be taken interpreting data in Fig. 3-31 as the very low CRSS values for <c>- component deformation below 6at.% AI are affected by compression twinning while only the CRSS values above 8at.% actually represent c-component slip. [Williams 2002]



Fig. 3-31: CRSS values for prismatic, basal and <c>-component slip from single crystal compression [Wiliiams 2002]

Recent investigations focus on the effect of the stacking fault energy on slip activity, which is discussed in the following chapter.

3.3.8.Stacking faults

Properties like electric resistivity, work hardening rate, creep and corrosion properties as well as phase morphology or crystallographic transformations and, most important for the current study, textures after recrystallization and deformation were linked previously to the stacking fault energy [Cahn 1996]. Smallmann and Green [Smallmann 1964] concluded that the SFE energy might be the governing factor in the rolling texture formation of Ag- and Cu-alloys. A decrease in SFE delays dynamic recovery in Cu-AI binary alloys [Rohatgi 2001], which may impede deformation of Ti alloy at high temperature [Williams 2007]. Rohatgi et al. also describe that low SFE promotes slip localisation [Rohatgi 2001], which is found at higher AI contents in Ti. Guo et al. even give the reduction of SFE with AI addition a major role in the strengthening but neglect literature reporting about the onset of SRO already from 7at.% [Namboodhiri 1973] instead of the 9at.% were Guo et al. consider ordering to start [Guo 2006].

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In the following stacking sequences and their faults are described followed by the effect of alloying on the SFE and its usefulness to describe dislocation activity.

3.3.9. Stacking sequences and faults

A perfect crystal has a perfect stacking as shown in Fig. 3-32 for fcc a) ABCABCA and hcp d) ABABAB structure. Deformation will change these perfect sequences and can introduce in principal three kinds of stacking errors. Slip between A and B layer in fcc results in ABCA|CAB stacking (b), which shows four layers of perfect hcp stacking: CACA. This intrinsic stacking fault (I₁) a removal of a close packed layer of atoms and is the most common fault, causing broadening and shift of diffraction peaks. An extrinsic stacking fault (I₂) denotes the insertion of an extra close packed layer of atoms and results in ABC|ACB|CA stacking, which is the original fcc sequence forward and reversed (in Fig. 3-32 c). As the extrinsic fault involves more partial dislocations and a more complex movement it occurs less frequently. The sequence ACB is called twin. The twin is a region with higher free energy than the fcc structure. The twin (or growth) fault (hcp) is bound in the fcc matrix by partial dislocations. [Cahn 1996]



Fig. 3-32: Faulted structures: a) perfect fcc packing, b) intrinsic stacking fault after slip in fcc, c) extrinsic stacking fault in fcc including twin and d) perfect hcp packing [Dieter 1986]

3.3.10. Stacking fault probability evolution when alloying Ti

A review by Gallagher shows a decrease in stacking fault energy or an increase in the inversely related stacking fault probability (SFP) for several alloying systems with increasing solute content, while some alloying systems show very little effect with concentration [Gallagher 1970]. More recently an increase in stacking fault probability was reported for addition of Sn to Zr [Sastry 1974] or AI to Cu [Rohatgi 2001 and most important for AI [Metzbower 1971, Arnas Fitzner, PhD Thesis, 2014

Shishmakov 1972, Guo 2006, Ghosh 2008] (see Fig. 3-33), Zr [Sen 1998] or Sn [Shishmakov 1972] to Ti. The effect of Zr seems strongest initially, but flattens out above 6at.% [Sen 1988], while Sn has a stronger effect than Al per at.% but similar effects per wt% [Shishmakov]. Sen et al. further conclude on complex Ti-Al alloying systems that the presence of Vanadium or Molybdenum raises the stacking fault energy [Sen 1998]. Furthermore, increasing stacking-fault probability was found with increasing levels of O, C, N and Fe [Biswas 1973].





At solute concentrations close to the solubility limit the stacking fault energy increases again towards the formation of Ti_{50} -Al₅₀ and is practically independent of Al content in ternary alloys Ti-Al-Nb [Zhang 2002]. An increase in SFE was also found in α -brasses with sufficient time for ordering at increased Zn content, as shown Fig. 3-34 [Thomas 1963]. SRO can increase the SFE furthermore supported by wider dislocation nodes in disordered Cu-Al compared to ordered samples as summarized by Cohen and Fine [Cohen 1962]. Contrary to those results Sastry and Ramaswami show for the Cu-Au system that Cu₃Au single crystals have a higher SFE in disordered state compared to an ordered state [Sastry 1976].



Fig. 3-34: The dependence of SFE of α-brass on Zn content and heat treatment [Thomas 1963]

While measurements of SFP clearly document an increase with addition of AI to Ti, as indicated with the black dashed line for the overall trend in Fig. 3-33 and upon O addition at different AI levels (as indicated in Fig. 3-33 for the results of Metzbower), it is unclear how the state of ordering affects the SFP or SFE in the Ti-AI system. Therefore, assumptions of the influence of the SFE on solution treated Ti-AI alloys can be made but not for aged and ordered variants.

Arguments on dislocation mobility are often based on SFE instead of the indirectly related SFP. Metzbower suggests an empirical relation, which was rewritten for the Ti-Al system by Guo et al. as given in Equation 3-8, with the Al concentration c_{Al} . However, a fully physically based relation between SFP and SFE is not available at present, which limits the power of any arguments based on SFE.

$$SFP = 0.003 \exp(0.133 c_{Al})$$

Equation 3-8: Relation between stacking fault probability and AI concentration [Guo 2006]

For CP-Ti, the hcp stacking sequence is ABAB... for basal planes and the stacking fault energy is high. The addition of Aluminium increases the likelihood for sequences of ABCABC... stacking, similar to the (111) planes in fcc structures. It is a fundamental difference to introduce a fcc stacking in a hcp structure compared to the case in fcc materials where stacking faults introduce a hcp structure. Previous investigations on stacking faults in fcc materials cannot directly be applied to stacking faults in hcp materials. Previous simulations of hcp-materials are not especially conclusive, mainly valid for cryogenic temperatures and depend on the used potential [Bacon-a 1981, Bacon-b 1981].

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3.3.11. Calculation and application to dislocation motion

Where experimental data are lacking, first principles are most appropriate to calculate the generalised stacking fault (GSF) energy, as shown in a comparison between modelling approaches and experimental values from Wu et al, on Mg [Wu 2010]. The same method applied to other hcp metals under consideration of spin polarisation suggests a dependency of the GSF from the volume of the hcp-unit cell and the c/a ratio between Be, Ti, Zr, Zn and Mg. Smaller c/a ratios compared to ideal c/a ratio and decreasing volumes can be connected with higher SFE in this calculations on pure metals. Energy maxima per material in Fig. 3-35 represent unstable stacking faults. The energy minima at the final positions of the burgers vector (1/3 <11-20> are intrinsic, stable stacking faults [Wu 2010]. Interestingly the position of the unstable stacking fault depends on the element.



Fig. 3-35: Generalised stacking fault energy for different hcp metals for basal <a> slip [Wu 2010]

Many of such calculations are required to plot the γ -surface, describing the energy requirement to shear the crystal on a given slip plane. Fig. 3-9 shows the γ -surfaces for the basal and prismatic plane in Ti. Minima reveal metastable stacking faults and help to describe the dislocation activity [Wu 2010, Pei 2013]. Prismatic planes in Ti and Zr for instance have lower SFE than basal planes and dislocations dissociate therefore easiest on prismatic planes [Domain 2006].

Theory and experiment confirmed that lowering stacking fault energy (SFE) leads to a greater separation of partial dislocations on the twin-matrix interface and therewith to a wider stacking fault and facilitated twin nucleation but impeded growth in fcc materials [Dieter 1986, Cahn 1996, Zhang 2009]. Practically, a lower SFE is related to increased twin nucleation but reduced width in fcc materials. The effect of SFE reduction on slip is described as a transition from a cellular dislocation structure in high SFE materials, where cross slip is active, to less cross slip activity and slip on rather defined slip bands in low SFE (fcc) materials [Rohatgi 2001]. Arnas Fitzner, PhD Thesis, 2014

Especially the observations of increased slip planarity can be confirmed for the Ti-Al and Ti-O systems but the reported loss of twinning is in contradiction [Wasz 1996, Williams 2002]. It is also known that metals with a lower SFE strain-harden more rapidly and twin easily on annealing [Dieter 1986], letting one expect that the addition of Al, Sn or Zr (which all reduce the SFE) increases the work hardening rate, twin activity and introduces planar slip.

3.3.12. Effect of alloying on twinning

Experimental evidence shows that alloying α Ti with elements like O and Al decreases the twin fraction [Wasz 1996, Williams 2002]. Also the ternary alloy Ti5Al2.5Sn is reported to twin less than CP-Ti under tension at ambient and elevated temperature [Li 2013].

However, substitutional elements can increase the likelihood for twinning in face centred cubic (fcc) materials and Zr alloys [Fundenberger 1990, Rohatgi 2001]. For instance an decreasing SFE with alloying in Cu-Al alloys (fcc) was connected to thicker twins [Zhang 2009] but also to a general decrease in the twin stress [Venables 1964, Meyers 2001] and twin activity [Rohatgi 2001]. Studies on other Ti-alloying systems, apart from Ti-Al and Ti-O, have not mentioned the development of twin activity with alloying previously but the SFE evolution would let one expect to see increased twin activity with addition of Al, Sn or Zr to Ti [Metzbower 1971, Shishmakov 1972, Cahn 1996, Sen 1998, Guo 2006, Ghosh 2008]. As Zr seems to increase the likelihood for faulting much more than Al, especially at low concentrations becoming much less effective towards concentrations of more than 10at.% [Sen 1998], twin activities would be expected to increase more rapidly than with Al addition. The effect of Sn per at.% is stronger than Al's effect on the SFP [Shishmakov 1972], but not as pronounced as the effect of Zr suggesting intermediate twin activity in Ti-Sn alloys compared to the other two alloying systems per atom percent solute.

3.4. Textures in Titanium alloys

'The sum of the crystallographic orientations of the crystallites within a polycrystalline aggregate is known as the texture of the material' [Humphreys 2004]. Textures develop during thermomechanical treatments and determine mechanical and environmental properties [Humphreys 2004]. Therefore it is necessary to understand texture development in various production routes and to develop processed titanium alloys in which the anisotropy of mechanical properties matches the most critical loading direction during service [Bache 2001].

Textures measured via X-ray or neutron diffraction are most comprehensively represented in pole figures (PF) or inverse pole figures (IPF) and additionally as orientation distribution function (ODF). However, local texture deviations, which might contribute to the failure of parts in service, can only be found with EBSD texture mappings. [Engler 2009]

3.4.1.Cold rolling texture

A cold rolled CP sheet shows no significant basal intensity in ND, with main intensities 30° from ND to TD and a spread of the basal pole to TD. Prismatic planes show strong intensity in RD Fig. 3-36 [Zherebtsov 2011]. Heavy cold working leads to refinement of microstructure, which results in increase of strength and better fatigue properties. During cold rolling three stages of microstructural evolution were observed by Zherebtsov et al. Stage one, up to 20% strain, is associated with deformation twinning and introduction of high misorientations locally. Compression twinning of type $\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ is dominant in CP-Ti during cold rolling and $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tensile twins are about half as frequent [Bozzolo 2010]. During stage two the dislocation density increases and the local texture changes only gradually, until the subsequent formation of high angle grain boundaries in stage three. In all strain levels is a formation of low angle boundaries present and the dislocation density is high, but the rate increase of high angle boundaries is higher above 50% strain. [Zherebtsov 2011]



Fig. 3-36: $\{0002\}$ and $\{10\overline{1}0\}$ pole figures of 266% cold rolled CP Titanium [Zherebtsov 2011]

The content of alloying elements has only a small influence on the texture evolution during cold rolling, as Fig. 3-37 shows. CP-Ti with high oxygen content shows a very strong intensity in ND Arnas Fitzner, PhD Thesis, 2014
with little spread to TD (Fig. 3-37 a), whereas 4% Al in Ti causing a symmetric distribution within 30° around ND (Fig. 3-37 b). Addition of both, Al and N leads to slightly less symmetry of the distribution around ND (Fig. 3-37 c). [Philippe 1988]



Fig. 3-37: Texture change after cold rolling with alloying elements: High oxygen CP-Ti a), Ti-7AI b), Ti5AI2.55N c) [Philippe 1988] and d) Ti6AI4V [Stapleton 2008]

The presence of second phases together with higher alloying contents leads to different texture developments during rolling and macro zone formation in more complex alloys like Ti6Al4V [Britton a 2010]. In an unidirectional rolled Ti6Al4V sheet basal planes of the crystallographic unit cell are aligned parallel to the transverse plane of the sheet (in Fig. 3-37 d) and in rolling direction elongated grains or grain clusters appear in a matrix of annealed α -grains [Bache 2001, Stapleton 2008]. The current literature does not explain the dramatically altered texture in a hot rolled sheet of Ti6Al4V compared to cold rolled sheets of CP-Ti.

3.4.2. Texture changes during deformation and the role of alloying

In various Ti and Zr alloys only minor changes could be observed in basal poles after tensile tests. A gradual rotation of the a-axis towards tensile axis could be observed when slip is active, as schematically shown in Fig. 3-38 a). However, $\{11\overline{2}2\}$ and $\{10\overline{1}2\}$ twins appeared after 10% tension along the former RD and lead to a more drastic texture changes, as schematically shown in Fig. 3-38 b) [Philippe 1988]. Fig. 3-39 is a schematic of the typical misorientations induced by twinning on a pole figure for a) $\{11\overline{2}2\}$ compression twinning, b) $\{10\overline{1}2\}$ tension and c) $\{11\overline{2}1\}$ tension twinning.



Fig. 3-38: Rotation of 0002 poles due to only slip after 5% deformation a) and with operation of $\{11\overline{2}2\}$ and $\{10\overline{1}2\}$ twins b) [Philippe 1988].

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Fig. 3-39: Lattice rotation of the basal pole for a) $\{11\overline{2}2\}$, b) $\{10\overline{1}2\}$ and c) $\{11\overline{2}1\}$ twinning systems for Zr [Philippe 1988].

Only specific twin systems can get activated under tensile or compressive loading in the same direction in respect to the c-axis in one loading situation due to the polar nature of twinning. The activation of slip systems depends on the crystal orientation in respect to the c-axis. The active deformation systems change texture, microstructure development and strain hardening behaviour in characteristic ways [Philippe 1988]. Fig. 3-40 presents stress strain curves; a) and the strain hardening behaviour; b) from simple compression test from textured CP-Ti; c) and high purity Ti (HP-Ti); d) in different loading directions. It can be seen in Fig. 3-40 that the work hardening rate is much increased in the CP-Ti compared to the HP-Ti, at any given loading direction [Wu X. 2008].



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Fig. 3-40: True stress-strain curves a) and strain-hardening behaviours b) in simple compression test on CP-Ti and HP-Ti in different loading directions and initial textures of annealed samples for CP-Ti b) and HP-Ti c) [Wu X. 2008]

Wu et al. summarise that compression perpendicular to c-axis (TD) leads to a lower yield stress and a high Stage B of the hardening rate with deformation twinning active in most grains. Compression parallel to c-axis (ND) leads to higher yield strength and twins are not appearing in all grains simultaneously which results in a lower work hardening rate [Wu X. 2008]. Intermediate loading situations between c-axes and loading direction result in intermediate flow stresses. But exceptions occurred, where intermediate angles leads to high flow stresses [Battaini 2007]. The difference in texture of a unidirectional rolled sheet of CP-Ti and Ti6Al4V is very pronounced. The industrial alloy Ti6Al4V has a predominant basal texture with the basal poles parallel to the transverse plane of a unidirectional rolled sheet after hot rolling [Fundenberger 1997, Bache 2001]. The basal pole intensity of cold rolled CP-Ti sheet is very little in the transverse and much more pronounced in the normal or rolling direction [Wu X. 2008]. Fundenberger et al. report that the compressive yield strength is higher in the transverse compared to rolling direction which is in contradiction to the results from Wu et al. on CP-Ti [Wu X. 2008]. Similar to the compressive behaviour the tensile yield strength [Fundenberger 1997] and the ultimate strength [Bache 2001] are higher during tensile loading parallel to the transverse direction compared to the rolling direction (longitudinal), as shown in Fig. 3-41 a), as the c-axis is stiffer and harder in comparison to the a-axis (Fig. 3-2). It shall be noted that the properties during high cycle fatigue (HCF) not necessarily correspond to static values [Bache 2001].



a)

b) Fig. 3-41: a) Texture sketch of a uniaxial rolled sheet Ti6Al4V and b) the corresponding stressstrain curves for tensile tests in transverse and rolling direction, parallel and perpendicular to caxis respectively. [Bache 2001]

From the presented work it can be seen that the loading direction not only influences the yield strength of the material but also the work hardening behaviour [Bache 2001]. Understanding the mechanical behaviour of a full range of alloys becomes more complicated as each alloy has its own yield strength and work hardening behaviour. In turn the relative activity of deformation systems in an alloy has its effect on texture evolution during forming. In order to forecast the Arnas Fitzner, PhD Thesis, 2014

texture of a product or to produce a mechanically isotropic part it is necessary to understand how the texture of the material develops at each hot and cold forming stage.

4. Experimental materials and methods

This chapter explains the choice of alloying compositions and describes their manufacturing at Timet - Witton, characterisation methodologies at the University of Manchester and at the neutron spallation source ISIS.

4.1. Compositional choices of binary model alloys

The current study investigates the effect of alloying elements on the deformation mechanism in α Ti. Due to the complexity of alloying the study focuses on effects in three binary alloying systems. Based on industrial relevance AI, Sn and Zr have been chosen. The Ti-AI system is represented by fractions of 3.5, 7, 10 and 13at.% AI (2,4,6 and 8 wt%), the Ti-Sn system by fractions 1 and 3.5at.% Sn (2.4 and 8.1wt%) and the Ti-Zr system by 3.5 and 10at.% Zr (6.6 and 17.5wt%). Additionally combined effects of AI and O are investigated on the model alloy Ti-10AI-O. Combined effects of AI and V or Sn are investigated on the industrial alloys Ti6AI4V and Ti5Al2.5Sn. The relation between weight percent and atomic percent for all alloys is given in Fig. 4-1.





The binary model alloys of the current study allow comparisons of macroscopic material properties on carefully chosen equal atomic fractions of different alloying elements and are therefore named in accordance to their solute content in at.%. The alloy Ti-1Sn, with only 1at.% Sn, gives the smallest atomic fraction and contains just more than 1 Sn in 96 atoms. A direct comparison between all three substitutional elements can be realised on a concentration of 3.5at.%, just more than one solute atom out of 32 atoms. This translates in wt% to a comparison between 2wt%AI, 6.5wt%Zr and 8.2wt%Sn. Effects of AI and Zr can be further

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compared on a concentration of 10at.%, corresponding to 6wt%Al and 17wt%Zr. With now more than 3 substitutional atoms per 32 solvent atoms ordering of the solute atoms can occur more likely. Superior strengthening effects of Al raise industrial and academic interest and therefore also Ti-Al alloys with 7at.% and 13at.% (4wt% and 8wt%) have been manufactured at Timet.

In order to visualise the quantities of substitutional atoms in the present alloys, structures were drawn in Fig. 4-2. The baseline is the hcp-structure without substitutional elements. When 25at.% of Al or Sn are dissolved in Ti the ordered DO₁₉-structure forms [Mishin 2000]. This so called α_2 phase contains 15.8wt%Al in the case of Ti₃Al and 45.3wt% Sn in the case of Ti₃Sn. The solute concentration of the present model alloys range between these two extreme concentrations (0 and 25at.%). Simple atomic fractions of the DO₁₉ structure with 12.5at.%, 9.375at.%, 6.35at.% 3.125at.% and 1at.% are depicted by filling the solute atoms with solvent atoms. Note that the structures are not calculated and only visualise the quantity of solute atoms in the matrix. The model alloys of the present study are written next to the structures in Fig. 4-2 according to their atomic concentrations, even though the actual atomic concentrations are slightly above the depicted concentrations. From a statistical point, solute atoms in these model alloys at equal atomic concentration should have the same chance to occupy lattice sites and form bonds. But driving forces to minimise the energy of the system result most likely in different arrangements. For instance first principles calculations (VASP) kindly conducted by Scotti, revealed that Sn atoms repel each other more than Al atoms do and Sn atoms attractwhile AI atoms repel vacancies [Scotti 2014]. Binding energies between Zr atoms are more than one magnitude smaller, but attractive for 1st nearest Zr atoms while second nearest Zr atoms repel each other.



Fig. 4-2: Possible arrangements of substitutional atoms in the HCP matrix for atomic fractions of the DO₁₉-structure [Graphics adapted from [Mishin 2000])

4.2. Practical aspects of model alloy manufacturing

Timet produced Titanium with low O contents (CP-Ti) and binary Ti-Al alloys with 2, 4, 6 and 8 weight percent (wt%) Al, based on the same batch of Titanium sponge containing 250-350ppm O. These wt% values equal 3.5, 6.9, 10.1 and 13.1 atomic per cent (at.%) respectively. These concentrations of one of the most effective solid solution strengthening elements in Ti [Donachi] allow insight into the gradual change of deformation twinning with Al content. To understand better how and why the rather high twin activity in CP-Ti vanishes nearly completely at concentrations of 6-8wt% Al also other solutes have been investigated.

According to the atomic concentrations of AI and practical aspects compositions with Tin and Zirconium were chosen and manufactured. Fig. 4-1 illustrates that 2wt% AI, 6.4wt% Zr and 8.1wt% Sn all posses roughly the same atomic solute concentration of 3.5at.%. The direct comparison at 10at.% is only possible for AI and Zr in the single-phase field, with 6.6wt% and 17.5wt% respectively. Sn is expected to form a considerable amount of precipitations at a concentration of 21wt% (10at.%) [Liu 2005]. Therefore the alloy is not considered and instead a commonly used concentration of 2.5wt%, or 1at.%, was manufactured as binary model alloy.

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With oxygen as one of the most important interstitial elements, the binary alloy Ti-10AI was infused with 4000ppm oxygen, labelled as Ti-10AI-O in Fig. 4-1. As benchmark, the industrial alloy Ti6AI4V has also been manufactured by the same route, with an overall AI content of 6.5wt%, 4.15wt% V and 2011ppm Fe. It should be kept in mind that the two phases of this α - β alloy have different compositions with V mostly in the β -phase and AI mostly in the α phase. The industrial alloy Ti5AI2.5Sn has also been investigated, but originates from an industrial forging route and contains in addition to 5.1wt.%AI and 2.7wt.%Sn also 1400ppm Fe. The latter three alloys have been plotted in Fig. 4-1 according to their AI concentration only.

The different alloying elements have, dependent on their atomic weight, positive or negative effects on the alloy density as shown in Fig. 4-3. Whilst AI makes the alloy lighter, all other chosen elements will lead to a higher density, which is generally detrimental when targeting light alloys. However, the industrial alloys Ti6Al4V and Ti5Al2.5Sn still have lower density than CP-Ti due to the high AI content.



Fig. 4-3: Alloy-density as function of solute content

It is helpful to revise a few atomic details from the alloying elements at that stage (see Tab. 4-1). This allows more fundamental comparisons and views on the alloys. Only Zr has an approximately 10% larger diameter compared to Ti, while all other elements have smaller diameters. Al has a small misfit of the atomic diameter, while Sn has a three times higher misfit.

Symbol	Element	Atomic	Relative	Diameter	Atomic	ΔV	Δd
		number	atomic	d [pm]	Volume V	[%]	[%]
			mass		(sphere)		
					[pm^3]		
Ті	Titanium	22	47.867	289.6	12717282	0	0
AI	Aluminium	13	26.982	286.4	12300355	-3	-1

Tab. 4-1: Atomic measures of used eleme	nts [Merck 2011]
Tab. 4-1. Atomic measures of used element	

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Zr	Zirconium	40	91.224	318.0	16837592	32	10
Sn	Tin	50	118.710	281.0	11617631	-9	-3
v	Vanadium	23	50.942	268.0	10078665	-21	-7
Si	Silicon	14	28.086	235.2	6812564	-46	-19
Fe	Iron	9	18.998	141.8	1492888	-88	-51
N	Nitrogen	7	14.007	142.0	1499214	-88	-51
С	Carbon	6	12.011	154.4	1927261	-85	-47
0	Oxygen	8	15.999	120.8	922995	-93	-58

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4.2.1.Casting, β -forge of model buttons

All model alloys were produced at Timet. – Witton, where they were double melted in a tungsten arc furnace under inert gas atmosphere to ensure a homogeneous distribution of alloying elements and low porosity. The 'as cast buttons', were completely transformed into β -phase during annealing at 1100°C for 1h. Buttons were β -forged using a screw press with 5 blows in one direction and after a 90° rotation another 5 blows in the other direction. Fig. 4-4 a) shows a cold as cast button in the screw press. Afterwards a third forging was conducted to ensure that the buttons are 26mmx26mm in cross section before the buttons were air cooled to room temperature (see Fig. 4-4 b).





Fig. 4-4: a) Forging of a "as cast button" (cold) and b) a β -forged button 4.2.2. α -cross roll of model buttons

Afterwards, the buttons were cross-rolled without lubricants on a 2 high Robertson mill made by WHA Robertson & Co Ltd (Fig. 4-5 a). The rolls were cold, separated in three gaps (Fig. 4-5 b) and about 130mm in diameter and have a length of 152 mm and spin with 26rpm. Before cross-rolling the β -forged buttons were heated up for 20min to 870°C in normal atmosphere.



Fig. 4-5: a) Rolling mill (2 high Robertson mill) and b) the rolls enlarged with gaps 1; 2; 3 (from left to right)

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The mill was initially totally open, so that 13.75 turns of the hand wheel were possible before it closes. With each turn of the hand wheel the rolls come 0.7mm closer together. The button was put in the first gap, with a cross section from 20mmx20mm, that the mill could grasp the button and pull it through. A worker took the button at the backside to twist it 90° and pass it to the front, where the button was put in the mill again. Now the height of the mill was reduced by 0.7mm (one revolution of the hand wheel) and the button was rolled two times with a 90° twist in between again. Two further cross-rolling steps were undertaken with one revolution of the hand wheel after each rolling pass. Reheating of the button followed for about 20min. The temperature after reheating could not be measured, but the thermocouple in the furnace reached the set temperature 15min after the first rolling step. Before further rolling steps, the height was reduced by two turns of the hand wheel. The button was cross-rolled again and 3 further height reductions were conducted with a cross rolling step for each reduction before the button was reheated in the furnace for 10min. The furnace picked up temperature now only 2 min after the rolling finished. Afterward the procedure was repeated one more time in the 20mmx20mm gap until the mill was nearly closed.

In order to use the second gap, with 15mmx15mm cross sectional area, the hand wheel was opened by 7.75 turns. The reheated button was cross-rolled in 4 steps. A reheating for 15min followed and the height from the mill was closed two more turns. Four steps of cross-rolling where conduced again with one turn of the hand wheel to reduce the height in between of each step. After seven min of reheating the button was cross-rolled in the final gap 3, with cross section of 10mmx10mm, and then straightened under a balance and finally air-cooled. The whole rolling procedure is visualised in Fig. 4-6.



Steps of reduction during cross rolling

Fig. 4-6: Visualised rolling plan, strain as function of rolling steps

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4.2.3.Heat treatments

The as-rolled bars were annealed to achieve homogeneous, recrystallised microstructures. The furnace (Carbolite CTF, CAR19 as shown in Fig. 4-7) was flushed with argon before heating to minimise oxygen contamination in the alumina tube. Temperatures were measured with a thermocouple before and after each treatment.



Fig. 4-7: Tube furnace (Carbolite furnaces, CTF, CAR19) for heat treatment

To establish equal grain size for all alloys, the samples were cut to 3 to 5mm thick pieces and annealed for 5hrs at distinct temperatures. As known from earlier work by Luke Marshall in collaboration with Timet and the University of Sheffield, the recrystallisation temperature for the Ti-Al alloys had to be 30°C below the respective β -transus temperature to achieve an equal grain size of approximately 80µm for the different alloys. Due to differing transus temperatures [ASM Handbook 1992] and diffusion rates [Perez 2003] the temperatures need to be chosen carefully to get different alloys with equal grain size. The temperatures for the Ti-Al alloys are listed in Tab. 4-2. Furthermore, ageing treatments were applied, where the samples were cooled slowly from the recrystallisation temperature (T_{RX}) with a rate of 10K/hour about 30K below the α_2 transus temperature, as reported by Nambhoodhiri [Namboodhiri 1983] and hold subsequently at this temperature for a week.

Annealing trials for the binary Ti-Sn and Ti-Zr alloys were accomplished with the same initial approach. The industrial alloys Ti6Al4V and Ti5Al2.5Sn were heat-treated as commonly reported in the literature, but using the same cooling rates as in the binary Ti-Al alloys of the present work. All heat treatments are given in Tab. 4-2.

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Alloy	T _{Forge}	T _{Roll}	T _{RX}	t _{RX}	Cooling rate	T _{AGE}	t _{AGE}
	[°C]	[°C]	[°C]	[hrs]	[K/hr]	[°C]	[hrs]
CP-Ti forge	Forging	-	700	0.5	>1000	-	-
СР-Ті 750	1100	750	700	5	>1000	-	-
СР-Ті 870	1100	870	700	5	>1000	-	-
Ti-3Al	1100	870	895	5	>1000	-	-
Ti-7Al	1100	870	933	5	>1000	-	-
Ti-7Al aged	1100	870	515	160	10	420	120
Ti-10Al	1100	870	968	5	>1000	-	-
Ti-10AI aged	1100	870	968	5	10	420	120
Ti-10Al low O	1100	870	968	5	>1000	-	-
Ti-10Al high O	1100	870	968	5	>1000	-	-
Ti-13Al	1100	870	990	5	>1000	-	-
Ti-1Sn	1100	820	860	8	>1000	-	-
Ti-1Sn aged	1100	820	860	8	>1000	450	120
Ti-3Sn	1100	820	860	25	>1000	-	-
Ti-3Sn aged	1100	820	860	25	>1000	450	120
Ti-3Zr	1100	750	834	25	>1000	-	-
Ti-3Zr SG	1100	750	824	5	>1000	-	-
Ti-10Zr SG	1100	750	750	25	>1000	-	-
Ti6Al4V	1100	870	860	24	>1000	-	-
Ti6Al4V aged	1100	870	860	24	10	420	120
Ti5Al2.5Sn	Forging	-	815	15	>1000	-	-
Ti5Al2.5Sn aged	Forging	-	815	15	10	400	48
Ti685	Forging	-	968	13	>1000	-	-

Tab. 4-2: Overview of alloys and heat treatments

4.2.4. Chemical Analysis

Timet – Savoie carried out all chemical analyses of the alloys used within the present study. Metallic elements were probed using ICP (Inductively coupled plasma) technique on a HORIBA Ultima2. C was probed on a HORIBA EMIA 820V combustion analyser, O and N on a LECO EF-400. The results in Tab. 5-1 are given in weight percentage where indicated, otherwise in ppm. While C, N and metallic elements were measured on anealed test pieces of 14x7x3mm, O concentrations were measured on halved compression samples to avoid the O intake during annealing. For fundamental purposes it is preferable to look into the compositions in atomic percentage. Therefore Equation 4-1 was applied to convert the concentrations of main alloying elements into at.% (see Tab. 5-2), while impurities were neglected. As alloys should be designed after atomistic considerations, Equation 4-2 gives the conversion from at.% of a complex alloy into wt%.

$$at\%_n = \frac{\frac{P_n}{A_n}}{\sum_{i=1}^{N} \frac{P_i}{A_{ni}}}$$

Equation 4-1: Conversion into at.% for complex alloys

$$wt\%_n = \frac{P_n A_n}{\sum_{i=1}^N P_i A_i}$$

Equation 4-2: Conversion into wt% for complex alloys

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4.3. Metallographic preparation

For the investigation by a optical microscopy the area of interest was cut free with an Al₂O₃particles reinforced blade. The wheel was set to 4000rpm and 1.0mm feed rate for most of the alloys. The Ti-Sn alloys needed cutting with 2000rpm and only 0.8mm feed rate to not break the blades. After cutting, samples were ground with P240 Silicon-Carbide grinding papers to remove sharp edges. Then, they were mounted in Bakelite by 7min heating at 180°C and 20 kN pressure. After 3 min cooling time the resin was cured and ready to grind. All samples were ground with sample-surface and resin-bottom being parallel to each other. By using Si-C grinding papers of the following steps P320, P600, P800, P1200, P2500 and P4000 a flat surface for polishing was prepared manually. Occasionally the final grinding step using P4000 paper was repeated using a single sample holder for 6 samples on a Struers TegraPol-31 with 10kN force, 150rpm for 1min to 5min. Few samples were polished manually with polycrystalline diamond suspension after grinding. The polishing behaviour differs strongly between titanium alloys and takes longer time in softer alloys [Donachi 2000]. Until all parallel scratches from grinding were replaced by the randomized polishing scratches on a shiny surface prolonged times were required (up to 120min) using a 6µm diamond paste. Good finishes have been achieved with further polishing using oil or water based suspensions from 3µm, 1µm and ¼µm diamonds. To avoid any deformed layer from metallographic preparation a combined chemicalmechanical polish was used for obtaining a mirror finish that yield high EBSD indexing rates. For the chemical etching, Kroll's reagent was applied with the following copmposition:



- 100 ml water (H₂O)
- 1-3 ml hydrofluoric acid (HF)
- 2-6 ml nitric acid (HNO₃)

Fig. 4-8: Semiautomatic polishing apparatus

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The etching times varied between 10s and 20s in dependence of alloying element as well as the state of the sample [Taylor 2008]. Samples were washed with water thoroughly and polished for two hours on a semiautomatic polishing machine (Buehler metaserv, see Fig. 4-8) with OPS (Oxide Particle Suspension) from Struers. The process was repeated three times. During the last hour water drops were slowly added to dilute the suspension on the polishing cloth and to reduce oxidation.

Good results with far reduced polishing times can also be achieved using OPS after a careful grind on the P4000 paper without the intermediate diamond polishing. The combined chemical and mechanical attack removes material very efficiently.

The automated grinding and polishing procedure after advices from Struers Application Notes for Titanium [Taylor 2008] can not be recommended because polishing twins occur. Also methods of electro polishing are possible on Titanium alloys, as described in [Piotrowski 1998, Tajima 2008, Mathieu 1978, Taylor 2008] but care has to be taken when the chemically different β -phase is present. Experimental trials in a beaker filled with 180ml laboratory grade methanol and 15ml perchloric acid (60% concentrated), as used by Bozzolo et al. [Bozzolo 2010], did not yield reproducible sample quality. Polishing trials stretched over a range Ti-alloys and 12 to 30V between the sample as anode (+ /positive) and the cathode (-/ negative). The temperature was kept between -40 and -30°C with liquid nitrogen. The produced surfaces were free of any polishing twins but often pitted or showed a wavy surface after 1min to 2min polishing time. Warmer solutions tend to burn the sample surface. As only about every tenth sample was useful for EBSD analysis only OPS finishes were used for any microstructural characterisation.

4.4. Optical microscopy

The optical micrographs were taken after the last step of OPS polishing with cross-polarised light (POL) or preferably with a differential interference contrast (DIC) filter on a Zeiss Axio (Scope.A1) and captured with a AxioCam MRc5 Fig. 4-9 a). Fig. 4-9 b) and c) show DIC micrographs, which use the pass difference of two polarised light beams gathered during the interaction with the sample to create a contrast during recombination of both light passes [Brandmaier 2013].

If the microstructure exhibits small scaled shadows within a grain as shown in Fig. 4-9 b) further OPS polishing is required to remove this layer. Fig. 4-9 c) shows a well-prepared sample surface, mostly free of preparation artefacts, which is usually sufficient to acquire good EBSD mappings. The polarised light image in Fig. 4-9 d) captures the same area as the DIC micrograph in Fig. 4-9 c). Both techniques show similar contrast and microstructural features are sometimes clearer using a DIC filter and another time with the POL filter. As exposure times with the POL filter are about 10 times longer, mostly DIC micrographs have been used for screening purposes and quality checks during sample preparation for EBSD analysis. Grain Arnas Fitzner, PhD Thesis, 2014

size (GS) analysis using the intercept method was conducted on DIC micrographs in accordance to DIN EN ISO 643. Five horizontal lines were placed on micrographs of 5x and 10x magnification to count interceptions with grain boundaries. The number of intercepts and the total length of measurement give the average grain size after Equation 4-3.



Equation 4-3: Grain size estimation after linear intercept method



fig. 19 – Zeiss Axiocam microscope used fig. 19 - MTS Alliance RT/100 Universal test Frigul 498caa) id Zeissov Axiong Scope Ayster by Machanier ography Matchine ufficiently prepared sample c) DIC micrograph of sufficiently prepared sample; d) same area with polarisation filter.

4.5. Mechanical properties

Macro hardness tests were used to confirm homogeneity of the bars and for initial mechanical characterisation. The strengthening effect from the alloying elements were further characterised by tensile tests in RD to failure and especially by compression testing parallel to the original RD, ND and 45° between these two directions, as indicated in Fig. 4-10. Nanoindentation was conducted to analyse "single crystal" anisotropy. Compression tests during lattice strain measurements at Engin-X are described separately in chapter 4.10.



Fig. 4-10: Schematic of alignment of compression samples in cross-rolled bar.

4.5.1.Macro hardness indentation

Macro hardness indentation offers a fast, reliable method to test mechanical properties. It measures the resistance of penetration into a material [Higgin 2006]. This resistance is multi dimensional and results less sensitive to anisotropic properties than uniaxial testing methods. Macro hardness was measured on a tester from Cooke, Troughthon and Simms, England, York (Fig. 4-11 a) with 20Kg load and a Vickers pyramid as shown in Fig. 4-11 b) and schematically in c). Also, micro-hardness indents with only 0.5Kg load were taken. The centreline-face angle is 68°, giving 136° inclination for opposing sites d). Adjusting the slit width manually for evaluation of the indent through an optical microscope gives the diagonal indentation width Fig. 4-11 e). Both diagonals are averaged and the size is proportional to the hardness of a material.



Fig. 4-11: Cooke, Troughthon and Simms Macro Hardness tester a) in full view and b) view on the stage with sample during test. c) shows the three dimensional pyramid shape, d) angle between the opposite faces of the diamond and e) the appearance of hardness indent [Higgins 2006]

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4.5.2. Nanoindentation

Another way of hardness measurements is nanoindentation where only very small indents within one grain are evaluated. Due to the mechanical anisotropy of the hcp-crystal, it is useful to plot nanohardness as a function of crystal orientation. To ultimately gain insight into the effect of alloying on crystal anisotropy samples from large-grained CP-Ti and binary Ti-Al alloys were indented along their former RD and ND. In accordance to the starting texture a sample cross-sectioned and polished along the RD offers mainly crystals with their c-axis nearly perpendicular to the indent direction. A polished surface with ND as normal direction offers the full range of c-axis inclination. For further insight into the influence of dislocation structures on nanohardness uniaxial compressed samples were also investigated. Multiple samples were compressed to either 3.7% or 8.7% plastic strain along the former RD or ND. Samples were cross-sectioned and polished with the LD as surface normal and indented parallel to the former compression direction. As for any other surface characterisation method a well-polished sample is required to test an artefact free subsurface layer of material with indents up to 2000nm depth and to acquire sharp electron back scattered patterns (EBSP).

Even though the interaction volume will be approximately three times larger than the actual indentation depth of 500nm in this study, a vibration free environment is required for reproducible results. Therefore, the indenter, Nanoindenter XP from MTS as shown in Fig. 4-12 a), sits in a sound insulated box on air suspension. It is equipped with a Diamond Bekovich tip (Fig. 4-12 b), a three-sided pyramid with a centrerline-to-face angle of 65.3°, similar to the Vickers indenter. Samples were mounted in Bakelite and fixed with superglue on an Al holder, which was then screwed into the indenter stage. In addition, samples have been glued onto Bakelite and indented that way. It should be remarked that results are not reproducable when the sample is not tightly fixed. To gather results a "Modulus-at depth" method was used with the parameters as listed in Tab. 4-3 and explained in the following: Before the actual indentation starts the indenter head needs to be already very close to the surface. To find the surface quickly a probe approaches the surface over 1000nm with 10nm/s and then waits until the drift between probe and sample surface drops below 0.15nm*s⁻¹. Afterwards the probe gets replaced with the diamond Berkovish indenter tip, which is pushed with a constant strain rate of 0.05s⁻¹ into the surface until a depth of 500nm. After 10s holding time at peak load unloading to 90% of the depth follows and the next indentation position will be approached. Finally, arrays are created as showcased in Fig. 4-13 a), with one indentation taking approximately 10min.



a)

b)

Fig. 4-12: a) MTS nano indenter XP in housing; b) Berkovich indenter head [Agilent]

Tab. 4-3: Parameters	and thresholds	for nanoindentation	method "Modu	ulus at a depth	" on <i>MT</i> S
Nanoindenter XP				-	

Surface Approach Velocity	Surface Approach Distance	∆X For Finding Surface	ΔY For Finding Surface	Allowable Drift Rate	Strain Rate Target	Depth Limit	Peak Hold Time	Percent To Unload	Poissons Ratio
nm/s	nm	μm	μm	nm/s	1/s	nm	s	%	1
10	1000	-50	-50	0.15	0.05	500	10	90	0.33



Fig. 4-13: a) Typical array of 20 μ m spaced indentations and b) experimental curve for one Nano-indentation to 500nm depth.

The presented hardness data were calculated automatically from the force-depth curves as shown exemplary in Fig. 4-13 b). The known geometry of the indenter allows estimation of the contact surface area A_P at the maximum displacement h_{max} , and any other height h_c . Calibration indents in Si account for tip wear by adjusting C_0 and C_1 after Equation 4-4. The tip wear Arnas Fitzner, PhD Thesis, 2014

becomes more important with decreasing indentation size as increasingly higher fractions of the worn tip interact with the sample.

$$A_P = C_0 h_{max}^2 + C_1 h_{max}$$

Equation 4-4: Projected area A_P

The maximum load F_{max} is read out from the test and divided by the estimated contact area, which equals the nanohardness H_N (Equation 4-5), which is finally related to orientation measurements from EBSD Mappings.

$$H_N = \frac{F_{max}}{A_P}$$

Equation 4-5: Nanohardness H_N

For the present work indentations arrays of typically 30x7 were obtained on polished samples. However, also much smaller arrays and single indents were made to target specific microstructural features. Spacings between indents were above 20µm and indentations closer than 20µm to a visible grain boundary on the polished surface were dismissed to avoid grain boundary effects and maintain the single crystal nature of this testing method. In most cases, indents were made in areas of previously taken EBSD maps, but for practical reasons some EBSD maps have been taken afterwards. In any case, the c-axis inclination was related to the hardness, with 0° being parallel to the c-axis and indenting into the basal plane and 90° being perpendicular to the c-axis. No distinction was made between indents closer to a $\{11\overline{2}0\}$ plane. The c-axis inclination is directly given by the Euler angle Φ from Tango in Channel 5, once a location is selected.

4.5.3.Compression tests

Rectangular and cylindrical samples were used with a height of 9mm and a cross section from 6*6mm (Fig. 4-14 a) or a diameter of 6mm (Fig. 4-14 b). Also samples with a height of 12mm and a diameter of 8mm (Fig. 4-14 c) were tested, with a height to width ratio of 1.5.



Fig. 4-14: Geometry for mechanical compression testing: a) rectangular compression sample; b) cylindrical compression sample with 6x9 and c) 8x12mm. Former normal directions are indicated.

Uniaxial mechanical tests were conducted on an Instron 5569 and a MTS RT100 compressiontension machine at room temperature and a strain rate of 1*10⁻³ 1/s. The crosshead movement and the force with a 50kN or 100kN loading cell were measured with a frequency of 3 or 10Hz.

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To consider the effective strain values in the samples, a compliance correction was applied under compression. To achieve an initial strain rate of 1*10⁻³ 1/s the crosshead speed was set to 0.54mm/min=0.009mm/s. Few samples were significantly smaller than the described dimensions due to material shortage. Therefore the crosshead speed was adjusted to maintain the initial strain rate. The interface of compression plunger and sample was lubricated to minimise barrelling and frictional forces. The tests were stopped at approximately 1.7%, 3.7% and 8.7% residual plastic strain for ex-situ characterisation of microstructural and textural development. To achieve reproducible values for the low strain level of 1.5% in samples of varying strength, the tests were stopped 15s after yielding rather than to consider absolute strain values. For the strain values of 3.7% and 8.7% the aimed height reduction was calculated in mm prior testing. Tests were terminated after samples had been deformed plastically by the calculated value in mm.

True stress and strain values were calculated as described in Equation 4-6. The following equation describes that the conversion from engineering to true strain leads to higher compressive and lower tensile strains. Stresses adjust inversely.

$$\begin{aligned} \epsilon_{true} &= \ln \left(\frac{l}{l_0} \right) = \ln \left(\frac{\Delta l + l_0}{l_0} \right) = \ln \left(1 + \frac{\Delta l}{l_0} \right) = \ln \left(1 + \epsilon_{eng} \right) \\ \sigma_{true} &= \sigma \left(1 + \frac{\Delta l}{l_0} \right) = \sigma \left(1 + \epsilon_{eng} \right) \end{aligned}$$

Equation 4-6: True strain and stress [Dieter 2003]

. .

The slope of the true stress-strain curve gives the work hardening rate θ according to Equation 4-7. In order to reduce scatter a floating average over 100 data points was used.

$$\theta = \frac{\delta \sigma_{true}}{\delta \varepsilon_{true}}$$

Equation 4-7: Work hardening rate

Also, lateral sample dimensions were measured before and after testing to calculate R-values according to Equation 4-8 to characterise the anisotropy of the barrelling in regard of the starting texture.

$$r_{ND} = \frac{\varepsilon_{RD}}{\varepsilon_{ND}} = \frac{l_{0RD} - l_{RD}}{l_{0ND} - l_{ND}}$$
$$r_{45} = \frac{\varepsilon_{45}}{\varepsilon_{ND}} = \frac{l_{045} - l_{45}}{l_{0ND} - l_{ND}}$$

Equation 4-8: Strain anisotropy against barrelling of compression samples, or R-values

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4.5.4. Tension tests

Tensile samples have been produced from cross-rolled model alloys and industrial forgings on different routes. Hounsfield tensile samples (Fig. 4-16 a) and sheet tensile samples (Fig. 4-16 b) were machined with tensile axis in RD. Sheet samples from Ti5Al2.5Sn were machined with the tensile axis along TD due to material availability. Their handling, advantages and disadvantages are outlined in the following.



Fig. 4-15: Geometries for mechanical tensile testing: (a) Hounsfield tensile sample, (b) Sheet tensile sample (c) Drawing for sheet tensile samples 1:1.

Hounsfield geometry

The advantage of the simplified grips section of the sample compared to usual tensile samples with threaded grips lies in the length saving of the whole sample, without sacrifices in gauge length or cross-sectional area. Sample production and handling are much easier than handling of threaded samples, as only the shoulder has to be placed into the holder. Rocking the sample slightly under a gentle elastic load settles the sample in the grips and avoids movements between sample and grips during a test. During the tests to failure the initial strain rate of $1*10^{-3}$ 1/s was equal to the compressive strain rates of the current study. All samples were slightly conical shaped, with increasing diameter from 4.94mm on the one to 4.99mm at the other side, which leads to an inhomogeneous stress throughout the sample. Tested samples were cut in sections perpendicular to the loading axis, as shown with the green lines in Fig. 4-16. Equation 4-9 calculates the local strain as function of the reduction in cross-sectional area, as shown in Fig. 4-17.

$$\varepsilon = ln\left(\frac{A}{A_0}\right)$$

$$\rightarrow A = A_0 \exp(\varepsilon_{true}) \varepsilon$$

Equation 4-9: True strain as function of reduction in area, resolved to area A where cross-sectional cuts have to be made

Together with the relation between diameter of the sample at a certain length and the area of a circle ($A = 2\pi d^2$) an estimate for a uniaxial strain state can be made. However, within and close Arnas Fitzner, PhD Thesis, 2014

to the necked region the stress state is not uniaxial, altering the affecting the activation of deformation systems. For simplicity the strain has been related to the stress in accordance to the stress-strain curve as shown Fig. 4-17.



Fig. 4-16: Schematic of strained Hounsfield sample for ex-situ characterisation of microstructure

Fig. 4-17: True stress-strain tensile curve with marked strain levels in green, as indicated in Fig. 4-16, for microstructural characterization and the elongation to failure in red.

Sheet samples

As the Hounsfield samples still require a substantial volume of the model buttons (14x14mm cross-section) sheet samples were produced from sub surface material, as shown in Fig. 4-15 b). Results from sheets samples are more sensitive to surface properties as sheet samples have a larger surface/volume ratio. More significantly, in the present case, samples were taken very close to the surface of the cross-rolled bars, which carries the risk of sampling volumes with varying grain size and contaminations from hot-rolling in air. Despite the small cross sectional area, which potentially increases the scatter of results, generally comparable results to tests on cylindrical samples were found. Even though the production was more cost and time intensive compared to Hounsfield samples and despite described further disadvantages, the material saving enabled performing compression and tension tests from the same material stock.

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Fig. 4-18: Tensile – sheet samples manufactured over the grinding route after testing with kept identity. The samples are, starting from the left: a) CP-Ti750, Ti-3Zr 37.6, Ti-3Zr 37.3, Ti-10Zr 30.25, Ti-10Zr 30.5 b) Ti-10Al aged, Ti-1Sn, Ti-1Sn 30.15, Ti-3Sn. The grip section measures 8x12mm.

In a first approach slices of the cross-rolled bars surfaces from ~ 3mm thickness were cut carefully using 0.5 mm thick Al_2O_3 abrasive cutting wheels. Subsequently, the slices were ground parallel to a final thickness of 1mm. The former bar surface was removed predominantly to minimise the risk of contaminations from hot-rolling in air and effects from a hardness increase close to the bar surface (see Fig. 5-3). Samples produced on this route are displayed after testing in Fig. 4-18.

After successful testing of the first batch of sheet tensile samples more alloys were manufactured on a slightly different route. An initial cut using by electronic discharge machining (EDM) took ~1mm off to remove surface contamination and a second, parallel cut produced a ~14x50mm sheet of 1mm in thickness. To ensure best comparability between the samples, the shortest sheet defined the full sample length of 30 mm. The dog bone shape was cut by EDM, according to the drawing in Fig. 4-16c, giving 10mm gauge length with 1x3mm cross sectional area. No significant deviations between samples from ground or EDM sliced sheets could be noticed during the quasi-static tests with an initial strain rate of 1*10⁻³ and set crosshead speed of 0.6mm/min in the Hounsfield setup Fig. 4-19 a) and b). In both geometries no suitable extensometers were available and strains were calculated from the crosshead movement Δl . Therefore it is assumed that all deformation occurs solely in the gauge length l_g . Stresses and strains for the plots have been converted into true values after Equation 4-10 and Equation 4-11, with l= actual length, l_g= initial gauge length and σ = engineering stress.

$$\epsilon_{true} = \ln \left(\frac{l}{l_G} \right) = \ln \left(\frac{\Delta l + l_G}{l_G} \right) = \ln \left(1 + \epsilon_{eng} \right)$$

Equation 4-10: True strain conversion [Dieter 2003]

$$\sigma_{true} = \sigma \left(1 + \frac{\Delta l}{l_G} \right) = \sigma \left(1 + \epsilon_{eng} \right)$$

Equation 4-11: True stress conversion

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Fig. 4-19: Setup for tensile tests with sheet sample in Hounsfield grips on a) Instron 5569 and b) MTS RT/100 and c) CP-Ti sample after test

The elongation to failure ϵ_F and the reduction in area R_A have been acquired by measuring the sample dimensions before and after the test and are therefore engineering values as described by Equation 4-12 and Equation 4-13, with I₀= initial length of complete sample, I_F= Final length of complete fractured sample, A₀=Cross sectional area before deformation and A_D=Cross sectional area in neck.

$$\epsilon_F = \frac{l_F - l_0}{l_G}$$

Equation 4-12: Elongation to failure

$$R_A = \frac{A_F - A_0}{A_0}$$

Equation 4-13: Reduction in Area

A useful comparison of elongation to failure values to literature data can be made from the stress strain curve, by simply applying the elastic slope to the last measured stress values. The true elongation to failure ϵ_{FTrue} is indicated in Fig. 4-17 with the red line in the graph, and usually higher than ϵ_F . Care has to be taken during comparisons of data from different sample length. A shorter gauge length is more affected by necking and strains appear higher during pronounced necking. [Dieter 2003]

4.6. Scanning electron microscopy

A modern scanning electron microscope (SEM) is a highly versatile tool: Details like surface topography, elemental composition, micro structures, crystallographic phase and orientation information can be resolved easily below the submicron scale, and even down to 1nm spatial resolution using modern microscopes.

4.6.1.Imaging with SEM

When the electron beam hits the sample, a part of these electrons will reflect directly as backscattered electrons. These highly energetic electrons escape from a relatively large interaction volume within a broad angular range in an almost straight flight pass to the scintillator where they are detected. As backscattered electrons barely interfere with electromagnetic fields, large area detectors are required to collect a high fraction of them for high quality images. Nowadays, annular detectors around the electron gun give images with good contrast in short times. Important for the image interpretation is that heavier elements, with higher atomic number, have a higher backscattering coefficient and appear brighter. This atomic number contrast (Z-contrast) is most pronounced at high acceleration voltage (for example 20kV). At low acceleration voltage (for example 8kV) channelling effects occur and orientation contrast can be more pronounced.

Next to the backscattered electrons the incident electrons also scatter inelastically from sample. The secondary electrons are low in energy and travel only a few nm between scattering events, until they escape eventually from the top 1nm layer of the sample. The amount of electrons escaping the surface depends on the inclination angle of the sample to the incident beam and gives a strong topography contrast. [Lloyd 1987, Echlin 2009]

4.6.2. Texture determination with EBSD (Electron Backscatter Diffraction)

Electron Backscatter Diffraction (EBSD) gives a multitude of information about the sample from small areas. At a usual acceleration voltage of 20 kV electrons penetrate only about 20nm into the surface and the EBSD patterns result from an interaction volume in the order of a few 1000 nm³ depending on the probe current. This value is about an order of magnitude larger than that of TEM diffraction techniques, but can be significantly reduced by reducing the primary beam energy down to a minimum of 3 kV. The spatial resolution of EBSD is generally better than 50nm [Zaefferer 2012, Schwartz 2009]. Due to such small interaction volume, specimen preparation requires highest standards to minimise artefacts from polishing or etching. For scans of large areas, samples have to have a very flat surface as well. The prepared sample surface needs to be focused under a 70° tilt to the incident beam in order to project the electron back-scattered pattern (EBSP) on the detector with high contrast. Therefore, tilt correction and dynamic focus are enabled in the microscope software to focus the full field of view. For optimal

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results, the beam must be aligned, focused and astigmatism has to be minimised for the desired acceleration voltage and spot size. Once the EBSD detector, a phosphor screen, is moved closely to the sample, as shown schematically in Fig. 4-20, the backscattered "Kikuchi" diffraction can be visualised where constructive interference on the EBSD detector occurs, as described by Bragg's law. Each crystal plane creates two cones (green in Fig. 4-20) enclosing two times the Bragg angle θ_{hkl} while the plane through the centre of these cones corresponds to the trace of the diffracting plane. The width w of the band on the screen relates after Braggs law (Equation 4-14) to the inter-planar spacing d_{hkl} for a given distance between sample and screen I. The angle between the traces is specific for the crystal planes and dependents on the c/a ratio of the hcp lattice. [Schwartz 2009]

$$n\lambda = 2d_{hkl}\sin\theta_{hkl}$$



Equation 4-14: Bragg's law for monochromatic beams [Schwartz 2009]

Fig. 4-20: Schematic of sample chamber with Kikuchi projection [Instruments 2011]

The working distance should be adjusted so that the centre of the Kikuchi pattern aligns roughly with the centre of the EBSD camera to optimise results. The system is calibrated according to the working distance. For an enhancement of the Kikuchi patterns background measurements have to be taken. Therefore, the electron beam is set to TV mode, which does not give Kikuchi bands but random intensity. The capturing time per frame can be optimised and lies depending on electron reflectivity of the sample, spot size, aperture and the quality of beam alignment, from 10ms to 24ms using 4x4 binning in the case for Ti-alloys. Once the screen is optimally lit, without being overexposed, the background measurement can be taken and the enhancements enabled. Now the crystal parameters are chosen and Kikuchi patterns are evaluated using the spot mode from the EBSD system. The electron beam is now stationary and band edges of 4-6 Arnas Fitzner, PhD Thesis, 2014





deviation (MAD) is below 0.5°. A successful refinement reveals the crystal orientation, which is generally given in respect to the orientation of the acquired surface.



Fig. 4-21: Part of Kikuchi map for hcp Ag₂Al with principal poles and directions [Carter 2009]

For optimal results, several refinements for several crystal orientations were performed across the area of measurement and averaged. Once all parameters for the indexing are set, the area of the measurement is defined and a step size chosen. In the present case, micro mapping were usually recorded with fine step sizes of 1µm or 0.5µm to resolve microstructural features. Within 12 hours areas bigger than 1mm² can be scanned when averaging 2 frames per beam position. Maps recorded in the described way usually exhibited indexing rates better than 80% using Flamenco acquisition software. Fig. 4-22 a) shows an example of deformed CP-Ti. The improved ACTEC acquisition software readily indexes more than 90% measuring only one frame per beam position. Maps were cleaned with the noise reduction function in tango (hkl, Channel 5), as seen in Fig. 4-22 b). First wild spikes were removed to then fill non-indexed pixel by the neighbouring orientation iteratively. The number of neighbours was decreased from 8 to 1 to receive finally fully cleaned maps. Afterwards, twin boundary artifacts at angles of 84°, 87° and 90° were removed using the Kuwahara filter on 5x5 pixel with a smoothing angle of 3°.

Maps recorded by Flamenco acquisition software sometimes suffer under a systematic misindexing, called pseudo symmetry. This 30° rotation of the crystal unit cell around the c-axis was removed until intermediate levels after a grain reconstruction. An improved algorithm of pattern identification in AZTEC reduces the amount of systematic misindexing and allows faster

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acquisition with higher indexing rates. In order to indicate twin types, their rotation axis and angle (see Tab. 3-1) have been input with a deviation of $\pm 5^{\circ}$. The data acquired from EBSD micro maps can be analysed in multiple ways. Information like grain size distributions or number, thickness and area fraction of twins, orientation analysis and neighbourhood effects etc. can be analysed automatically [Marshall 2010]. However, due to the very complex deformation-twin networks, manual analyses were performed. Especially problematic are situations where a grain is nearly fully consumed by the twin and secondary or tertiary twinning, even though Schmid factors have been considered. Instead twins have been identified manually with help of their boundary criteria and morphology and subsets have been taken. Finally the percentage value of data points within one subset from all data points was taken as twin fraction.



Fig. 4-22: Example for EBSD mapping of a 9% deformed sample as measured a) and after the cleaning procedure b). IPF colouring is applied and twin boundaries are marked in black, grey and white for specific twin types.

Once the micro scaled maps show trustful results, large scaled macro texture maps can be recorded and analysed confidently. Therefore a stepsize similar to the grain size was chosen to capture at least one orientation per grain. Accordingly, the binary model alloys were measured with 40µm, while the industrial alloys were measured using a 10µm step size. Measurements were carried out combining stage- and beam-scan to acquire more than 3000 data points across 16mm² per sample. The increased step size leads to a significant decrease of the indexing, in some cases even below 60%. The singled macro texture maps were combined using the map stitcher from channel 5 and the full project used to plot pole figures using 5° angular averaging in Mambo. The principle of contour maps on a stereographic projection is depicted in Fig. 4-23. The beam comes from the top (labeled with ND) and reflects on specific lattice planes after Bragg's law. The reflected beam crosses the sphere and is from there projected to the bottom of the sphere (a). In this way, the projection plane is crossed and the crystal orientation is marked (b). A polycrystalline material, and also deformed single crystals, will create multiple projections for each reflecting plane (c) resulting in scattered areas with a specific pole density distribution (d). Contour plots show the density distribution projected onto Arnas Fitzner, PhD Thesis, 2014

two dimensions (e). Usually projections of the basal planes and the prismatic planes are plot on separate stereographic projections in mud (multiples of uniform density) to describe the texture of hcp materials. In the present case, four FEGSEM EBSD systems were used: Most micro mapping with 0.5µm step size and macro texture measurements were performed on a Camscan FEGSEM with a large chamber and HKL EBSD system with a fast Nordlys II camera and Flamenco software. A FEI Sirion FEGSEM, also running Flamenco, was used for the same purposes, but primarily for micro mapping with 1µm step size. Additionally, a FEI Quanta 650 FEGSEM, applied with the Nordlys II EBSD camera and additionally with EDX X-Max 50 detector was used. Fine EBSD was performed on a FEI Magellan FEGSEM using a step size of 0.25µm. High resolution EBSD using only 10kV acceleration voltage, a step size of 0.025µm and simultaneous EDS analysis was also performed on the Quanta 650 and the Magellan FEGSEM both run AZTEC acquisition software instead of Flamenco, which uses an improved pattern recognition algorithm.



Fig. 4-23: Reference sphere and projection plane around a orientated sheet (a), projection of poles for basal and prismatic planes of one single grain (b) and similar orientated grains (c), the pole density distribution of scattered projections (d) and the final contour map of pole density (e) [Hatherley 1979]

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4.6.3. Element analysis

The X-rays photons, which are created when the electron beam hits the surface, were resolved by energy dispersive spectrometry (EDS), giving information about the elemental composition of the interaction volume between electron beam and sample. High beam current leads, just like in imaging and EBSD, to large activation volumes, which increases the signal and reduces counting times but also spatial resolution. The beam was hold in one place for prolonged time (more than 1min) using the spot mode function to acquire accurate spectra from a specific location. Also, mapping was undertaken, where the beam rests only very short times (usually 20ms) over each position and spectra were acquired for each point. The amount of data points over a map gives a qualitative indication for elemental distributions within the sample. Multiple scans of the same area increase the accuracy of the data, and give generally quantitative maps after 10-30min. Ideally, any EDS measurement should be taken on a flat, non tilted sample to minimise differences in beam energy at different working distances. However, only when the sample is tilted to 70° simultaneous EBSD measurements are possible. This allows simultaneous acquisition of phase and composition over the same area with high spatial resolution. [Echlin 2009]

Three FEGSEM's were used for the analyses: Phillips XL 30 with Rontec detector, FEI Quanta 650 equipped with XMax 50mm², FEI Magellan with windowless Silicon Drift Detector XMax 80mm² from Oxford instruments.

4.7. Digital image correlation

In the present work digital image correlation (DIC) in sub-micron resolution was applied to visualise slip traces and their development especially in connection with twinning during compression of different Ti alloys. Historically, different imaging techniques have been used to reveal slip traces on polished surfaces. Optical microscopy on first polished and subsequently deformed samples revealed slip traces as surface ledges [Dieter 1986]. Secondary electron images give the same topographical information but with much better spatial resolution [Echlin 2009]. Most detailed is the analysis of crystalline defects using transmission electron microscopy (TEM), but results may be affected from sample preparation and have limited statistical significance. More recently, electron channelling contrast imaging (ECCI) has been applied to identify slip traces using a SEM [Crimp 2001, Crimp 2006, Gutierrez-Urrutia 2009]. One of the most recent developments is digital image correlation, where slip traces can be visualised and associated with strain vectors as demonstrated by Quinta da Fonseca et al. [Quinta da Fonseca 2005, Di Gioacchino 2012] and outlined in this chapter. Even though the method does not always offers unique answers to which deformation system is activated, much larger areas can be covered than during TEM investigations.

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4.7.1. Principle of DIC in submicron resolution

Submicron resolution can be achieved when nano-scaled patterns are imaged in the SEM before and after deformation. Images of the same area are subsequently correlated to each other to visualise the local pattern displacement, which is finally converted into strain vectors. Those strain vectors are mapped and reflect the deformation of the underlying microstructure. Features in the strain maps are finally compared to the theoretical alignment of slip-traces and their Schmid factors, which are both calculated from orientation measurements using EBSD. The identification of one single slip system is not always certain and Schmid factor analysis might indicates which slip mode is more likely to be active.

4.7.2.Gold pattern application

The polished current of ~4(subsequently random distri evaporate wa clips (Fig. 4-2 environment f remodelled fo



iold in an Edwards S150B sputter coater for 5min at a o of ~3x10⁻¹ atmospheres (ATM). The gold layer was . 4-24 a), into fine speckles of 20-100nm in size with c plate was set to full power (~300°C) to boil and pour flows through a bigger beaker, rested on bulldog before it escapes the setup. Samples were left in this e refills of water were required. The sample T-6AI was pattern distribution.



Fig. 4-24: a) Gold remodelling setup for DIC b) with gold pattern at 3000 As magnifications and c) require 2: A vapour assisted remodelling section from pattern at 1000x magnification to resolve single pixels, with one pixel being 36x36nm in 1992

Figure **4.7.3:** (Curves used with permission courtesy of Arnas Fitzner).

BSE images were acquired at a working distance of ~ 4.5mm, 20kV acceleration voltage and spot size 3 on the Sirion FEG-SEM. A resolution of 32nm per pixel within one image was achieved at 1000x magnification in extra high definition mode (XHD), with images of 3872x2904 Arnas Fitzner, PhD Thesis, 2014

pixels. Brightness and contrast were adjusted to see speckles of approximately 3x3 pixels (see Fig. 4-24 c) on images of 1000x magnification (Fig. 4-24 b). A matrix of 4x4 images was taken with 10µm overlap between adjacent frames in order to create a large field of view.

Images were processed using La Vision DaVis digital image correlation software. In order to correlate overlaying frames between subsequent deformation steps a good alignment is required, but the recorded images suffered from poor alignment and insufficient overlap. The alignment was improved manually post acquisition using Adobe Photoshop, but rotation and stitching of BSE images introduced artefacts in the strain maps. Non-linear filters were applied to the aligned images in DaVis to average brightness and contrast of the different sets of images. Images were subsequently cross-correlated over areas of 512x512 pixel with 2 passes and finished with 3 passes at 12x12 pixel without overlap. Window shape (called window weight in DaVis) was square and circular respectively. Cross correlation of an image to the first image displays the overall strain accumulation. Cross-correlation of subsequently taken images displays incremental strain accumulation, labelled as $\Delta\epsilon$ later on. Standard correlation function was applied, allowing for zero padding via fast fourier transform (FFT) and subpixel resolution through linear interpolation of vectors with 100 pixels as upper ceiling. For purposes of noise reduction, vector post processing was applied by means of a median filter. Vectors were removed if over 2 times the difference of average route mean squared distance (rms) of a neighbouring pixel and iteratively replaced if below 3 times average rms. Dynamic removal and reinsertion of data followed by interpolation allows for smoothing of displacement maps.

Prolonged time spans between the imaging sessions result in slightly altered beam alignments and can cause noise. Also a lack of software drift correction, and the necessity to remount the samples after each compression step, cause different drift rates between the image sets and causes noise towards the bottom of the image.

4.7.4.Slip trace analysis

Once a slip trace was identified the corresponding grain orientation was read out as Euler angles from EBSD orientation maps. The theoretical alignment of the slip trace or the twin habit plane on the sample surface was calculated from the grain orientation, while only the deformation systems listed in Tab. 3-1 were considered. Furthermore the Schmid factor m was calculated for possible slip- and twin-systems assuming a uniaxial stress state. Theoretical slip traces and Schmid factors were calculated with the "BPW PC Crystal Math tool" from the University of Sheffield and the donation is highly appreciated. To compare the imaged slip traces with the theoretical lines, the image had to be aligned on the EBSD map, as shown in Fig. 4-25. The 70° tilt of sample during the EBSD mapping creates, together with astigmatism and drift, a disadvantageous mismatches between EBSD map and image. Furthermore the activated sample volumes are different under 70° and 0° tilt. The angular accuracy for EBSD orientation measurements is in the order of 1°.

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Mismatches of 3° between the theoretical and measured slip trace are accepted, because of the manual alignment from strain- and EBSD map.

Slip traces on the manually aligned image were compared to the theoretical slip lines, as shown in Fig. 4-25 for two grains. If the observed and theoretical slip traces matched better than $\pm 3^{\circ}$, the slip system was considered to be active, as shown on the example in Tab. 4-4, and got accounted as 1. Multiple slip bands of the same slip system were also accounted for only 1 system per grain. In few occasions multiple slip bands matched more than one theoretical trace angle. Pyramidal <a> and pyramidal <c+a> slip even share the slip trace. Here the Schmid factor was used to decide which slip system is more likely to be active. To avoid ambiguity the activity of pyramidal <a> and <c+a> slip traces exhibit nano-atomistic jogs and appear a serrated, as shown for Ti-5Al by Williams et al. [Williams 2002], which makes their identification essentially impossible by DIC. The procedure of identifying twin types and variants is analogous.

Now it is important to normalise these counts against all possible slip systems per Schmid factor bin. Therefore a second frequency chart with all Schmid factors of all possible deformation systems in all grains was calculated. The fraction of active slip systems from all possible slip systems gives an indication about the relative likelihood for the different slip systems. Finally the normalised frequencies were plot in Schmid factor bins of 0.1 to characterise the likelihood of each slip system.



Grain 5 - — Prismatic <a> m=0.40 - — Grain 6 Prismatic <a> m=0.50 Twin 85° m=0.48

Fig. 4-25: Example for slip trace analysis: Part of EBSD map (right) and aligned DIC strain map (left), theoretical slip traces and Schmid factors for activated slip systems for grain 5 (e1=50°, e2=35°, e3=45°) and grain 6 (e1=0.3°, e2=132°, e3=12°) in Ti-10AI.

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Tab. 4-4: Evaluation of theoretical Schmid factors and trace angles for various slip systems and the $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tension twin for the examples of grain 5 and 6 in Ti-10Al shown in Fig. 4-25.

						Grair	۱D			5-e1		5-e2	5-e3	6-e1	6-e2	6-e3
Clin	Custore	Dise	+:			Euler	r angl	es 1-2	2-3	Colore i d Er	50	, 	25 45	0.3	132	12
Slip	System	Direc	tion	t	w	h	Slip	Plane i		Schmid Fa	actor	i race angle	Comment	Schmid Factor	i race angle	Comment
hasal	<a> B1	1	1	-2	0	0	0	0	1	-0.16		50.00		0.00	0.30	
50501	<a> B2	1	-2	1	0	0	0	0	1	0.31		50.00		0.00	0.30	
		-2	1	1	0	0	0	0	1	-0.14		50.00		0.00	0.30	
	<a>_B4	1	1	-2	0	0	0	0	-1	0.16		50.00		0.00	0.30	
	<a>_B5	1	-2	1	0	0	0	0	-1	-0.31		50.00		0.00	0.30	
	<a>_86	-2	1	1	0	0	0	0	-1	0.14		50.00		0.00	0.30	
prismatic	<a>_Pr1	-2	-2	1	0	1	1	-1	0	-0.03		2.19		-0.30	26.20	
	<a> Pr3	1	1	-2	0	1	-1	0	0	-0.40		126.35		0.50	126.92	active
	_ <a>_Pr4	1	1	-2	0	-1	1	0	0	0.40		126.35	active	-0.50	126.92	
	<a>_Pr5	1	-2	1	0	-1	0	1	0	0.03		2.19		-0.20	82.21	
	<a>_Pr6	-2	1	1	0	0	-1	1	0	-0.37	·	66.47		0.30	26.20	
pyramidal a	<a>_Py1	1	1	-2	0	1	-1	0	1	-0.43		114.37		0.44	98.38	
	<a>_Py2	1	-2	-2	0	1	-1	-1	-1	-0.26	'	170 23		0.44	61 34	
	<a> Py4	1	-2	1	0	1	0	-1	-1	-0.18		10.88		0.18	105.36	
	<a>_Py5	-2	1	1	0	0	-1	1	1	-0.39	1	63.19		0.26	53.15	
	<a>_Py6	-2	1	1	0	0	-1	1	-1	-0.26	i	71.81		0.26	16.87	
	<a>_Py7	1	1	-2	0	-1	1	0	-1	0.43		114.37		-0.44	98.38	
	<a>_Py8	1	1	-2	0	-1	1	1	-1	-0.12		139.65		-0.44	143.65	
	<a>_ry3 <a> Pv10	1	-2	1	0	-1	0	1	1	0.12		10.88		-0.18	105.36	
	<a>_Py11	-2	1	1	0	0	1	-1	-1	0.39		63.19		-0.26	53.15	
	<a>_Py12	-2	1	1	0	0	1	-1	1	0.26		71.81		-0.26	16.87	
pyramidal c+a	<c+a>_Py1</c+a>	1	1	-2	3	1	0	-1	-1	0.00		10.88		0.34	105.36	
	<c+a>_Py2</c+a>	2	-1	-1	3	1	0	-1	-1	-0.09	1	10.88		0.44	105.36	
	<c+a>_Py3</c+a>	-1	-1	2	3	1	0	-1	1	0.07		1/0.23		-0.34	61.34	
	<c+a>_ry4</c+a>	-2	1	1	3	1	-1	0	1	0.00		114.37		-0.29	98.38	
	<c+a>_Py6</c+a>	-1	2	-1	3	1	-1	0	1	-0.19		114.37		-0.06	98.38	
	<c+a>_Py7</c+a>	1	-2	1	3	1	-1	0	-1	0.43		139.65		0.07	143.65	
	<c+a>_Py8</c+a>	2	-1	-1	3	1	-1	0	-1	0.28		139.65		0.30	143.65	
	<c+a>_Py9</c+a>	1	1	-2	3	0	-1	1	1	0.01		63.19		-0.11	53.15	
	$_Py10$	-1	-1	-1	ר ר	0	-1	1	-1	-0.20		71 81		0.03	16.87	
	<c+a> Py12</c+a>	1	-2	1	3	0	-1	1	-1	0.45		71.81		-0.03	16.87	
	<c+a>_Py13</c+a>	1	1	-2	-3	-1	0	1	-1	0.07		170.23		-0.34	61.34	
	<c+a>_Py14</c+a>	2	-1	-1	-3	-1	0	1	-1	0.00		170.23		-0.43	61.34	
	<c+a>_Py15</c+a>	-1	-1	2	-3	-1	0	1	1	0.00		10.88		0.34	105.36	
	<c+a>_Py16</c+a>	-2 -2	1	1	-3	-1	1	0	1	-0.05		10.88		0.44	105.36	
	<c+a> Py18</c+a>	-1	2	-1	-3	-1	1	0	1	0.43		139.65		0.07	143.65	
	<c+a>_Py19</c+a>	1	-2	1	-3	-1	1	0	-1	-0.19		114.37		-0.06	98.38	
	<c+a>_Py20</c+a>	2	-1	-1	-3	-1	1	0	-1	0.03		114.37		-0.29	98.38	
	<c+a>_Py21</c+a>	1	1	-2	-3	0	1	-1	1	0.32		71.81		0.11	16.87	
		-1	-1	-1	-3	0	1	-1	1	0.45		/1.81		-0.03	16.87	
	<c+a>_ry23</c+a>	1	-2	1	-3	0	1	-1	-1	-0.20	,	63.19		0.03	53.15	
pyramidal c+a	<c+a> P2v1</c+a>	-1	2	-1	3	1	-2	1	2	-0.22		88.00		-0.02	132.73	
	<c+a>_P2y2</c+a>	-1	-1	2	3	1	1	-2	2	-0.14		27.05		-0.25	39.47	
	<c+a>_P2y3</c+a>	2	-1	-1	3	-2	1	1	2	-0.10		167.31		-0.41	125.51	
	<c+a>_P2y4</c+a>	1	-2	1	3	1	-2	1	-2	0.49		111.95		0.02	169.77	
	<c+a>_P2y5</c+a>	1	1	-2	3	1	1	-2	-2	0.00		37.20		0.25	91.59 75.14	
	<c+a>_P2y0</c+a>	-1	2	-1	-3	-1	2	-1	2	0.49		111.95		0.02	169.77	
	<c+a>_P2y8</c+a>	-1	-1	2	-3	-1	-1	2	2	0.00		37.20		0.25	91.59	
	<c+a>_P2y9</c+a>	2	-1	-1	-3	2	-1	-1	2	-0.02		138.25		0.40	75.14	
	<c+a>_P2y10</c+a>	1	-2	1	-3	-1	2	1	-2	-0.22		88.00		-0.02	132.73	
	$_P2y11$ $_P2y12$	-2	1	-2	-3 -3	-1	-1 -1	-1	-2 -2	-0.14		27.05		-0.25	39.47	
Twin	System	Shea	r dire	ction	5	Twin	plane	2	-	0.10				0.41	120.01	
Tension	Σ11a_T1	-1	0	1	1	1	0	-1	2		0.05	154.	54	-0.48	46.33	
	Σ11a_T2	1	0	-1	1	-1	0	1	2		0.05	17.2	23	-0.48	124.52	
	Σ11a_T3	0	1	-1	1	0	-1	1	2		0.32	60.9	99	-0.05	118.84	
	211a_14 Σ11a_T5	0	-1	1	1	0	1	-1	2		0.28	81.	28	-0.05	12.40	
	Σ11a_15 Σ11a T6	-1	-1	0	1	-1	-1 1	0	2		0.29	104.	00	-0.22	153.04	
	Σ11a_T7	1	0	-1	1	1	0	-1	-2		0.05	17.2	23	0.48	124.52	
	Σ11a_T8	-1	0	1	1	-1	0	1	-2		0.05	154.	54	0.48	46.33	active
	Σ11a_T9	0	-1	1	1	0	-1	1	-2		0.28	81.7	77	0.05	12.40	
	Σ11a_T10	0	1	-1	1	0	1	-1	-2		0.32	60.9	99	0.05	118.84	
	Σ11a_111 Σ11a T12	-1	-1	0	1	-1	-1 1	0	-2 -2		0.25	153.0	38	0.22	153.10	

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4.8. TEM

TEM selected area diffraction has been applied to gain insight into the state of ordering, particularly to obtain evidence of the presence of Ti_3AI in DO_{19} -strucutre in the diffraction pattern (DP). Dark field images were taken to visualise the ordered regions.

4.8.1.TEM foil preparation

First, slices of around 500-700µm thicknesses were cut out of the bulk material. The normal of the foil aligns mostly with RD and in a few cases with ND (only quenched Ti-Al samples and aged Ti-10Al). In order to obtain foils of a final thickness of ~100µm the slices were thinned manually down to P1200 grinding papers and finally punched with 3mm diameter. Afterwards sharp edges were smoothed with P1200 paper. The final preparation step is electro thinning to achieve electron transparent regions. Best results, with high repeatability, were achieved by using a double-jet polishing apparatus (STRUERS, Tenupol 5) and an attached recirculation cooler unit (Julabo FP50). Voltages of 14-15.5V result in good sample quality at currents of 50-90µA after 1-3min polishing. Either of following electrolytes were mixed up to 11 and used at -30°C, depending on availability. Both mixtures contain 3.6% pure perchloric acid. It is advised to add perchloric acid only when the methanol measures below -20°C to slow down the exothermal reaction.

Electrolyte A

0	6% Perchloric Acid (60%)	HCIO ₄	60ml	
0	94% Methanol, anular grade	CH ₄ O	940ml	
	Electrolyte B			
0	5% Perchloric Acid (70%)	HCIO ₄	50ml	
0	95% Methanol, anular grade	CH₄O	950ml	

The procedure is also possible without cooler unit and instead frequent use of liquid nitrogen to keep the electrolyte below -30°C, but results vary in quality.

4.8.2.TEM diffraction and DF imaging

The foils aligned with their normal parallel to the RD allow easy access to the $\{1\overline{1}00\}$ -zone axis, which was previously used for visualising extra super-lattice diffraction spots from DO₁₉-structures of Ti₃Al [Gysler 1982]. With the help of a Kikuchi map (Fig. 4-26), the $\{1\overline{1}00\}$ -zone axis could be found and indexed with the help of Williams TEM guide [Williams 2009] (see Fig. 4-27). The higher dynamic range of image plates in comparison to a CCD camera allows substantial image enhancement post acquisition. Disadvantage is that some images cannot be used when patterns of previous images have not been entirely deleted and appear faint in the Arnas Fitzner, PhD Thesis, 2014
background. This can cause great confusion. In samples where the super-lattice reflection was visible, the objective aperture was put on top to eliminate any other contributions to the DF image. DF-images were taken subsequently.



Fig. 4-26: Kikuchi bands of hcp-structures with $\{10\overline{1}0\}$ -zone axis at the bottom centre [Engler 2009]

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FIGURES 18.21. Six standard, indexed, DPs for hcp crystals in the $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$, [0001], $[01\bar{1}2]$, $[01\bar{1}1]$ and $[1\bar{2}1\bar{3}]$ beam directions. Ratios of the principal spot spacings are shown as well as the angles between the principal plane normals. Forbidden reflections are indicated by x.

Fig. 4-27: Patterns used for indexed experimental diffraction patterns [Williams 2009]

4.8.3.DITABIS image plates

TEM images and diffraction patterns were recorded on high resolution Imaging Plates from DITABIS. These plates have a higher dynamic range than CCD cameras and photographic film, which makes them ideal to record diffraction patterns in the presence of both, strong primary reflections and faint super lattice reflections (compare Fig. 4-29 b and c). A disadvantage is that the images have to be digitized before they can be viewed. Suggested exposure times from the system range between 0.5s and 90s when the luminescence screen is well lit and result in reasonable images.



Fig. 4-28: a) Ditabis reader and eraser b) Tecnai G20



Fig. 4-29: Quality demonstration of the DITABIS image plates from the same diffraction pattern of aged Ti-10AI on the $\langle 10\overline{1}0\rangle$ zone axis. a) Recorded with DITABIS image plate b) and after enhancement c) Recorded with CCD camera and enhanced. b) and c) are enhanced similarly to maximise the appearance of the faint super lattice reflection in b).

The image plates contain doted barium fluoro-bromide crystals embedded in a blue resin, based on a metallic base layer for mechanical stability. Electrons irradiate these crystals and excite their luminescence centre to a semi-stable state. But stored information will degrade slowly and the image quality decreases dramatically when plates come in contact with daylight. Therefore the plates should be scanned soon after recording and handled in dark rooms. The plates were digitised using the DITABIS reader with standard settings, shown in Fig. 4-28 a). Red laser light in the reader stimulates the crystals in the plates to emit blue light linearly proportional to the electron dose that was captured during the exposure in the TEM. The digitized images (Fig.

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4-29 a) were subsequently enhanced. Brightness, contrast and the tone curve were adjusted using ADOBE LIGHTROOM 3 to maximise the intensity from the super lattice reflection visually (Fig. 4-29 b).

The DITABIS image plates were reused after deleting the stored information by an illumination with light on the DITABIS eraser for about 15min-60min. Experience has shown that 60min on the eraser was insufficient to remove the strong intensity after diffraction experiments, while overnight erasing was successful.

Example for pronounced precipitation

Due to very weak super lattice reflections in samples of this work a highly ordered sample was used to proof the method. For this purpose Professor Mike Loretto from the University of Birmingham kindly offered a Ti6Al4V sample, aged for 20 weeks at 500°C. Fig. 4-30 a) shows a BF image of a grain tilted into the $\{10\overline{1}0\}$ -ZA. The corresponding selected area diffraction pattern is shown in Fig. 4-30 b). The smallest objective aperture was placed on one of the super lattice reflections from Ti₃Al to obtain the darkfield image shown in Fig. 4-30 c), exhibiting precipitations on dislocations and a few spherical precipitates.



Fig. 4-30: The "Loretto sample", Ti6Al4V 20weeks aged at 500°C. a) BF image of observed area with speckle contrast, b) DP on ZA $(10\overline{1}0)$ with clear Ti₃Al superlattice reflection and c) the corresponding DF image on Ti₃Al super lattice reflection

4.9. Diffraction spectra on WISH, ISIS

WISH is a powder diffractometer optimised for diffraction experiments on magnetic structures with interest in high d-spacing. In the present case the instrument was chosen to identify short range ordering towards Ti₃AI in the Ti-AI system. Major advantage of neutron diffraction is the higher contrast between Ti and Al in neutron diffraction compared to X-ray or electron diffraction [Thirumalai 2000]. Furthermore the sample volume at WISH exceeds 1mio grains and results are insensitive to surface effects, as they occur readily in electron and X-ray diffraction from sample preparation. A full technical description of the beam line WISH and how the low background is technically achieved, can be found in reference [Chapon 2011]. At this point it should be only noted that the detector banks cover vertically +10° and -5°, 20 and horizontally nearly a full circle from 10° to 170° 20, subdivided in 9 banks in symmetrical arrangement. While bank 1 receives backscattered neutrons up to a high d-spacing of 50Å, bank 5 and 6 are symmetrically arranged around the beam stop to receive forward scattered neutrons with high resolution at short d-spacing. Bank 4 and 7 lack, just like bank 5 and 6, on intensity at high dspacing, while bank 2 and 9 exhibit not as good intensity at low d-spacing. Bank 3 and 8 receive neutrons at 20=90° and show visually best signal/noise ratio over the d-spacing range from 2Å to 7Å. For simplicity only bank 3 has been chosen for comparisons of data in the d-spacing range of interest for Ti-alloys.



Fig. 4-31: WISH diffractometer at ISIS a) and Spectra for the different banks in WISH spectrometer on example of aged Ti-10AI, with bank numbers indicated (b)

4.9.1. Setup and data manipulation

The gauge volume of the beam on WISH is 80x20mm and covers fully the sample. Measurements were taken at a pressure of 0.05 bar to reduce background. The raw data can be found at Wish, ISIS under RB RB1320274, measured on 25th September with supervision of Pascal Manuel.

Cylindrical Samples of 8mm diameter but varying length (12, 24 and 40mm as indicated in Tab. 4-5) were loaded in a Vanadium can with 0.3mm wall thickness and placed in the beam on a candlestick. The holding mechanism, made from Al and stainless steel, was covered with a cubic Bornitride cylinder to avoid scattering, as shown in Fig. 4-32. The centre of the sample was aligned in the beam centre. The holder for a shorter sample sits higher, meaning less V is illuminated. Vanadium activates significantly during the measurement with neutron radiation. To minimise the handling of "hot" material a second V-can was used, and the whole Al holder (marked in Figure 3) was exchanged with V-can and sample. The two different V-cans give rise to different backgrounds, and a small Bragg peak from V at 2.16Å. A measurements of each empty V-can were used to subtract background and the V reflection using the neutron diffraction software MantidPlot 2.6.1. Background corrected data have been smoothed using the rebunch function in Mantid with a factor of 10, and data have been plotted with a moving average over 10 data points using Microsoft Excel.



Fig. 4-32: Two Vanadium (V) cans (left) and a V can mount to the AI candlestick with attached boron nitride shield as applied for the measurements (right).

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Run number	Sample	Dimensions [mm]	Orientat ion	Holder	Counts [µA]
25470	Ti-10Al aged	~30x8.02	RD	Al holder no V can	13.6
25471	Ti-10Al aged	39.96x8.02	RD	A Vanadium can	13.6
25472	Ti-10Al aged	39.96x8.02	RD	A Vanadium can	40
25473	Ti-7Al RX	38.97x7.94	RD	B Vanadium can	40
25474	CP-Ti870	39.97x8.01	RD	A Vanadium can	40
25475	Ti-10Al II RX	38.5x7.96	RD	B Vanadium can	30
25476	Ti-7Al aged	38.95x8.02	RD	A Vanadium can	30
25477	Ti-10Al low O	39.44x7.99	RD	B Vanadium can	30
25478	Ti-13Al	38.96x7.98	RD	A Vanadium can	30
25479	Ti-3Sn	24.05x8.03	ND/45°	B Vanadium can	40
25480	Ti-1Sn	24.07x8	ND/45°	A Vanadium can	18.8
25482	Ti-10Al high O	39.85x7.95-8.02	RD	B Vanadium can	30
25483	Ti-10Zr	24.07x8	ND/45°	A Vanadium can	30
25484	Ti-3Zr	24.04x8.02	ND/45°	B Vanadium can	80
25485	Ti6Al4V	39.73x7-95-8.00	RD	A Vanadium can	30
25486	CP-Ti750	13.69x7	RD	B Vanadium can	35.4
25487	Ti5Al2.5Sn	39.97x7.96	RD	A Vanadium can	23.4
25488	Empty can B	40mm height	-	B Vanadium can	20
25863	Empty can A	40mm height	-	A Vanadium can	20
25865	CP-Ti forge	12x8	RD	A Vanadium can	22
25868	CP-Ti 870 7hrs@700°C	12x8	RD	A Vanadium can	22
25870	CP-Ti 870 & CP-Ti forge	24x8	RD	A Vanadium can	22
-	Ti-3Al			Not measured	-

Tab. 4-5: ISIS, Wish HRPD: Run numbers and associated sample details

4.9.2. Practical aspects for result interpretation

Due to sample availability measurements were taken on two different sample dimensions and textures. The big detector coverage from wish allows neglecting texture effects. Even though sample size effects have been stated as correctable prior to the experiment, no acceptable way was found to match diffraction spectra from different samples sizes. Measurements of CP-Ti on three different sample sizes have been taken to evaluate possible correction methods and show that larger samples have higher background levels (Fig. 4-33). Linear scaling by a factor (for example volumetric ratio) to match intensities of multiple alloys at one particular d spacing or subtracting a general background curve have been found to distort the data. Corrections have neither been applied for the effect of sample sizes nor for the effect of alloying on the neutron scattering properties. Therefore only data from samples of approximately the same size are compared. Effects of alloying elements can be compared directly in all Al containing samples, but separately for the Ti-Sn and Ti-Zr system where the sample length was only 24mm.



Fig. 4-33: Sample size effect on background in WISH for CP-Ti

An increased background level is not only caused by bigger sample sizes but also by an increased incoherent cross section. Neutron scattering properties for the elements of interest in this study (see Tab. 4-6) show that any element but V should decrease the background noise.

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Element	Charge- number	Bound coherent scattering length	Coherent cross section	In- coherent cross section	Total cross section	Thermal absorption cross section for 0.0253 eV
Symbol	Z	b _c [fm]	σ _{coh} [barn]	σ _{inc} [barn]	σ _{scatt} [barn]	σ _{abs} [barn]
Ti	22	-3.3	1.485	2.87	4.35	6.09
AI	13	3.449	1.495	0.0082	1.503	0.231
Sn	50	6.225	4.871	0.0022	4.892	0.629
Zr	40	7.16	6.44	0.02	6.46	0.185
0	8	5.805	4.232	0	4.232	0.00019
V	23	-0.443	0.018	5.08	5.10	5.08

Tab. 4-6: Neutron scattering properties for important alloying elements of Ti [Dianoux 2002]

4.10. In-situ compression tests at Engin-X

Major purpose of in situ lattice strain measurements during the mechanical loading is the characterisation of the intergranular strain response. The following chapter describes measurement strategies and how data have to be treated specifically for the setup on Engin-X.

4.10.1. Measurement strategies

Many strategies for in-situ mechanical testing have been used and compared in recent years. Ideally, lattice strain data are acquired during mechanical loading using a constant strain rate. But titanium's poor neutron scattering properties leads to long measuring times and force the experimenters to compromise to avoid cold creep from about 60% of the yield stress [Hasija 2003]. Skippon et al. experimented on that issue and showed Zr-data for two constant strain rates and step loading using position; stress and strain control (Fig. 4-34) [Skippon 2013]. The two different strain rates show in principal the same lattice strain behaviour of the $\{11\overline{2}0\}$ plane, but the faster strain rate shows higher lattice strain and macroscopic stress for twin initiation. While the incremental stress controlled measurement reflects the onset of twinning rather poor, the strain controlled data points underestimate the typical s-shape of the lattice strain response from twin initiation. Best match, to particularly the slow strain rate, seems the position controlled loading. However, that research article was only available after a major part of experiments for this PhD project had been accomplished. Instead most in-situ loading experiments were carried out using the approach followed from Warwick and Dye [Warwick 2012] undertaking Arnas Fitzner, PhD Thesis, 2014

measurements in the unloaded rather than loaded condition in order to minimise cold creep. The reloading to go to the next macroscopic strain level was shown to have little effect on the stress-strain curves [Nemat-Nasser 1999]. That approach measures only the residual lattice strains $\varepsilon_{hkl-residual}$ and not the lattice strains under the applied stress. In order to extrapolate the measured residual lattice strains to a situation under load diffraction elastic constants DEC_{hkl} are required. Therefore several lattice strain measurements at full stress $\varepsilon_{hkl-true}$ were taken in the elastic regime of the material to then calculate DEC_{hkl} from the stress increment $\Delta \sigma_{Elastic}$ according to Equation 4-15. The residual lattice strains were extrapolated to the apparent lattice strains at full stress in the plastic regime according to Equation 4-16.

$$DEC_{hkl} = \frac{\Delta \sigma_{Elastic}}{\varepsilon_{hkl-true}}$$

Equation 4-15: Diffraction elastic constants

$$\varepsilon_{hkl-extrapolated} = \frac{\Delta\sigma}{DEC_{hkl}} + \varepsilon_{hkl-residual}$$





Fig. 4-34: Effect of loading mode on lattice strain development [Skippon 2013]

4.10.2. Engin-X setup

Engin-X is a time of flight (ToF) instrument with stationary detectors 90° inclined to the pulsed and polychromatic incident beam. The 90° detector banks at Engin-X span their reception area in real space (20) horizontally from 76° to 104° from the incident beam and vertically from +21 to -21° (Fig. 4-35 a) and detect diffracted neutrons. A vertical subdivision in 5 modules of 8.5° range, with their centres in 0°, ±8.5° and ±17° allows rough orientations of eg. single crystals or polycrystals with only very limited amount of grains in the gauge volume. However, the horizontal subdivision is smaller than 1° and allows very good angular resolution. More important for twin fraction estimations are the full horizontal range of 28° (90° +14/-14°) and the full vertical range of 42° (0° ±21.25), resulting in a reception area reaching to nearly 30° in the corners of the detector. Bragg's law can be rewritten for ToF methods (see Equation 4-17), describing the relationship between the scattering angle θ and the lattice spacing d_{hkl} to the wavelength λ_{hkl} of the white neutron beam. The detector coverage was approximated on a stereographic projection with ±7° horizontally and ± 10.5° vertically for the axial and transverse detector (Fig. 4-35 b). A more accurate projection can be found in reference [Malamud 2014].

 $n\lambda_{hkl} = 2d_{hkl}\sin\theta$



Equation 4-17: Bragg's law for ToF [Dianoux 2002]

Fig. 4-35: Setup at Engin-X a} seen from transverse direction with labels on crucial parts for the experimenter and b) coverage of detectors on stereographic projection together with a 30° circle as usually applied for twin fraction analysis from EBSD texture measurements.

Samples of 8mm diameter and 12mm length were compressed using a hydraulic Instron 100kN stress rig equipped with compression plungers from hardened H13 steel. The diffraction data were collected using a 8mm vertical slit and 4mm horizontal slit on the incident side (Fig. 4-36 b) and 4mm collimators (Fig. 4-36 a) on the reception side. The diffracting gauge volume within Arnas Fitzner, PhD Thesis, 2014

the sample was therefore a rectangular cuboid measuring 4mmx4mm in the horizontal plane, and with a height in the vertical direction of 8mm, which corresponds to the full diameter of the sample and allows quicker measurements. Deformation hot spots and higher stress levels in the compression axis, compared to the edge of the sample are neglected and it is assumed that uniform deformation behavior throughout the gauge volume takes place. Because of the 45° angle between the incoming neutron beam and the stress axis of the loading rig, as visible in Fig. 4-36 a), the cuboid is rotated by 45 degrees in the horizontal plane. This means the diagonal of the horizontal faces of the cuboid are parallel to the loading and transverse axis, and the top and bottom corners will stick out the cylindrical sample (Fig. 4-36 b). Using uniform sample dimensions allows neglecting these details, but a significant deviation from the sample diameter will decrease the illuminated material in the gauge volume and obscure intensity data. A simple volume correction as presented in Equation 4-18 gives reasonably comparable intensity values.

I_{Corrected}=I_{Deviation}*V_{Original}/V_{Deviation}





Fig. 4-36: Setup at Engin-X a) Overview from axial direction with 4mm collimators on north and south bank, 100kN loading rig in place b) the compression sample held between the grips with horizontal and vertical slit moved close to sample c) Co-worker aligning the sample in x-axis and z-axis.

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However, smaller sample volumes decrease the accuracy in lattice strain and intensity data using the same measurement times. To ensure comparability between samples a perfect sample alignment in x-, y- and z-axis is essential. Fig. 4-36 c) shows colleague Peter Honniball checking the x and z-alignment in an optical scope. Subsequently a beam scan was carried out to align the sample in the y-direction.

The setup is drawn schematically in Fig. 4-37 a). The schematic shows the incident beam, transverse and axial detector, 45° inclined from the loading axis in the sample, as described above. Fig. 4-37 b) shows the angular divisions of the subdivided detector banks.





Considering the crystal structure of Ti, Tab. 4-7 lists theoretical d-spacing and angles between planes for a given lattice parameter.

For the result interpretation the crystal geometry has to be considered. After trigonometric laws the values in Tab. 4-7 can be calculated for the hcp crystal structure of CP-Ti. It can be seen that none of these major lattice planes is inclined within $\pm 5^{\circ}$ to another one. Thus reflections of one single grain will always be more than 10° apart from each other on the stereographic projection and making it unlikely that multiple planes of one grain diffract into the same detector. As a consequence, the full diffraction spectrum in one of both Engin-X detectors will originate from different grain families, with each peak belonging to a certain set of grains. However, the same grain may diffract into multiple grain families between both detectors. As each diffraction peak consist of specific grain families only, the results have to be understood as jigsaw from multiple grain families. This is shown on an example in the following.

Lattice plane	Length in unit cell [Å]	d- spacing [Å]	Angle to c (around a)	Angle to a (around c)	Angle to a (around a)
$\{10\overline{1}0\}$	2.953	2.55	90	0	0
{0002}	4.685	2.34	0	90	90
$\{10\overline{1}1\}$	5.56	2.24	32.22	57.77	0
$\{10\overline{1}2\}$	3.77	1.73	51.57	38.4	0
$\{11\overline{2}0\}$	3.406	1.46	90	0	30
$\{10\overline{1}3\}$	3.34	1.33	62.14	27.87	0
$\{11\overline{2}2\}$	3.49	1.24	32.22	57.78	30

Tab. 4-7: Length and angular values for the major lattice planes in hcp lattice for CP-Ti.

4.10.3. Observation of twinning on Engin-X while loading in RD

As only little of the total diffracted beam is captured, it is important to align the sample according to its starting texture. In the example in Fig. 4-38 samples are loaded along the previous RD and only very low intensity of $\{0002\}$ and $\{10\overline{1}3\}$ can be measured axially before loading, but therefore a good signal for instance $\{11\overline{2}0\}$ and $\{10\overline{1}1\}$. The transverse detector exhibits high intensity of the $\{0002\}$ peak. Also the corresponding $\{0002\}$ pole figure from EBSD macro texture measurements in Fig. 4-38 shows little intensity of basal planes in LD, but higher intensity in the transverse plane. Intensities of the $\{0002\}$ peak and the $\{10\overline{1}3\}$ peak in the axial detector both increase with increasing plastic strain and load. Due to the crystal symmetry the $\{10\overline{1}0\}$ peak decreases its intensity in the axial detector and intensity changes in the transverse detector are inversed. The pole figures of the $\{0002\}$ and $\{10\overline{1}0\}$ planes reflect the trends from the Engin-X diffraction patterns and are shown for approximately the same plastic strains. These dramatic intensity changes during loading are introduced by crystal reorientation due to twinning.



Fig. 4-38: Example for development of basal and prismatic pole figures from ex-situ EBSD macro texture measurements and raw diffraction spectra during the in-situ compression test. Shown are diffraction patterns in transverse and axial detector banks, the major lattice planes are indexed. The first row depicts the situation prior to loading and before the onset of deformation twinning, row two an intermediate state and row three after extensive twinning (~25%).

From EBSD orientation maps, as presented in Fig. 4-39, it can be seen that the $\{10\overline{1}2\}(10\overline{1}1)$ tension twin is the dominant twin system. Studying the colour code in Fig. 4-39, or the twin geometry, also shows that this twin systems signature is a rotation of the c-axis into the compressive loading direction and a rotation of the a-axis out of the compression direction. Intensity developments in the transverse detector are somewhat inversely proportional compared to the axial detector.

As shown in Fig. 4-35 b), the detectors cover only a small angular range in axial and transverse direction. In order to visualize the orientations of the diffracting grains these ranges have been input as texture component in channel 5 and applied to detailed orientation maps. Set is a fiber texture $\pm 10^{\circ}$ to Z, which corresponds to the LD and $\pm 10^{\circ}$ to X, corresponding to the transverse detector as indicated by the green circles in Fig. 4-35 b). In fact the detectors at Engin-X cover a roughly rectangular area instead of the circular area used here. The six major diffracting planes are indexed in the diffraction spectra shown in Fig. 4-38. The same example, CP-Ti compressed to 9% along the original RD (Fig. 4-39), was used to visualize grains contributing to these diffraction peaks. Each reflection is highlighted separately for axial and transverse detector on the EBSD map (Fig. 4-40). It can be seen that the {0002} reflection in axial direction (Fig. 4-40 a) covers mostly tension twins, but also few parent grains, undergoing compression twinning.

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Also the $\{10\overline{1}3\}$ and the $\{10\overline{1}2\}$ reflections in axial direction cover mainly tension twins (Fig. 4-40 c and e). Any sudden intensity increase of these three reflections can therefore be related to twin activity. The axial $\{10\overline{1}1\}$ reflection (Fig. 4-40 g) originates from twins and parent grains and cannot be used for evaluations of the twin activity. The reflections of the prismatic planes in axial direction (Fig. 4-40 i and k) originate from the parents of the twins. The transverse detector shows obviously a different picture: The $\{0002\}$ and the $\{10\overline{1}3\}$ reflections, both with significant c-component in transverse direction, cover mostly the parent grains of tension twins. Grains, which have a high Schmid factor for basal slip are covered by the $\{10\overline{1}2\}$ and the $\{10\overline{1}1\}$ reflections in the transverse direction (Fig. 4-40 f and h). These two reflections also include compression twins and some of the parent grains of tension twins. The prismatic reflections in the transverse detector (Fig. 4-40 j and I) originate from a mix of compression and tension twins, their parents and untwinned grains. When the six major reflections for one detector are highlighted together on the same EBSD map (Fig. 4-41 a and b) it becomes clear that only about 50% of the grains contribute to the diffraction peaks on Engin-X, with only few grains contributing to multiple reflections. The stereographic projections in Fig. 4-41 c) illustrate the origin of the colouring in the orientation maps for the axial detector (Fig. 4-40 a, c, e, g, i and k as well as Fig. 4-41 a). The texture component used to colour the orientation maps results in a 10° circle around the LD for the corresponding crystallographic plane. The $\{10\overline{1}2\}$ reflection is somewhat overshadowed by the $\{10\overline{1}3\}$ reflection due to the vast amount of data in the same plot. Fig. 4-41 d) illustrates the orientations in transverse direction, as used to colour the orientation maps in (Fig. 4-40 b, d, f, h, j and I as well as Fig. 4-41 b). Observations on a much bigger area from compressed, big grained CP-Ti (EBSD map Fig. 4-43 a) also show only about 50% coverage in the Engin-X detectors of the material in the gauge volume. The reflections in the axial detector cover regions in the full EBSD map as: 1.8% from the {0002} reflection, 15% from the $\{10\overline{1}3\}$, 10% from the $\{10\overline{1}2\}$, 6% from the $\{10\overline{1}1\}$, 1% from the $\{10\overline{1}0\}$ and 8% from the $\{11\overline{2}0\}$ reflection. In transverse direction only 0.8% are covered from the $\{0002\}$ reflection, 8.6% from the $\{10\overline{1}3\}$, 9.5% from the $\{10\overline{1}2\}$, 7.7% from the $\{10\overline{1}1\}$, 5.3% from the $\{10\overline{1}0\}$ and 4.2% from the $\{11\overline{2}0\}$ reflection.

The analysis of diffraction data during compressive deformation regarding twin formation uses these situations. The twin activity can be seen on the intensity increase of especially the $\{0002\}$ but theoretically also the $\{10\overline{1}3\}$ and the $\{10\overline{1}2\}$ reflection in axial direction. But due to different structure factors of these three crystallographic planes their intensity change can't be summed up directly. Practically, the increase of the $\{10\overline{1}3\}$ and the $\{10\overline{1}2\}$ reflection in axial direction is not as clear as the increase of the $\{0002\}$ reflection. When the global Schmid factor for twinning is highest, earliest onset is expected, as it is the case for grains aligned with their $\{0002\}$ pole in transverse direction. Therefore only the lattice strain of the $\{0002\}$ reflection is evaluated for direct measure of twin activity. Information about the strain and stress state of the grain families prone to twinning are revealed from the same reflection in the transverse detector.

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Fig. 4-39: Example EBSD map from CP-Ti after 9% compression in a) IPF Z colouring with twin boundaries indicated as: Black= $\{10\overline{1}2\}<10\overline{1}1>$, Grey= $\{11\overline{2}1\}<\overline{11}26>$, White= $\{11\overline{2}2\}<\overline{11}23>$. b) shows the same are as band contrast map as used in Fig. 4-40 and Fig. 4-41. Twin boundaries are indicated in red= $\{10\overline{1}2\}<10\overline{1}1>$, green= $\{11\overline{2}1\}<\overline{11}26>$ and blue= $\{11\overline{2}2\}<\overline{11}23>$.



a) axial {0002}



b) transverse {0002}



c) axial {1013}



d) transverse {1013}



e) axial {1012}

Fig. 4-41: a-f. Caption on following page

f) transverse {1012}

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Fig. 4-40: EBSD map from Fig. 4-39 with band contrast as background and regions coloured when diffracting $\pm 10^{\circ}$ to LD or TD as: a) axial {0002}; b) transverse {0002}, c) axial {1013}; d) transverse {1013}; e) axial {1012}; f) transverse {1012}; g) axial {1011}; h) transverse {1011}; i) axial {1010}; j) transverse {1010}; k) axial {1120}; l) transverse {1120}.

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Fig. 4-41: Example EBSD map from Fig. 4-39 with the six major crystallographic planes reflecting a) $\pm 10^{\circ}$ from axial direction, approximately as in the axial detector at Engin-X and b) $\pm 10^{\circ}$ to transverse direction, as approximately in the transverse detector at Engin-X. The corresponding stereographic projections are shown as scatter plot in c) and d) respectively. The angular ranges of the axial and transverse detectors are indicated on the {0002} reflection in c) and the 10° and 30° circles are indicated.



Fig. 4-42: Intensity as function of maximal applied stress for a) axial detector and b) transverse detector

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Fig. 4-43: EBSD example microstructure after compression at Engin-X in different colourings: a) IPF Z with indicated twin boundaries; b) Captured intensities in axial detector, b) Captured intensities in transverse detector

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4.10.4. Twin observation in different loading directions at Engin-X

If the loading direction of the sample is altered, also the initial diffracted intensities for each reflection alter. The basal pole figures in Fig. 4-44 are rotated into three different cases. The loading direction is indicated by red dots. The previous chapter described detailed that the basal intensity is low when LD//RD. A similar situation is present when loading the sample 45° between the original RD and ND, labelled as 45° in Fig. 4-44. Little basal intensity is present axially before loading, while good intensity is present in transverse direction. A sample loaded along the former ND exhibits significant {0002} intensity in the axial detector. But the sample can be loaded in two ways, leading to different situations in the transverse detector: The split direction of the basal pole can be either aligned vertically (variant A in Fig. 4-44) or horizontally (variant B in Fig. 4-44). For variant A no basal intensity is present in the transverse detector, which allows the detection of compression twinning. Therefore, Variant A has been chosen during experimentation.





In the following, the orientations of the three active twin systems are compared for these three described loading situations. Fig. 4-45 shows the orientations of twins on scatter plots from orientation maps recorded by EBSD on the example of CP-Ti compressed to approximately 9%. It can be seen that the basal pole of the dominant $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twin always aligns within 30° to the LD. Accordingly, the prismatic planes build a ring in the transverse plane. The basal pole of the $\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twin aligns not exactly in LD, but as ring between ~15° and ~45° to LD and therefore having orientations like some of the $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ twins. The compression twins predominately have their basal pole perpendicular to the LD, and one of the prismatic planes close to LD. The orientation of a particular twin type is almost independent to the loading direction but the probability for each twin type is dramatically affected.

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Fig. 4-45: Scatter plots of three twin types on a stereographic projection for three different loading directions. The axial and transverse detectors from Engin-X are shown in grey.

A more complete picture of these three twin systems is shown in Fig. 4-46, where orientations of the six major reflections have been plotted on the stereographic projection for a) the twinned fraction and b) the parent grains. Different samples have been chosen, to maximise the number of data points per twin system. The case for CP-Ti loaded in RD, with a high fraction of the $\{10\overline{1}2\}$ ($10\overline{1}1$) tension twins, has been discussed above. The $\{11\overline{2}1\}$ ($\overline{11}26$) tension twin system is more pronounced in other alloys, especially in Ti-3Sn. Instead of the alignment of the basal pole in LD as at the $\{10\overline{1}2\}$ $(10\overline{1}1)$ twin, one of the 6 $\{10\overline{1}3\}$ planes aligns close to LD and the basal pole aligns within a ring around LD, as shown in Fig. 4-46 a). The orientations from the $\{11\overline{2}1\}\langle\overline{11}26\rangle$ and $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ twins (Fig. 4-46 a) and their parents (Fig. 4-46 b) can be equal. As the $\{10\overline{1}2\}$ ($10\overline{1}1$) twin is far more frequent, no clear states about activity or strain stated from the $\{11\overline{2}1\}\langle\overline{11}26\rangle$ twin can be made. However, the comparably rare CT can be detected during the neutron experiment as no other deformation mode offers this sudden alignment of the basal pole in the transverse plane. An increase in intensity of the {0002} reflection in the transverse detector indicates the onset of compression twinning. Unfortunately only a very small angular range in the TD is captured from the transverse detector, which strongly limits the power of investigations of compression twin activity.



Fig. 4-46: Scatter plots for a) three twin systems major pole projections after 9% compression and b) their parents orientation. Underlying samples are CP-Ti loaded in RD for TT1, Ti-3Sn loaded in RD for TT2 and CP-Ti loaded in 45° for CT.

5. Baseline characterisation

This chapter outlines the different manufactured alloys and provides an estimate of the homogeneity of the bars in different aspects to understand in how conclusions can be drawn across the proposed publications.

5.1. Chemistry of alloys

The binary alloys from this study exhibit all roughly the same level of impurities, as it can be seen in Tab. 5-1. While the concentrations of Carbon (C) and Nitrogen (N) are negligible; the content of O is with approximately 1000ppm rather important. The content of O seemed to increase with prolonged heat treatments in argon atmosphere as found on the Ti-Zr system. The O content increased from 758ppm to 1098ppm and 1508ppm in Ti-10Zr during recrystallization treatment of test samples at 750°C in Argon shield for 5, 25 and 60 hours respectively.

Alloy batch	AI	Sn	Zr	V	С	Fe	Ν	0	Si
CP-Ti forge	-	-	-	-	-	-	37	694	-
CP-Ti-750	<10	110	<10	<20	55	46	13	507	40
CP-Ti-870	<10	<100	<10	<20	53	48	31	625	39
Ti-3Al	2.00%	<100	<10	<20	72	45	39	474	40
Ti-7Al-l	3.95%	<100	<10	<20	58	77	55	413	38
Ti-7Al-II	3.87%	<100	<10	<20	42	49	7	-	<50
Ti-7Al-II ^a	-	-	-	-	-	-	-	592	-
Ti-10Al-l	5.92%	<100	<10	<20	94	61	85	756	39
Ti-10Al-II	5.87%	<100	<10	<20	35	59	12	620	<50
Ti-10Al-II ^a	-	-	-	-	-	-	-	567	-
Ti-10Al-LowO	5.92%	<100	<10	<20	83	47	31	763	<50
Ti-10Al-HighO	5.85%	<100	<10	<20	55	46	33	4349	<50
Ti-13Al	7.85%	<100	<10	<20	55	47	94	377	<50
Ti-1Sn	<10	2.41%	<10	<20	48	53	36	1227	46
Ti-3Sn	<10	8.08%	<10	<20	42	48	25	589	37
Ti-3Zr	<10	<100	6.63%	<20	67	74	33	636	40
Ti-3Zr SG	-	-	-	-	-	-	-	534	-
Ti-10Zr	<60	<100	17.49%	<20	83	81	24	580	41
Ti6Al4V									
Ti6Al4V ^a	Accurate compositions are confidential but correspond to AMS 4911,								
Ti5Al2.5Sn	Titanium alloy grade 6 and Timetal 685 respectively.								
Ti5Al2.5Sn ^a									
Timetal 685									

Tab. 5-1: Chemical composition of observed Ti-alloys during this project in ppm unless stated as wt%. Aged samples marked by superscriped a.

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It remains doubtful if such increased O concentration is also present in the centre of annealed button where samples for mechanical tests have been taken from. Therefore it may be assumed that the impurity levels of the binary Ti-AI and Ti-Zr alloys are comparable. No distinction between the three batches of Ti-10AI (Ti-10AI-I, Ti-10AI-II and Ti-10AI-LowO) or of the two batches Ti-7AI (Ti-7AI-I, Ti-7AI-II) were made, but the binary Ti-10AI-HighO was purposely infused with additional 4000ppm Oxygen.

The binary Ti-Sn alloys do not match the low Oxygen concentrations, as Ti-1Sn with shorter recrystallization time at the same temperature, shows nearly twice the O content of Ti3Sn and overall the highest O content of the binary model alloys, indicating increased O concentration in Ti-1Sn. However, the difference could also be related to O contamination from insufficiently removed α case of the annealed test pieces.

Alloy batch	AI	Sn	Zr	V	Fe	0	Si
CP-Ti forge	-	-	-	-	-	0.02%	-
CP-Ti-750	<10	110	<10	<20	<100	0.02%	<50
CP-Ti-870	<10	<100	<10	<20	<100	0.02%	<50
Ti-3Al	3.49%	<100	<10	<20	<100	0.01%	<50
Ti-7Al-l	6.80%	<100	<10	<20	<100	0.01%	<50
Ti-7Al-ll	6.67%	<100	<10	<20	<100	0.00%	<50
Ti-7Al-II ^a	-	-	-	-	-	0.02%	-
Ti-10Al-l	10.01%	<100	<10	<20	<100	0.02%	<50
Ti-10Al-II	9.99%	<100	<10	<20	<100	0.02%	<50
Ti-10Al-II ^a	-	-	-	-	-	0.02%	-
Ti-10Al-LowO	10.05%	<100	<10	<20	<100	0.02%	<50
Ti-10Al-HighO	9.88%	<100	<10	<20	<100	1.20%	<50
Ti-13Al	13.13%	<100	<10	<20	<100	0.01%	<50
Ti-1Sn	<10	0.99%	<10	<20	<100	0.37%	<50
Ti-3Sn	<10	3.42%	<10	<20	<100	0.02%	<50
Ti-3Zr	<10	<100	3.58%	<20	<100	0.02%	<50
Ti-3Zr SG	-	-	-	-	-	0.02%	-
Ti-10Zr	<60	-	10.02%	<20	<100	0.02%	<50
Ti6Al4V	Acour	to compos	itiana ara a	opfidential	hut corroon	and to AMC	4011
Ti6Al4V ^a	Accura	ate compos	sitions are co	onndential	but corresp		4911,
Ti5Al2.5Sn	Titanium alloy grade 6 and Timetal 685 respectively.						
Ti5Al2.5Sn ^ª							
Timetal 685							

Tab. 5-2: Chemistry of model alloys in atomic percentage indicated by % and impurities in ppm

The industrial alloys Ti6Al4V and Ti5Al2.5Sn exhibit increased Iron (Fe) and Silicon (Si) contents but otherwise comparable interstitial concentrations. The industrial alloy TIMETAL 685 exhibits much increased Si content and cannot be compared to any other alloy. Subsequently, with minor variations in the Oxygen content, all binary alloys can be compared with focus on their concentration of substitutional elements. Those were chosen to achieve comparable atomic fractions between the different alloys, as listed in Tab. 5-2 and described more detailed in chapter 4.1 and 4.2. From a chemical pointy of view direct comparison between Ti3Al, Ti3Sn and Ti3Zr are possible as well as between Ti-10Al and Ti-10Zr. Additionally, ternary effects can be studied between Ti-10Al-HighO, Ti6Al4V and Ti5Al2.5Sn having both roughly a content of 10at.% Al.

5.2. Homogeneity of received material

5.2.1. Mechanical homogeneity

When the material was received a careful screening regarding its homogeneity was accomplished using Vickers hardness indentations on OPS polished surfaces. First, the axial homogeneity of the bars was confirmed by macro hardness test (HV20) in surfaces parallel to the former RD at the centre of the bar and 2cm from the end of the bars. The as rolled state shows no significant difference within one bar axially but a significant increase with solute concentration as shown in Fig. 5-1.



Fig. 5-1: Macro hardness on as rolled state in RD for four Al concentrations in the middle and at the end of the button, $n \ge 3$

Furthermore the cross sectional areas were tested for homogeneity by micro hardness indents (HV0.5). The first two indents were made close to the surface with a ~1.5mm spacing in RD so that the 10th indent is again within the top 0.5mm from the surface, as shown in Fig. 5-2. The indents close to the bar surface show significantly higher hardness values (see Fig. 5-3 a) than in the central plateau. Values more than 1mm away from the surface did not show any anomalies compared to the central plateau. The dramatic difference in hardness towards the

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surface could not be picked up with macro hardness indents (HV20), measuring diagonally between 200µm to 500µm, thus also suggesting that this layer may be smaller than 1mm in thickness. The layer possibly suffers from contaminations from the thermo-mechanical processing and is therefore disregarded for material characterisation. The central indents only measure ~50µm diagonally (see Fig. 5-3 b and c). The affected zone of the indent measures at least three times that value and expands over few grains. Thus hardness can be affected by the dominating orientation of the indented region. Also, the symmetric slip lines around the indents suggest orientation effects.



Fig. 5-2: Schematic of hardness indent layout for macro hardness test for homogeneity of bars a) and experimental profiles for three AI concentrations b)



b)

Fig. 5-3: Example indents on Ti-10AI. a) indent 7; b) indent 10.

a)

Afterwards, the anisotropy of the bars was tested with macro indentations parallel to the former RD and ND. Results from at least three indents have been averaged to gain the graph shown in Fig. 5-4. While in CP-Ti barely any difference occurs between both directions, Ti-3AI and Ti-7AI show higher hardness in the ND than in the RD. The difference diminishes in Ti-10AI and both directions have again equal hardness in Ti-13AI. The anisotropy increases with initial AI addition but at 13at.%=8wt% AI concentration the material seems isotropic to the hardness indenter Arnas Fitzner, PhD Thesis, 2014

again. A more detailed discussion about the effect of alloying on anisotropy is given in the proposed publication in 8"The relationship between nanohardness and the flow stress of Ti alloys: Effect of straining and solute content".



Fig. 5-4: Macro hardness as function of AI concentration in different orientations, n≥3

In order to have a fair comparison between the different alloys, only indentations along the former RD are compared in Fig. 5-5. While Zr shows a linear strengthening effect, Sn shows strong effect initially but levels of quickly and none of them reach hardness values of binary Ti-Al alloys. The hardest alloy is Ti-10Al-O, closely followed by the industrial alloy Ti6Al4V and Ti5Al2.5Sn.

Hardness measurements were previously linearly related to 0.2% proof strength and ultimate tensile strength in β Ti alloys [Okazaki 1993] and the still complex effects of the different alloying elements are described and discussed in chapters **Error! Reference source not found.** to 12.



Fig. 5-5: Macro hardness along the former RD as function of solute content in at.%. Ti6Al4V and Ti5Al2.5Sn are listed according to their atomic Al concentration.

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5.2.2. Microstructural homogeneity

The as rolled microstructure from CP-Ti is homogeneous and rather equiaxed, only a slightly elongated grain structure along the former RD is present (not shown). The binary model alloys exhibit mostly homogeneous microstructure in the ND-ND plane, but grains are highly elongated along the RD. Partly large patches of grains with seemingly similar orientations are present, as far as seen on optical micrographs after rolling. Grain sizes of all alloys are smaller than from CP-Ti and somewhat comparable for the Ti-AI, Ti-Sn alloys and Ti-3Zr in the as rolled state. Ti-10Zr exhibits significantly smaller grains and only Ti6Al4V exhibits even smaller grain size and pronounced striations in the microstructure along ND. However, for the current deformation study only microstructures after the recrystallisation heat treatments are of interest. The recrystallisation heat treatments grew equiaxed grains in most binary alloys of approximately 100µm±20µm diameter (see Fig. 5-6), measured using the linear intercept method. It was only possible to grow grains of Ti-10Zr up to 30µm and efforts to grow larger grains were not successful. Therefore, a heat treatment for Ti-3Zr with shorter annealing time and a forged CP-Ti bar were introduced to match the smaller grain size of Ti-10Zr. Ti6Al4V shows a α -grain size of ~10µm and comparisons to the binary alloys have to be accomplished under consideration of the smaller grain size. The industrial alloy Ti5Al2.5Sn has a well matching grain size with the binary alloys after recrystallization. Values for the grain sizes showing therefore a plateau around 100µm and around 30µm as summarised in Fig. 5-6, only the large grained CP-Ti 870 and Ti6Al4V lay out of these plateaus.



Fig. 5-6: Grain size as function of concentration for recrystallized state as function of the solute content and for the industrial compositions according to their Al content.

5.2.3. Textural homogeneity

Fig. 5-7 shows an EBSD micro mapping of Ti-3Al with locally highly inhomogeneous texture of the as rolled bar. The micro texture in the as rolled state shows signs of twinning and plenty of grains exhibiting significant orientation gradients above 10°. While most grains have their c-axis perpendicular to RD, shown in blue and green tones, a small fraction of lenticular shaped tension twins (red, orange and pink) exhibit local misorientation from 85° and 35°, directing the c-axis close to the former RD.



Fig. 5-7: EBSD microstructure of as rolled Ti-3AI along RD, from centre of bar in the ND-ND plane, along the former RD in IPF Z colouring. 0.25µm stepsize, scale bar indicates 100µm.

EBSD measurements on the as rolled state of Ti-10Al show large non-indexed regions, which are shown in white in Fig. 5-8 for Ti-3Al and Ti-10Al. Due to poor indexing maps have only been cleaned to the 4th neighbour to avoid artificial "grain growth" during the data processing in channel5. While only small bands exist in Ti-3Al, large patches in Ti-10Al dominate the map. Work by Luke Marshall in Sheffield University connected these to increased likelihood of shear banding with higher Al concentration, in accordance to the literature [Luetjering 2007].

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Fig. 5-8: EBSD micro maps 2cm from the end of the as rolled bar (step size 0.25µm) and after RX treatment according to Tab. 4-2 (step size 1µm) along the former RD from Ti-3AI and Ti-10AI.

Recrystalisation treatments have been applied to create a more homogeneous microstructure, which facilitates investigations of microstructural changes during further deformation in uniaxial tests. As already seen on optical micrographs in the previous chapter, the recrystallized microstructures have rather equiaxed grains. EBSB micro mapping reveals misorientations beneath 2° within the recrystallized grains, visible on plain colours per grain in Fig. 5-8. Large scaled EBSD macro texture scans with measurement direction parallel to the RD show a clockwork texture of the basal plane, in which the {0001} pole aligns roughly perpendicular to the rolling direction, without clear preference between ND₁ and ND₁₁ as shown in Fig. 5-9. The recrystallisation textures of all binary buttons are similar with respect to the c-axis orientation, but distributions vary throughout the alloys. Calculations of the Schmid factor using Hexaschmid show the dramatic effect of the c-axis orientation for the likelihood of different twinning modes. The Schmid factor for $\{10\overline{1}2\}(10\overline{1}1)$ tension twinning is maximised when the compression direction is perpendicular to the c-axis, while compression twinning is rather unlikely under compression but preferred under macroscopic tensile stress along the c-axis. The $\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twin is most likely in grains which c-axis is inclined ~45° to the LD [Stark 2010]. Textures therefore suggest that the likelihood for different twinning modes is altered in especially the complex alloys Ti6Al4V and Ti5Al2.5Sn.

Differences of preferred a-axis orientation exist between alloys, but affect twinning less significant compared to the c-axis orientation. As in Fig. 5-9 the prismatic $\{10\overline{1}0\}$ planes show in CP-Ti a 2 times random preferred orientation along the RD. But with increasing AI concentration increasingly more crystals are aligned with the $\{11\overline{2}0\}$ planes along the former RD, seen here as ring of the $\{10\overline{1}0\}$ plane around the RD.

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The homogeneity of the texture for bulk samples was additionally evaluated using neutron time of flight diffraction spectra on Engin-X, ISIS. Compression samples of 8x12mm with the former RD parallel to the LD were held with 15MPa in the loading rig, with the rig positioned in a 45° angle to the incident beam. Thus, the intensity of a reflection in the axial detector directly reflects the frequency of the underlying crystallographic planes in the gauge volume (4x4x8mm) along the RD. The reception angles of each detector are approximately $\pm 14^{\circ}$ vertically and $\pm 21^{\circ}$ horizontally. Intensities of individual peaks were fitted using the ISIS in-house software opengenie.

EBSD macro texture scans with measurement direction parallel to the RD show a clockwork texture of the basal plane, in which the {0001} pole aligns roughly perpendicular to the rolling direction, without clear preference between ND_I and ND_{II}, Only Ti5Al2.5Sn and Ti6Al4V show different textures, with increased intensity of the basal pole along the RD. The intensity measurements of the basal pole in the axial detector of Engin-X verify this result. Only CP-Ti with 100µm grain size shows little intensity (10 counts/neutron) and the industrial alloys Ti6Al4V and Ti5Al2.5Sn with 41 and 49 counts per neutron respectively. All other binary alloys show no basal pole in axial direction in the stress free condition (even though the automated peak fitting results in random intensities). It should be noted that Ti5Al2.5Sn and CP-Ti forge were manufactured on a forging route and are consequently plotted parallel to the forging direction (FD) instead parallel to RD.

Minor differences of preferred a-axis orientation exist between alloys. However, the c-axis orientation affects twinning more significant [Christian 1995]. The prismatic $\{10\overline{1}0\}$ planes show in the macro texture measurements for CP-Ti a 2 times random preferred orientation along the RD. Such orientation preference was explained by Rosi et al. from simultaneous slip on two $(11\overline{2}0)$ directions on two $(10\overline{1}0)$ prismatic planes [Rosi 1953]. But with increasing Al or Zr concentration the intensity of the $10\overline{1}0$ pole in RD becomes more diffuse, indicating a change of the active slip systems with alloying addition from the rolling texture, possibly due to SFE reduction [Philippe 1988, Smallman 1999]. The intensity measurements of the 1010 pole in relation to the $11\overline{2}0$ pole in the axial detector of Engin-X verify these trends. Closer examination of Fig. 5-10 reveals also decreasing intensity of the prismatic pole for the Ti-Sn system. This discrepancy might be caused by indexing rates of only around 50% during EBSD measurements on the Ti-Sn system, caused by a chemical reaction on the surface during polishing. The industrial alloys Ti-64 and Ti5Al2.5Sn show both higher intensities of the prismatic pole along RD in the pole figures and in to the neutron measurements. Macro zones in the industrial alloys, and the comparatively small measured areas by EBSD against the big gauge volume captured by neutron diffraction can cause these fluctuations. Due to the surface sensitivity and the statistic limitation of EBSD, the neutron results are more reliable.

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Fig. 5-9: $\{10\overline{1}0\}$ and $\{0002\}$ pole figures from EBSD macrotexture measurements for compared alloys along the former RD or FD respectively. Note that the Ti-3Sn suffers from bad indexing.

The rotation of the crystal unit cell around the c-axis causes slightly different situations for the $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ twinning system. When the a-axis, correspondingly the first order prismatic plane, is well aligned with the LD the Schmid factor is maximised (m=0.5) on 2 out of 6 planes, while 4 out of 6 planes have a high Schmid factor from 0.37 when the LD is parallel to the second order prismatic plane.



Fig. 5-10: Intensity ratio of $\{10\overline{1}0\}$ to $\{11\overline{2}0\}$ pole in axial detector ($2\theta = LD \pm 10^{\circ}$) from Engin-X for the tested alloys

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5.3. Crystal structure

The lattice spacing was determined by Rietfeld refinements of the Engin-X spectra under stress free condition recorded in the transverse detector, along the former ND of the samples. The results for the lattice parameters and the c/a ratios are presented in Fig. 5-11. The three measured samples of CP-Ti with grain sizes of 30µm, 80µm and 200µm exhibit the same lattice parameters, as expected from only minor variations of the oxygen concentration and match well with the literature value for CP-Ti [Leyens 2003].

According to the atomic radii of Al and Ti [Merck 2011] and the Hulme-Rothery rule [Dieter 1986] Al is ~1.1% smaller than Ti. The lattice spacing reduces when adding the 6% smaller substituent Al to Ti. The <a> lattice parameter reduces about three times as fast as the <c> lattice parameter but the change in <c> direction becomes more pronounced at higher concentration, while <a>- decreases somewhat linearly, leading overall to an increasing c/a ratio. Ageing has no significant effect on the lattice spacing and data points of aged (red triangles) and RX (blue triangles) Ti-7Al or Ti-10Al overlap in Fig. 5-11.

Zr atoms have 9.6% bigger radius than Ti atoms according to the Hulme-Rothery rule. Therefore Zr addition shows linear increase in the c-direction, slightly more pronounced than in a-direction, resulting in a slightly decreasing c/a ratio. Values are presented separately for the small and big grain size level in Fig. 5-11 by green crosses.

Sn has a 3% smaller atomic diameter compared to Ti, and is therefore the smallest alloying element even though it has the highest atomic mass. Surprisingly the crystal unit cell expands less than with Zr addition. The c-axis expands similarly to the effect of Zr, but less linearly. The <a>-axis barely changes dimensions; only a very slight decrease from less than 0.001Å can be noted with Sn addition.

Fig. 5-11 plots the complex alloys are according to their AI concentration in at.%. The data show that addition of O (4000ppm) to Ti-10AI very slightly increases the a-parameter, while the c-parameter increases significantly. O addition therefore increases the c/a ratio. The industrial Ti-1Sn5AI alloy has a slightly lower a-parameter and a slightly higher c-parameter than expected from the AI content only. Even though the Sn amount is similar to 1at.%, the values from the binary alloy Ti-1Sn cannot be added on values for Ti-5AI to match the measured value.

The α phase of Ti6Al4V shows for a- and c-parameter smaller values than expected from the Al concentration compared to the Ti-Al binaries and a higher c/a ratio. If one wants to put Ti6Al4V in context with the binary Ti-Al alloys, it has an equivalent effect to 13at.% Al. Especially V may contribute to this deviation with a 7.5% smaller diameter than Ti. Also Fe and O contents are higher than from the binary Ti-Al alloys, which doesn't allow direct comparison.

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In summary, the c/a ratio is increased strongest per at.% Sn, while Zr has only almost no effect. Al is less effective per at.%, but the total effect after more than 10at.% Al is strongest for the investigated binary alloys. Ageing of the binary Ti-Al alloys has no significant effect on the c/a ratio, but decreases it by trend. O clearly increases the c/a ratio. The industrial alloys show an increased aspect ratio. Ordering of Ti₃Al was observed by neutron and electron diffraction in alloys containing more than 7at.% Al, especially after ageing treatments, but not in the binary Ti-Zr or Ti-Sn alloys. Diffraction spectra are presented in the proposed publications separately.



Fig. 5-11: Lattice spacing development as function of solute content in at.% for <a>- and <c>parameter as well as the c/a ratio.

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5.4. Microstructural similarities and differences of investigated alloy range

The buttons, as produced by Timet show, homogenous hardness throughout the full length of 26cm, until 2cm from the edges. The cross section shows increased hardness in the outer layer of approximately 1mm thickness. Therefore material out of the outer 1mm layer was disregarded and only material from the core was utilised. After recrystallization treatments, most alloys exhibit a comparable grain size of about 80 μ m with similar distributions of the basal pole in the transverse plane. However, minor but systematic differences from the prismatic poles exist between the alloys. Alloying weakens the 1010 fibre along RD and the 1120 fibre strengthens instead. The lattice spacing varies for all alloys systematically, with Sn and Zr expanding the lattice and Al contracting it. The c/a ratio increases similarly with addition of Al or Sn, but does not change with addition of Zr. The more complex, Al rich alloys follow mostly the trends according to the Al concentration.

The binary alloys in the Ti-Al and Ti-Sn system as well as Ti-3Zr can be compared focusing on the substitutional content without having to consider major effects from texture and grain size. Comparisons of the deformation behaviour between the buttons and the industrial alloys and forgings are not straightforward. Special care has to be taken when looking at the Ti-Zr binary system with smaller grain size and the industrial alloys Ti6Al4V and Ti5Al2.5Sn with significant basal intensity in the RD, smaller grain size for the former one and slightly increased impurity levels. Furthermore, the different distributions of the basal pole in the transverse plane of the forged materials (CP-Ti forge and Ti5Al2.5Sn) do not allow direct comparisons to the cross-rolled model alloys.

6. The effect of Aluminium on deformation by twinning in α titanium

ABSTRACT

The deformation mechanisms of binary Ti-Al model alloys (0-13.1at.% Al) in recrystallized and aged conditions have been investigated in respect to nucleation and growth of twins using insitu loading in combination with neutron diffraction as well as detailed post mortem EBSD analysis. A consistent starting microstructure and texture was generated for all alloys promoting tensile twinning during compression testing. Two trends were identified, one for alloys showing no ordering of Al and the ones that do.

It was found that raising the AI content does first enhance twinning in Ti. While {1012}<1011> tensile twins were by far the dominant twinning type, growing substantially during deformation particularly in alloys with slightly increased AI content, small fractions of $\{11\overline{2}1\}<\overline{11}26>$ tensile twins were also identified. Titanium without any AI additions displayed additional $\{11\overline{2}2\}<\overline{11}23>$ compression twins, which were not found in any other Ti-Al alloy. Analysis of the residual intergranular strains of the twinning grain family revealed that twin nucleation becomes initially easier with increasing AI in solution, which might be an effect of increasing stacking fault energy. However, the initial correlation between AI content and twin activity might be a simple result of increasing yield strength resulting in higher misfit stresses when twinning becomes active. At high AI content, large d-spacing neutron diffraction analysis revealed short range ordering, which increased with additional ageing or further increase of AI content and was also eventually accompanied by weak α_2 formation identified by TEM selective aperture diffraction pattern imaging. A strong correlation between the dramatic drop in twin activity and increasing levels of ordering, including short range ordering, were found. Intragranular strain analysis by neutron diffraction revealed twin nucleation becoming significantly more difficult with degree of ordering while twin morphology studies by EBSD showed that ordering severely hinders growth of twin boundaries.

6.1. Introduction

Despite the importance of Aluminium (AI) as an alloying element in commercial Ti alloys, its effect on deformation mechanisms is still poorly understood. This is particularly true regarding its effect on twinning. In metals with a hexagonal close packed (hcp) crystal structure, twinning is often considered an important deformation mechanism. As it offers shear with a <c> component. This is otherwise only obtained by pyramidal <c+a> slip, which is known to have a critical resolved shear stress (CRSS) about 3-4 times that of prismatic <a> slip [Williams 2002, Lütjering 2007]. In principle, twinning increases formability and improves impact resistance because twins increase the work hardening rate during deformation [JIANG 2008], in contrast Arnas Fitzner, PhD Thesis, 2014

adding AI to Ti is known to reduce ductility [TRUAX 1974] and cause unstable shear [Williams 2002]. An increased understanding of the effects of alloying additions on twinning and associated ductility is required in order to elucidate this contradiction.

Aluminium and Oxygen (O) are potent solid solution strengthening elements in α -Ti [Donachie 2000]. Al is a substitutional element whereas O is an interstitial [Schofield 1957]. The effect of Al on slip modes and twin activity has been studied in some detail in large single-crystal compression samples [Williams 2002]. Their work showed that the CRSS for basal and prismatic <a>-slip increases with increasing Al content, and that this strengthening is higher for prismatic slip. So, although in CP-Ti the CRSS for prismatic slip is lower than that for basal slip, at 12 at.% Al they have the same CRSS. In principle, this trend can be explained by Al decreasing stacking fault energy on the basal plane [Metzbower 1971 & 1978], which is also known to have a significant effect on high temperature creep performance in α -Ti alloys [Neeraj 2001, Guo 2006]. The work of Williams et al. [Williams 2002] also showed that CRSS for <c+a> slip is consistently more difficult than <a> slip.

Regarding twin activity and twin morphology, significant differences have been observed when comparing commercially pure (CP) Ti [Chun 2005 & 2010] and for instance Ti-6Al-4V [Prakash 2010, Zaefferer 2003]. While in CP-Ti twin activity tends to be very high during the early stage of deformation and twins are readily observable due to their morphology, twin activity has often been reported to be less frequent, or even absent, in Ti-6Al-4V. The reason for this is not entirely clear but it has been suggested it is related to the small grain size, high solute content and presence of Ti₃Al precipitates [Lütjering 2007]. However, more recently, compression test of Ti-6Al-4V at room temperature have demonstrated development of a normal basal texture, which is generally associated with activation of $\{10\overline{12}\}<10\overline{11}>$ tensile twinning. Moreover, the same study suggests that despite the difficulty of twin nucleation in Ti-6Al-4V, twin growth is very rapid resulting in the consumption of entire parent grains, making the detection of twins by conventional means difficult [Prakash 2010].

For metals with a fcc crystal structure it has long been established that the propensity for twin nucleation is related to the stacking fault energy as the stacking fault can act as a nucleation site for twin formation [Venables1964, Rohatgi 2001, Zhang 2009]. Interestingly, in the absence of ordering, AI does lower the SFE on the basal plane in Ti very substantially [Guo 2006, Ghosh 2008]. Although twins in Ti do not usually involve stacking faults on the basal plane, according to one of the models of heterogeneous twin nucleation, twins initiate and grow from stacking faults on twinning planes, forming zonal dislocations with a $<10\overline{11}$ > Burgers vector in the case of $\{10\overline{12}\}<10\overline{11}>$ tensile twins [Christian 1995]. Although the effect of increasing AI content on this process cannot be easily estimated, its effect on basal SFE suggests it should make twinning nucleation easier.

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Another potential effect of Al on twin activity is its significant contribution to solute solution strengthening in Ti [Truax 1974, Donachie 2000]. The effect of Al in Ti alloys is further complicated by its tendency of first forming short range ordering (SRO) followed by long range ordering (LRO), i.e. Ti₃Al (α_2 - DO₁₉ structure), depending on the level of Al additions and heat treatment procedure. Such an ordered domain or phase is expected to strengthen the material as shearing will either result in the formation of a diffuse anti-phase boundary (DAPB) in the case of SRO or the more familiar anti-phase boundary (APB) when LRO is fully developed [Van de Walle 2002]. First principle calculations suggest that the energy for the formation of a DAPB is about 4-8 times smaller than the APB energy for Ti₃AI. It has long been suggested that ordering promotes slip localisation [Williams 1969] and more recent TEM investigations have indeed confirmed the formation of coupled dislocations in deformed Ti-6wt%AI [Neeraj 2000]. The effect of solid solution strengthening on twinning activity is difficult to estimate. On one hand, if solid solution strengthening affects the CRSS for slip but not for twinning, a higher flow stress should lead to higher twinning activity, simply because plastic deformation occurs at higher stress levels. On the other hand, the change in slip character to more localized slip with increased AI content could make the accommodation of the twinning strain in both the parent grain and the twinned volume more difficult, and hence make twinning more difficult. The effects of ordering further complicate this.

Detailed characterisation of ordering in Ti-Al alloys has been notoriously difficult. TEM analysis of Ti-15at.%Al (500ppm O) after ageing for 80h at 550°C identified spherical α_2 precipitates [Wood 1998], which coarsened to ellipsoidal precipitates along the <c>-axis during continued ageing [Wood 1998, Lütjering 1970]. Signs of ordering have also been commonly reported at Al concentration as low as 8.5at.% [Williams 2002, Truax 1974, Sircar 1986, Chaze 1987, Koike 1996]. Namboodhiri identified signs of SRO down to 7at.% Al by resistivity measurements [Namboodhiri 1973]. An adapted version of Namboodhiri's phase diagram [Namboodhiri 1983] is presented in Fig. 6-1. Reported Ti₃Al domain sizes and ageing times are given for several concentrations and temperatures as marked in the phase diagram [Williams 2002, Truax 1974, Lütjering 1970 & 1969]. For comparison, the heat treatments used in the current study are indicated. Research on the TiAl-Ti₃Al system has consistently demonstrated that although TiAl twins during deformation Ti₃Al does not [Umakoshi 1981, Thomas 1989, Minonishi 1991, Umakoshi 1993, Legros 1996, Yakovenkova 2007], suggesting that ordering hinders twinning. In addition some interesting recent studies of twin boundary mobility in a Mg-Gd alloy have also shown that ordering on twin boundaries exerts a very strong pinning force [Nie 2013].



Fig. 6-1: Ti-rich side of the Ti-Al phase diagram, adapted from [Namboodhiri 1983; Massalski 1986; Leyens 2003], edited with the current alloy treatments and positions of α_2 domain sizes. The bottom crystal unit cell depicts the full DO₁₉-structure [Mishin 2000] with stoichiometric 25at.% Al as present in the α_2 -phase, while the upper crystal unit cell depicts an ordering possibility for 6.25at.% Al (1/4 of DO₁₉).

In summary, there is no convincing explanation for how adding AI to Ti affects twinning. Increasing the AI content increases the flow stress and decreases the SFE, all of which should promote twinning. On the other hand, it leads to slip localization and ordering, both of which might suppress twinning. In light of the lack of a clear understanding of the role of AI on twinning in Ti, a series of deformation studies were carried out on binary Ti-AI alloys with AI contents ranging from 0 to 13 at.%. To facilitate a meaningful comparison, great care was taken to generate starting microstructures with very similar recrystallized grain size and macroscopic texture. The microstructure was first characterised by SEM/EBSD, TEM and neutron diffraction to determine starting texture, grain size, lattice spacing and provide evidence of α_2 and SRO. Insitu neutron diffraction compression experiments were carried out to quantify twin activity and measure the elastic strains in the parent grains. The methodology used is similar to previous work carried out on commercially pure Ti, Ti-6AI-4V, Zr alloys and Mg alloys [Oliver 2004, Warwick a&b 2012, Abdolvand, 2012, Lentz 2013, Preuss 2010] to monitor the {1012}<1011> tensile twin activity during compression testing. In the present work, the twin analysis was further complemented by detailed post-mortem EBSD analysis.

6.2. Materials and Methods

6.2.1. Material preparation

For the purpose of this research, 200g binary Ti-Al alloy buttons, with different Al content up to 13at.% Al (8wt% Al), were double melted in a tungsten arc furnace under inert gas atmosphere.

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This was followed by β forging at 1100°C at the TIMET research facility in Witton, UK. Subsequently, the buttons were cross-rolled in bar shape (14× 14× 260mm) on a "2 high Robertson mill" (WHA Robertson & Co Ltd) at 750°C for Ti-0AI and 870°C for the AI containing alloys. Ti-0AI was recrystallised (RX) at 750°C, 130°C below the β transus temperature, in a tube furnace under Argon shield for 5 hours followed by air-cooling, while recrystallisation treatments for the AI containing bars were carried out 30°C below the β -transus followed again by air cooling. The β -transus depends on AI content and therefore, Ti-3AI, Ti-7AI, Ti-10AI and Ti-13AI were recrystallized at 895°C, 933°C, 968°C and 990°C, respectively. The β -transus temperatures were determined using Thermocalc, which is known to provide reasonable results for the given range of alloys [Namboodhiri 1983, Schuster 2006, Massalski 1986].

Alloy	Т	t	GS	
	°C	h	μm	
Ti-0Al	750	5	94	
Ti-3Al	895	5	82	
Ti-7Al	933	5	73	
Ti-7Al ^a	380	120	74	
Ti-10Al	968	5	71	
Ti-10Al ^a	420	120	77	
Ti-13Al	990	5	78	

Tab. 6-1: Heat treatments of the model alloys in this study and resulting grain size

Ti-0Al was annealed at a lower temperature than the binary alloys in order to achieve a similar final grain size. In addition, some Ti-7Al and Ti-10Al samples were cooled at 10°C/hour from RX temperature to 380°C and 420°C respectively, around 30°C below the α - α ₂-transus temperature suggested by Namboodhiri [Namboodhiri 1983], and aged for 120 hours. The different heat treatment procedures and the according grain size estimates are listed in Tab. 6-1. Chemical analyses were performed after annealing by TIMET, Savoie, France using inductively coupled plasma mass spectrometry on a HORIBA Ultima2 for metallic elements, on a HORIBA EIMA 820V for C and on a LECO EF-400 for O and N. Tab. 2 lists the measured chemical composition of the binary alloys displaying oxygen (O) concentration of 1000±500ppm, while carbon and nitrogen are below 100ppm. Rectangular and cylindrical samples of $6x6x9mm^3$ and 6mm diameter and 9mm length were machined for ex-situ compression testing while for in-situ loading using neutron diffraction cylindrical samples of 8mm diameter and 12mm length were required.

6.2.2. Microstructure analysis

Cross sections with the plane normal parallel to the former rolling direction (RD) were cut from the middle of non-deformed and deformed samples and prepared by mechanical grinding to P4000 paper followed by oxide particle suspension (OPS) polishing for 5min at a force of 20N, Arnas Fitzner, PhD Thesis, 2014

15N and 10N in contra rotation and finally 5min with 10N in counter rotation. Three rounds of Kroll's etching for 10s (3% hydrofluoric acid, 6% nitric acid and balance water) and semiautomatic OPS polishing with 5N for 60min produced a sufficiently good finish for optical microscopy (OM), X-ray diffraction (XRD) and electron backscattered diffraction (EBSD). The presented textures were measured on a CamScan Maxim 2500FEG SEM with NordLYS detector. The CamScan was operated at 20 kV using an aperture of 100µm and a spot size of 6.25 resulting in 6.8nA probe current. Detailed orientation maps were also recorded on a FEI Sirion FEG SEM using 100µm aperture and spot size 4, resulting in 5.06nA probe current. A step size of 1µm allowed recording maps covering typically more than 100 grains. Data were cleaned and analysed using the HKL software package Channel5. Twin boundary criteria, as given by Bozzolo et al. [Bozzolo 2010], were used to identify twins and quantify relative area fractions for each system manually. For texture analysis, areas of at least 4×4 mm², covering more than 3500 grains, were scanned using a 40 µm step size. In addition, the macrotexture measurements were used to approximate the $\{10\overline{1}2\}<10\overline{1}1>$ twin activity A_{twin} based on texture changes by using equation 6-1, where N_{RX} is all indexed EBSD data points before deformation, n_{RX} is a subset within 30° to the loading direction (LD), N_s is all EBSD data points of the deformed sample and n_s is a subset within 30° to LD.

$$A_{twin} = n_S / N_s - n_{RX} / N_{RX}$$

Equation 6-1

It should be pointed out that any great degree of reorientation of the hexagonal close packed (hcp) crystal at small strain levels is unlikely to be related to slip, as slip creates a more gradual texture change [Philippe 1988]. It should also be noted that 65° compression twins would decrease A_{twin} , while 35° tensile twins could increase it [Philippe 1988]. However, the contribution of these other twinning modes is much smaller than those of $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning. Schmid factors for each individual slip and twin system were calculated for individual grains using HEXASCHMID to evaluate their likelihoods.

Thin foils for transmission electron microscopy (TEM) were prepared of solution treated and aged material (~100µm thickness) by electro polishing (6% perchloric acid (60%) and 94% methanol) between -50 and -35°C at 15V using a Tenupol 5. A FEI Tecnai G20 with a LaB₆ filament was used at 200 kV equipped with Ditabis image plates that provide a high dynamic range enabling the detection of faint Ti₃Al superlattice reflections. Long wavelength powder diffraction type measurements were carried out at the time-of-flight beamline WISH, ISIS, to assess the state of ordering (SRO, LRO) [Chapon 2011]. Cylindrical bulk samples of 8mm diameter and 40mm length were loaded in one of two Vanadium cans of 0.3mm wall thickness and mounted on an Al candlestick. Boron nitride shielding was used to avoid scattering from the Al holder. The sample was aligned in the centre of the beam gauge volume (20x80mm) and measurements were taken below pressures of 0.05 bar for 60min. Background subtracted

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spectra from bank 3, which provided the highest flux at 90° from the incident beam, were smoothed with moving average over 20 points.

6.2.3. Mechanical testing

Standard compression tests were conducted on an Instron 5569 at room temperature and an initial strain rate of 10^{-3} 1/s. The use of Lubriplate grease minimized barrelling of the sample and helped ensure a uniaxial stress state during deformation. Samples for microstructural and texture observation were monotonically strained to $\epsilon_{pl} = 1.7\%$, 3.7% and 8.7% parallel to the rolling direction (RD).

6.2.4.In-situ loading using neutron diffraction

In-situ compression experiments using neutron diffraction were carried out at beam line ENGIN-X, ISIS, UK. ENGIN-X is a time of flight (ToF) instrument with two detectors installed at 90° to the incoming beam [Daymond 2004, Santisteban 2006]. With a loading rig (an Instron 8562 with 100kN load cell) positioned at a 45° angle to the incident neutron beam, as shown schematically in Fig. 6-2, the two detectors allow recording of diffraction spectra parallel (red areas) and transverse (blue areas) to the loading direction (LD). The samples were incrementally loaded and diffraction patterns obtained at every increment until 75% of the expected yield stress from the ex-situ compression tests, providing data for the determination of the diffraction elastic constants. Above 75% of the yield stress, measurements were carried out in the unloaded condition to avoid significant cold creep during neutron diffraction measurements. For each loading experiment about 14 diffraction measurements were carried out within the plastic regime up to 9% plastic strain. A current of 30 µA was collected for each data point to ensure a good signal-noise ratio, which took 24 minutes under optimal beam conditions. The most common twinning mode in Ti alloys is the $\{10\overline{1}2\}<10\overline{1}1>$ tensile twin, which provides a near 90° rotation of the c-axis from a tensile to a compressive stress condition, causing an increase in the 0002 peak intensity along the loading direction which can be monitored using the axial detector. In addition, shifts in the position of the 0002 reflection in the transverse detector can be used to monitor the (residual) elastic strain of the grains that are most likely to twin. Single peaks were fitted using the in-house ISIS software Open Genie. The lattice strains evolution was calculated as described by Warwick et al. [Warwick b 2012]. The initial lattice spacing of each alloy was determined by Rietveld analysis of the spectra recorded on each detector before loading using. The results were averaged from the two detectors and are listed in Tab. 6-2.



Fig. 6-2: Schematic of experimental setup at ENGIN-X, ISIS for in-situ loading experiment with detector areas axially in red and transverse in blue and {0002}-pole figure before (left) and after loading (right).

6.3. Results

6.3.1. Starting material

Neutron diffraction results presented in Tab. 6-2 show that the *a* lattice parameter decreases comparatively linearly with increasing AI content while the *c* lattice parameter decreases more rapidly at high AI concentrations. The corresponding *c/a* ratios are plotted in Fig. 6-3, and are in excellent agreement with previously reported values [Leyens 2003, Ghosh 2008]. The data show a clear non-linear relationship between AI concentration and c/a ratio, which indicates that with increasing AI content some of it is not kept in solution.

Tab. 6-2: Chemical	composition o	f the	model	alloys	in this	study	and	lattice	parameters	from
neutron diffraction a	at Engin-X, ISIS									

Alloy	Al	Al	С	Ν	0	Ti	<a>	<c></c>	<c>/ <a></c>
	wt%	at.%	ppm	ppm	ppm		nm	nm	
Ti-0Al	0.00	0.0	55	13	507	bal.	2.949	4.683	1.5880
Ti-3Al	2.00	3.49	72	39	474	bal.	2.942	4.681	1.5911
Ti-7Al	3.90	6.67	50	23	413	bal.	2.935	4.678	1.5939
Ti-7Al ^a	3.90	6.80	50	23	592	bal.	2.935	4.677	1.5935
Ti-10Al	5.88	10.01	76	53	756	bal.	2.929	4.675	1.5961
Ti-10Al ^a	5.88	9.99	76	53	567	bal.	2.928	4.673	1.5960
Ti-13Al	7.85	13.13	55	94	377	bal.	2.922	4.669	1.5979

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Fig. 6-3: Calculated c/a ratio as function of the Aluminum concentration in comparison to literature values. Values for α_2 were doubled.

Interestingly, when extrapolating the nonlinear trend to higher AI levels, the c/a ratio seems to assume a value, which is in good agreement with literature values for Ti₃AI [Froes 1992, Banumathy 2005]. The WISH beamline was used to characterise the long range part of the neutron diffraction and look for order. Fig. 6-4a shows the patterns recorded for Ti-0AI, Ti-7AI, Ti-10AI. Fig. 6-4b shows a comparison between the materials in the recrystallised and in the aged condition. None of the patterns showed any evidence of a superlattice reflection corresponding to Ti₃AI indicated in Fig. 6-4 b). However, a broad intensity increase becomes noticeable in the region where one would expect the $\{11\overline{2}0\} \alpha_2$ reflection in the case of Ti-10AI and Ti-13AI, Fig. 6-4 a). Ageing of Ti-7-AI also causes a small intensity increase in this range while ageing Ti-10AI makes this shoulder even more pronounced, Fig. 6-4 b).



Fig. 6-4: a) WISH spectra from ISIS, showing only the root of the major hcp-alpha peaks but increasingly diffuse $(10\overline{1}1)$ and $(11\overline{2}0)$ peaks from α_2 with a) increased AI concentration and b) with aging

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Extensive TEM analysis was carried out in order to detect α_2 formation in the binary alloys with relatively high Al content. Selective area electron diffraction pattern analyses with the zone axis along [1010] showed no indication of an α_2 superlattice reflection in Ti-10Al, Fig. 6-5a, while the aged Ti-10Al displayed a very weak superlattice reflection spot, Fig. 6-5b. In both cases very significant scattering was seen in the region of the expected superlattice reflection, which impaired the clear visualisation of the superlattice spot in the aged Ti-10Al.





a) Ti-10AI: RX

b) Ti-10AI: Aged

Fig. 6-5: TEM diffraction pattern with 600mm camera length on $(10\overline{1}0)$ zone axis of a) Ti-10AI in recrystallised condition and b) after ageing, diffuse α_2 reflections marked with white arrow.

EBSD was used to map the starting microstructure and at strains of 0.02, 0.04 and 0.09. The first row of Fig. 6-6 shows typical inverse pole figure (IPF) colour orientation maps of the starting microstructures, with the corresponding 0002 and $10\overline{10}$ pole figures (obtained from larger areas) shown in Fig. 6-7. While the grain size distribution appears to be somewhat heterogeneous for all alloys, no significant differences between the alloys was noticeable,



Fig. 6-6: EBSD micro maps of the recrystallised binary alloys in IPF colouring //LD//RD, after recrystallisation (0% strain) and at strains of 0.02, 0.04 and 0.09. Twin boundaries are indicated as: Black= $\{10\overline{12}\}<10\overline{11}>$, Grey= $\{11\overline{21}\}<\overline{112}$, White= $\{11\overline{22}\}<\overline{112}$.

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Large EBSD maps did not reveal any regions of strong microtexture (macrozones). The mean grain size in all alloys was about 80 μ m with very low misorientations (<2°) within grains. All starting microstructures displayed a very low mud (multiples of uniform density) value along RD in the 0002 pole figure. The distribution of the basal poles within the ring texture is rather random in Ti-0AI and Ti-3AI and Ti-13AI, while Ti-7AI and Ti-10AI display intensity maxima 45° between both ND directions. In Ti-0AI and Ti-3AI the 1010 pole along RD is more intense, while in the other alloys the 1010 pole along RD is more spread out.



Fig. 6-7: a) Texture maps of the starting microstructure and b) after approximately 9% compression parallel to RD. In addition, c) displays close up Band contrast maps highlighting twin types by different boundary colors: Red= $\{10\overline{1}2\}<10\overline{1}1>$, Green= $\{11\overline{2}1\}<\overline{11}26>$, Blue= $\{11\overline{2}2\}<\overline{11}23>$.

6.3.2.Flow curves

The compression flow curves for uniaxial compression along the original rolling direction (RD) are presented in Fig. 6-8 a). The mechanical response during the interrupted in-situ loading experiment using neutron diffraction reflects the behaviour of monotonic compression tests well, as indicated by the crosses for Ti-13AI. As one would expect, the yield strength increases

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significantly with AI content. It is noticeable that the increase in strength is most significant until 10 at.% AI, but far less pronounced for a further increase to 13 at.% AI. The applied ageing treatments show no further increase of the 0.2% yield strength but a noticeable drop in work hardening rate. Fig. 6-8 b) plots the work hardening rate as a function of compression strain. It can be seen that the ability to work harden increases with AI content but reaches a maximum for recrystallized Ti-7AI. Higher AI contents give lower work hardening ability, as does ageing with aged Ti-10AI displaying the minimal work hardening rate θ_{min} during the early stage of plasticity.



Fig. 6-8: a) True stress-strain curves under quasi-static compression in RD for binary Ti-Al alloys in solution treatment and after ageing with indication of neutron measurements for Ti-13Al and the onset of twinning with circles in the corresponding line styles b) Work hardening rate θ as function of the true strain (data averaged and smoothed). The minimal work hardening rate θ_{min} , related to the onset of twinning, is indicated for Ti-10Al in aged condition.

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6.3.3.Deformation microstructures and textures

As described earlier, the texture development during uniaxial compression testing gives a good indication of the development of $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning. Any c-axis rotation caused by tensile twinning will result in the c-axis "rotating" towards the loading direction (LD), and a corresponding increase in intensity in the basal pole figures. Fig. 6-7b shows the 0002 and 10\overline{10} pole figures after a true strain of about 0.09 and it can be clearly seen that at aluminium contents of up to Ti-7Al a strong basal pole does indeed develop along LD. However, Ti-10Al still shows a much weaker pole in this direction whereas the Ti-13Al pole figures are relatively unchanged after a true strain of 0.09.

These changes in macrotexture are consistent with the higher resolution EBSD maps. Fig. 6-6 (small crop from significantly larger EBSD maps) displays representative IPF colour orientation maps after about 0.02, 0.04 and 0.09 true strain. It can be seen that with increasing AI content up to 7 at.% AI twin growth becomes more significant eventually showing almost complete grain consumption in some cases for Ti-7AI. At higher AI contents, twin coarsening diminishes with Ti-13AI showing a large number of twins that have only just started to grow from one side of the grain boundary. Fig. 6-7c confirms the overall dominance of $\{10\overline{12}\}<10\overline{11}>$ tensile twinning (TT₁). Overall, the EBSD analysis suggests an increasing fraction of $\{10\overline{12}\}<10\overline{11}>$ twins until 7at.%AI, which drops dramatically with further AI addition. Only in the case of Ti-0AI about 4% $\{11\overline{22}\}<\overline{11}23>$ compression twins (CP₁) were observed. The detailed EBSD analysis also revealed that there is a very small fraction of $\{11\overline{21}\}<\overline{11}26>$ tensile twins (TT₂), which increases slightly with AI concentration, especially from to Ti-3AI to Ti-7AI and again peaks for Ti-7AI.

The maximum accommodated strain from twinning can be approximated by using equation 6-2, where s is the twin shear for a specific twinning systems and the corresponding twinning volume fraction V_{Twin} , [Battaini 2007].

$$\varepsilon_{max_{i}} = \sum \left(\sqrt{1/2} \, sV_{Twin} \right)_{i} \text{ Equation 6-2}$$

$$\varepsilon_{max} = \sqrt{1/2} \, 0.176 \cdot V_{TT1} + \sqrt{1/2} \, 0.630 \cdot V_{TT2} + \sqrt{1/2} \, 0.217 \cdot V_{CT} \text{ Equation 6-3}$$

Assuming that the measured area fractions by EBSD equal the volume fraction V_{Twin} and the shear values for the three identified twin systems the total twin strain ε_{max} was calculated for each alloy. This analysis revealed that after 0.09 true strain, 50-60% of the total strain had been accommodated by twinning in the case of Ti-OAI, Ti-4AI and Ti-7AI while this number dropped very rapidly to values of around 30% and 15% for Ti-10AI and Ti-13AI, respectively.

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6.3.4. Diffraction peak evolution

In most cases, the starting texture of the different alloys and the choice of loading direction (RD) meant that no 0002 reflection that was amenable to fitting could be recorded along the loading direction (axial detector) at the start. The change in the 0002 integrated intensity as a function of true strain is given in Fig. 6-9. As discussed previously, TT₁ will cause the twin volume to reorient the lattice so that the c-axis lies close to loading direction. Consequently, the slope in Fig. 6-9 is an indication of the twinning activity. Fig. 6-9 a) offers a comparison between different Al contents while Fig. 6-9 b) illustrates the effect of ageing for Ti-7Al and Ti-10Al. The slopes for Ti-0Al, Ti-3Al and Ti-7Al in Fig. 6-9 a) are essentially identical, indicating similar twinning activities. However, when the Al content is further increased, the twinning activity is substantially reduced with almost no sign of twinning for Ti-13Al. In addition, the true strain at which twinning starts increases to more than 0.04 true strain for Ti-13Al from values close to 0.01 for the low Al contents. Fig. 6-9 b) demonstrates that ageing Ti-7Al has only a minor effect on twin activity, while ageing Ti-10Al causes a more significant drop in twinning activity.

The 0002 diffraction peak along the transverse direction represents a grain family that includes grains ideally orientated for twinning, that is, it contains the parent grains of the twins that form during deformation. Because of the texture, these grains make up the majority of the grains in this family. The shifts of these peaks are a measure of the residual lattice strains in these grains, since these measurement were made with the samples unloaded. As can be seen in Fig. 6-10, these grains are in residual tension after unloading. This strain increases up until twinning starts, which can be inferred from the intensity plots in Fig. 6-9, and then decreases steadily after that. As with Fig. 6-9, Fig. 6-10 is split into comparing the effect of Al (Fig. 6-10 a) and the effect of ageing (Fig. 6-10 b). The maximum residual lattice strain in this grain family first decreases with Al content before increasing dramatically for Ti-10Al and Ti-13Al. With the exception of Ti-13Al, the moment at which twinning starts also represents a sharp turning point regarding the residual lattice strain evolution. Ageing increases the residual lattice strain significantly for both Ti-7Al and Ti-10Al.



Fig. 6-9: Axial intensity evolution of {0002}-plane $\Delta I_{(0002)}$ related to 85° tensile twinning as function of true strain derived from neutron diffraction at Engin-X for a) recrystallised material and (b) the effect of SRO ageing.



Fig. 6-10: Evolution of transverse residual lattice strain on {0002}-plane $\mu \epsilon_{0002}$ as function of true strain derived from neutron diffraction at Engin-X for a) recrystallised material and (b) the effect of SRO ageing. The onset point of twinning is marked in grey.

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6.3.5.Summary of results

A summary of the results obtained from the single phase α -Ti alloys with Al contents ranging from 1 to 13at.% is presented in Fig. 6-11. It demonstrates that the greatest gain in 0.2% yield strength was achieved between Ti-3AI and Ti-10AI while the ageing procedure applied for Ti-7AI and Ti-10AI had no noticeable effect on strength, Fig. 6-11 a). The minimum work hardening rate θ_{min} , which for uniaxial compression along RD is in principle obtained before the onset of twinning, showed a slight maximum for Ti-7AI. Here, ageing resulted in a very significant drop of θ_{min} particularly in the case of Ti-10AI, Fig. 6-11 b). The approximated TT₁ twin fraction suggests an increase of TT₁ twinning activity with increasing AI content up to Ti-7AI but a sharp fall after that resulting in almost no TT₁ twinning for Ti-13AI. Ageing of T-7AI and Ti-10AI further reduces TT_1 twinning, Fig. 6-11 c). Analysis of the detailed orientation maps revealed some CP₁ only in the case of Ti-0AI and a small volume fraction of TT₂ increasing with AI content and seemingly independent of the final heat treatment condition, Fig. 6-11 d). Overall, similar trends were seen when monitoring the evolution of the change of (0002) integrated intensity during the in-situ loading experiments using neutron diffraction. In Fig. 6-11 e) the TT₁ twin activity is represented by a simple linear regression of $\delta\Delta I_{(0002)}$ / $\delta \epsilon$ for each alloy composition. Although the increasing twinning activity up from Ti-0AI to Ti-3AI or even Ti-7AL is not obvious, the drop after that is dramatic. The corresponding macroscopic stress values for twin initiation σ_{nuc} are plotted in Fig. 6-11 f) demonstrating a significant increase in macroscopic stress level with AI addition. The intercept of that slope with $\Delta I_{(0002}=0$ indicates the onset for twinning $\varepsilon_{\Lambda I}$ and is given as plastic strain in Fig. 6-11 g). It can be seen that the plastic strain at the onset of twinning decreases initially until 7at.% AI. For the highest AI content a sharp increase is noted.

Finally, Fig. 6-11 h) summarises the critical twin nucleation lattice strain $\epsilon \mu_{\{0002\}}$ along the c-axis, extrapolated to values at full stress, in the grain family that includes the grains most likely to twin. This value seems to be lowest for Ti-3Al but increases significantly beyond Ti-7Al, similarly to the evolution of the residual lattice strains. Ageing Ti-7Al or Ti-10Al slightly increases the critical lattice strain value.

6.4. Discussion

The initial increase in twinning followed by the dramatic drop in twin activity implies that adding Al to Ti promotes twinning at lower Al contents and hinders it after a critical Al content is reached. In order to elucidate this observation, the different microstructural and plasticity aspects are critically discussed in terms of their possible contribution to twin activity.

6.4.1.Ordering in Ti-Al

Several of the experimental results provide evidence of ordering starting with Ti-10Al. In the case of Ti-7Al, the aged condition seems to show a very slight indication of ordering in the long-range diffraction pattern. However, the long-range neutron diffraction data provide no clear evidence of α_2 formation for any of the alloys investigated. The detailed TEM analysis provided only evidence of very weak α_2 reflections once Ti-10Al had been aged. Hence, both characterisation studies combined suggest that once the Al content reaches 7 at.%, SRO develops during ageing, which clearly becomes very dominant with increasing Al content and ageing. From about Ti-10Al aged, in addition to SRO, a small degree of LRO seems to be present. It is particularly interesting to note that the start of LRO does not result in a reduction of SRO. These observations are further supported by a more indirect observation in Fig. 6-2 showing a non-linear relationship between c/a ratio and Al concentration. Such deviation from linearity has been previously attributed to increased levels of ordering in other systems. For instance see [Dienes 1958] attributing it to Cu₃Au formation in the Cu-Au system. The present observations are also consistent with results from Nambodhiri's resistivity measurements, showing effects of SRO down to 6.8at.% Al [Namboodhiri 1973], as indicated in Fig. 6-1.

It might surprise somewhat that Ti-10Al and particularly Ti-13Al did not form α_2 more readily. However, the reader is reminded here that cooling rates from recrystallisation temperatures were in the range of 100K/min (air cool of 14 x 14 mm² cross sectional samples) and ageing temperatures were substantially lower (see Tab. 6-1) than in cases when α_2 has been observed previously. For instance, α_2 in primary α of Ti-6Al-4V is normally induced by ageing at 500°C [Lütjering 2007].

Regarding the effect of SRO on deformation mechanisms and twinning, the dramatic increase of 0.2% yield strength between Ti-3AI and Ti-10AI demonstrates that SRO does have a strong strengthening effect. However, it also clearly reduces work hardening rates and promotes planar slip [Van de Walle 2002].

6.4.2.Twinning in Ti-AI

When studying the effect of alloying elements on twin activity the first important parameter is to achieve a similar starting texture and grain size as both aspects will affect twin activity to a great extent. In the present case, the common starting texture had a strong preferred orientation of the c-axis perpendicular to the compressive loading direction and high Schmid factors for tensile twinning. The mechanisms of twin nucleation and growth mechanisms in metals with a hcp crystal structure are still not well understood. Heterogeneous twin nucleation and growth have been discussed in terms of formation of zonal twinning dislocations and stress concentrations at grain boundaries [Christian 1995]. It is further complicated by the need of the local twin shear to be accommodated, which means that ease of deformation by slip will also impact twin activity.

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On the other hand, since in Ti like in Zr twinning is preceded by slip, an increase of the yield strength also means that twinning occurs at higher stresses.



Fig. 6-11: Summary of results as function of Al concentration and for aged conditions: a) 0.2% proof strength $\sigma_{0.2}$; b) Minimal work hardening rate θ_{min} ; c) Fractions of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ -twin TT₁; d) Fractions of $\{11\overline{2}1\}\langle\overline{11}26\rangle$ -twin TT₂ and $\{10\overline{1}1\}\langle10\overline{1}2\rangle$ -twin CT; e) Twin activity $\delta\Delta I/\delta\epsilon$, as the rate at which the axial $\{0002\}$ -intensity changes with true plastic strain ϵ ; f) True stress to nucleate twin σ_{nuc} , from first indication in axial $\{0002\}$ reflection; g) Extrapolated plastic strain for onset of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ -twin ϵ_{nuc} , from intercept of linear regression of ΔI with ϵ axis $\Delta I=0$; h) Residual microstrain on <c> axis $\epsilon\mu_{nuc\{0002\}}$ at the onset of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ -twinning from favorably orientated grain family.

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Combining information from neutron diffraction and EBSD suggests that the initial increase of twin activity with increasing AI content is related to easier growth rather than more nucleation. It is not clear at the moment if this observation is driven by a decrease in SFE [Metzbower 1971 & 1978, Guo 2006, Ghosh 2008, Shishmakov 1972], which in principle affects dissociation of basal dislocations or if growth is driven simply by higher stresses at which plasticity starts and misfit strains are generated. It is however noticeable that the residual lattice strain for twin nucleation does initially decrease giving indication that twin formation becomes easier before ordering is observed.

Once ordering is observed, there is a clear reduction in twin activity and with increasing evidence of ordering this trend becomes more pronounced resulting in almost a complete suppression of twinning for Ti-13AI. Interestingly, ordering in the present case means mainly SRO. Calculations of the anti phase boundary (APB) energy created by a single basal or prismatic dislocation shearing SRO (diffuse) in the Ti-Al system gave a value of 25 mJ/m², which compares with 100 – 250 mJ/m² when shearing α_2 (defined) [Van de Walle 2002]. Those calculations suggest that any diffuse APB energy required for twinning a SRO cluster is comparatively small. However, it is worth remembering that Ti₃AI as an alloy is known not to twin [Umakoshi 1981, Thomas 1989, Minonishi 1991, Umakoshi 1993, Legros 1996, Yakovenkova 2007] and the EBSD maps of the deformed samples show very clearly that once ordering is observed, twin growth declines very sharply. In the case of Ti-13AI, many twins have not even grown lengthwise to reach the opposite grain boundary, suggesting that any type of ordering has a significant impact on twin boundary migration as previously reported for Mg-Gd alloys [Nie 2013]. Another, perhaps less plausible, factor for the dramatic decline of twin activity might be found in the promotion of severe slip planarity in the presence of SRO and α_2 . Fig. 6-8 b) and Fig. 6-11 b) demonstrate that ordering reduces the work hardening capability of the material, which has been reported previously [Truax 1974, Neeraj 2000]. The absence of cross slip and dislocation interaction might reduce the ability of heterogeneous twin nucleation by twin dislocations. A suppression of cross slip makes dislocation jogs less common, which have been described as possible twin nuclei [Venables 1961]. The jogs lower the energy for the separation of partial dislocations, and facilitate twin growth. In any case, ordering appears to be the reason why twinning is suppressed in Ti at higher AI contents, either because it pins twin boundaries or because it promotes slip localization.

6.5. Conclusion

A systematic study of twin activity in Ti binary alloys with 0 to 13 at.% Al during uniaxial compression testing has been carried out in order to provide new insight into the effects of Al on twin activity in these alloys. Great care was taken to obtain similar starting microstructures including textures to enable such comparison. One of the key microstructural features, ordering of Al in Ti, was characterised using large d-spacing neutron diffraction and selective diffraction

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aperture pattern imaging in the TEM. It is important to note that while Ti 10 at.% AI and Ti 13 at.% AI are known to form α_2 when aged in a certain temperature range and for long time, the heat treatments applied in the present study focused the work on the effect of short range ordering. In order to monitor twin evolution in-situ, loading experiments were carried out in combination with neutron diffraction in order to capture peak intensity changes, peak broadening and the evolution of intergranular strains. In addition, detailed post mortem microstructure analysis by EBSD was carried out in order to identify twin types and quantify them. The main findings of the work can be summarised as follows:

- The neutron diffraction study on WISH revealed that Ti-Al alloys with up to 7 at.% Al showed practically no indication of SRO after recrystallisation heat treatment followed by air cooling (100'sK/min). In contrast, Ti-10at.%Al showed clear indication of short range ordering that became stronger with ageing or by further increasing Al content to 13 at.%. Aged Ti-7at.%Al also showed a very slight indication of SRO. Long range ordering, i.e. α_2 , was only identified for aged Ti-10at.% Al and recrystallised Ti-13at.%Al. In both cases only weak α_2 reflections were identified by TEM analysis and α_2 formed additionally to SRO.
- In the absence of ordering, alloys showed an increase in work hardenability with rising Al content, which can be correlated to a slight increase in {1012}<1011> tensile twin activity confirmed by neutron diffraction and EBSD analysis. The increase in twin activity can be associated with ease of twin growth.
- In addition to the extremely dominant $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning mode, about 4% $\{11\overline{2}2\}<\overline{11}23>$ compression twins were observed in Ti without any AI addition after a true strain of 0.09. In addition, EBSD analysis also revealed a small fraction of $\{11\overline{2}1\}<\overline{11}26>$ tensile twins, which increases slightly with AI concentration, especially from to Ti-3AI to Ti-7AI.
- SRO significantly reduces the work hardenability of these alloys, which, apart from increased strain localisation, can be related to a dramatic reduction of twinning activity as identified during the in-situ loading experiments using neutron diffraction and post mortem EBSD analysis. Additional α₂ formation further emphasis this trend.
- It was found that with increasing AI content, in the absence of ordering, the critical residual intergranular strain required for twin nucleation decreases. This observation

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was interpreted as an indication that with increasing AI content in solution the intrinsic energy requirement for twin formation reduces, which could be due to an increase in stacking fault energy. However, the generally higher stress with increasing AI solute solution strengthening at which plasticity occurs might be the most important factor to increase twin activity.

- Evaluation of the prismatic peak width evolution as a function of plastic strain revealed that the alloys that contained ordering developed significantly larger peak broadening than alloys without any indication of ordering. Since hardening by slip is generally very low in hcp metals, the difference in peak broadening is most likely an indication of a significant increase in strain localisation in the presence of ordering.
- The dramatic fall in twin activity in the presence of ordering including short range ordering is accompanied with a dramatic decrease in twin growth. It seems most likely that ordering dramatically reduces twin boundary mobility.

It should be noted that the initial increase in twinning activity with increasing AI content has not been shown previously as most studies have only focused on either commercially pure Ti or Ti with 6-7 wt% AI. Considering the significant impact on work hardenability identified in the present study, Ti alloys with relatively low AI content might be of particular importance when considering formability and sudden impact applications.

7. The Effect of AI on slip and slip-twin interactions in Ti using DIC

Abstract

Strain maps were acquired patterns during compression on binary Ti-Al alloys using high resolution digital image corelation (DIC). The data show highly heterogeneous deformation patterns by slip with varying twin activity and increasing strain localisation with Al addiition. Slip traces in Ti-OAl are commonly of prismatic type but basal slip becomes prominent with Al addition and nearly as common as prismatic slip in Ti-10Al. Slip trace analyses around twinned areas suggests that the formation of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twinning is assisted from prismatic slip and the formation of $\{11\overline{2}1\}\langle\overline{1126}\rangle$ twinning from pyramidal 2nd order and basal slip. Slip traces on pyramidal 1st order planes with low shear strain could be observed prior $\{11\overline{2}2\}\langle11\overline{2}3\rangle$ compression twinning. The results are discussed in relation to the ease of basal and prismatic slip in single crystals and theories on twin nucleation, propagation and growth.

7.1. Introduction

Plastic deformation in metals with an hcp crystal structure usually relies on both slip and twinning at low temperatures and a loss in the ability of the material to twin can coincide with reduction of ductility [Truax 1974, Williams 2002]. Empirical studies have revealed that the twin activity in a material depends on parameters like temperature, stress state, strain rate and alloy chemistry [Paton 1970, Chichili 1998, Nemat-Nasser 1999, Williams 2002]. In the case of Ti-Al alloys, it is well established that twin activity is dramatically reduced for Al concentration of 6wt%=10at.%Al [Williams 2002], which coincides with the onset of short and/or long-range ordering [Namboodhiri 1973 & 1983], increased basal slip activity [Williams 2002] and enhanced slip planarity [Neeraj 2001].

In the case of Ti, $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tension twinning is by far the most frequently observed twin mode resulting in a shear strain of s=0.17, which is slightly smaller than the shear strain of the less commonly observed $\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ compression twin (s=0.22) and significantly smaller than the shear strain of the rarely reported $\{11\overline{2}1\}\langle \overline{11}26\rangle$ tension twin (s=0.63) [Yoo 1981, Chun 2005]. However, the $\{10\overline{1}1\}\langle 10\overline{1}2\rangle$ compression twin generates by far the smallest shear strain of s=0.09 but has been reported to only occur at high temperature [Paton 1970]. Yoo et al. and Chun et al. have explained the low twinning activity of the $\{10\overline{1}1\}\langle 10\overline{1}2\rangle$ compression twin at ambient temperature by considering the associated level of atomic shuffle [Yoo 1981, Chun 2005]. Further, Yoo et al. described in their review [Yoo 2002] that ab-initio calculations based on empirical potentials predicts twin boundary energy to be lowest for the rare $\{10\overline{1}1\}\langle 10\overline{1}2\rangle$ high temperature compression twin. Those calculations predicted higher twin boundary energy

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for the $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ than the $\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twin, which suggests twin boundary energy is not a critical parameter in predicting twin mode activities.

Instead of focusing on static properties of twin boundaries one has to understand the dynamics of twinning. Deformation twinning is generally described by a nucleation, propagation and growth mechanism [Christian 1995, Yoo 2002]. However, the detailed dislocation reactions are not well understood and partly contrary observations have been summarised by Christian and Mahajan or more recently by Yoo et al. [Christian 1995, Yoo 2002]. Along this line of arguments, it has been suggested that twin nucleation is a heterogeneous process, where twins emerge by a dissociation of dislocation into two partial dislocations from an already existing stacking fault [Christian 1995]. Density functional theory (DFT) calculations support the zonal-twinning mechanism, as simultaneous nucleation from a partial dislocations and multiple twinning dislocations lower the required elastic energy to form $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twins [Wang-a 2009]. However, the situation may be different for other twin types [Wang-b 2009].

Recent modelling and experimental work in metals with an hcp crystal structure has concentrated on the role of stress concentrations at grain boundaries and the general stress state in the twinning grain [Capolungo b 2009, Beyerlein 2010a&b, Beyerlein 2011, Yu-b 2012, Abdolvand a&b 2012] as well as on precipitates (in Mg) [Robson 2010] and on slip transfer across grain boundaries [Wang 2010 a&b, Bieler 2014] to further understand twin formation. In general, it is still unclear if twin nucleation and growth is determined by a stress criterion, similar to a critical resolved shear stress (CRSS) value for slip, or if slip activity in the twinning grain or neighbouring grains are of bigger importance [Serra 1996, Capolungo-b 2009, Bieler 2014]. The importance of slip in connection with twinning has already been suggested by Paton and Backofen, who found <c+a>-slip bands prior to the formation of $\{11\overline{2}2\}$ -compression twins [Paton 1970]. It is also worth noting that slip prior to twinning has been observed during numerous in-situ measurements in various hcp metals although not always mentioned or discussed explicitly [Agnew 2003, Xu 2008, Preuss 2010, Oliver 2004, Abdolvand 2011, Abdolvand c 2012, Warwick a & b 2012, Bieler 2014].

To further investigate the role of slip and stress localisation from slip bands on twinning detailed two-dimensional (2D) strain maps were created by means of high-resolution digital image correlation (DIC) during compressive loading of binary Ti-Al alloys. The strain maps were analysed in conjunction with EBSD to identify slip traces and twin types. The chosen starting texture of the material offered a broad distribution of grains favourably orientated for basal, prismatic <a> slip and pyramidal <a> or <c+a> slip. Accordingly those grains are also well aligned to undergo either $\{11\overline{2}1\}\langle\overline{1126}\rangle$, $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twinning or $\{10\overline{1}1\}\langle10\overline{1}2\rangle$ compression twinning, respectively. It was possible to characterise slip localisation and the appearance of different slip systems for binary Ti alloys with different Al concentration on those DIC-2D strain patterns and the interaction of slip and twinning on a sub-micrometer scale is discussed.

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7.2. Experimental methods

7.2.1.Sample preparation and experimental procedure

The measured chemical composition of the alloys used in the present study is presented in Tab. 7-1. The alloys were produced in form of 200g buttons by double melting in a tungsten arc furnace under inert gas atmosphere. The cast structure was broken up by β forging at 1100°C and subsequent cross-rolling of the samples in symmetric bar shape (14 × 14 × 260mm) on a "2 high Robertson mill" (WHA Robertson & Co Ltd) at 750°C for Ti-0Al and 870°C for the Al containing alloys. Ti-0Al was recrystallised (RX) at 750°C, 130°C below the β transus temperature, in a tube furnace under Argon shield for 5 hours followed by air-cooling, while recrystallisation treatments for the Al containing bars were carried out 30°C below the β -transus, which translates into 933°C for Ti-7Al and 968°C for Ti-10Al, followed again by air cooling.

Tab. 7-1: Chemical composition of the model alloys in this study

Alloy	Al	Al	С	Ν	0	Ti
	wt%	at.%	ppm	ppm	ppm	
Ti-0Al	0.00	0.0	55	13	859	bal.
Ti-7Al	3.95	6.80	58	55	961	bal.
Ti-10Al	5.92	10.01	94	85	1491	bal.

For the purpose of imaging the surface and undertaking high resolution 2D strain analysis by DIC rectangular compression samples of $6x6x9mm^3$ were cut from the bars and mechanically ground and polished using oxide particle suspension (OPS) on their face along the former ND_{II}. See Fig. 7-1 for relationship between rolling direction and orientations by which the samples were extracted.



Fig. 7-1: Schematic allignment of compression samples along ND and 45° between ND and RD in respect to the rolling direction.

The compression direction of the samples was parallel to the former ND₁ for Ti-0AI, and 45° between RD and ND₁ in the Ti-AI alloys. The polished surface was gold sputtered in an Edwards S150B sputter coater for 5min at a current of ~40 μ A and a chamber pressure of ~3x10⁻¹ atmospheres (ATM). The gold layer was subsequently remodelled into fine speckles of 20-100nm in size with random distribution, using the same setup as presented by Fig. 7-1 in [Di Gioacchino 2012]. A hot plate was set to ~300°C to boil and evaporate water in a small beaker.

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The vapour flows through a bigger beaker, rested on bulldog clips and passes the sample before it escapes the setup. Samples were left in this environment for 180min, while intermediate refills of water were required. The Ti-10Al sample was remodelled for another 90min for optimal pattern distribution.

Microhardness indentations with 0.5kg load were used to mark arbitrary regions in the centre of each specimen. These regions were imaged before and after uniaxial compression in order to produce strain maps by digital image correlation, as described in detail in [Fonseca 2005, Di Gioacchino 2012, Smith 2013]. The compression experiments were carried out using a MTS RT100 compression-tension rig at room temperature and an initial strain rate of 1*10⁻³ 1/s. Ti-OAI was compressed to 1.7%, 2.5% and 5% strain. Unfortunately, after the last strain increment the gold pattern was damaged during handling, which meant that the DIC analysis was limited up to 2.5% macroscopic strain. Ti-7AI was compressed to 1.6%, 2.5% and 6.9% strain. Images of Ti-10AI were taken after 1.1%, 1.2%, 2.6 and 6.3% compressive strain. It should be noted that some buckling was noticed after the Ti-10AI sample had been strained to 6.3% strain. All strain increments are indicated in Fig. 7-2 by grey lines.



Fig. 7-2: a) Strain steps investigated with DIC are marked by a grey line as: Ti-OAI (S1=1.7%, S2=2.5%), Ti-7AI (S1=1.6%, S2=2.5%, S3=6.9%) and Ti-10AI (S1~1.1%, S2~1.2%, S3~2.6, S4~6.3%). The strain for EBSD mappings is indicated by the grey rectangular. Note that in Ti-OAI the macroscopic strain of the DIC map and EBSD map differ. b) Shows the global starting texture for the materials measured with macro texture scans.

7.2.2.Imaging and image processing

Backscatter electron (BSE) images of the gold patterns were acquired before deformation and after each compressive loading step at a working distance of ~ 4.5mm without sample tilt, 20kV acceleration voltage and spot size 3 on a Sirion FEG-SEM. A resolution of 32nm per pixel within one image was achieved at 1000x magnification in extra high definition mode (XHD), with Arnas Fitzner, PhD Thesis, 2014

images of 3872x2904 pixels. This enabled to have in average 3x3 pixels describing a gold speckle with appropriate brightness and contrast settings. A matrix of 4x4 images was taken with 10µm overlap between adjacent frames in order to create a large field of view and cover a sufficient number of grains to visualise possible macroscopic strain patterns [Efstathiou 2010]. Images were processed using La Vision DaVis 7 digital image correlation software. During analysis it became apparent that the overlap between images was insufficient to generate a single large field image without artefacts. The alignment was somewhat improved manually post acquisition using Adobe Photoshop, however resulting in some artefacts in the strain maps. Non-linear filters were applied to the aligned images in DaVis to average brightness and contrast of the different sets of images. Images were subsequently cross-correlated over areas of 512x512 pixel with 2 passes and finished with 3 passes at 12x12 pixel without overlap. Window shape (called window weight in DaVis) was square and circular respectively. Crosscorrelation of an image relative to the first image displays the integral strain accumulation, labelled as ϵ later on. Cross-correlation of successive images displays differential strain accumulation, labelled as $\Delta \varepsilon$ later on. In one presented case the integral mode did not work in the final strain step and instead the sum of differential vector fields $\Delta \epsilon$ was used to calculate the accumulated strain, labelled as $\Sigma \Delta \epsilon$. Standard correlation function was applied, allowing for zero padding via fast Fourier transform (FFT) and subpixel resolution through linear interpolation of vectors with 100 pixels as upper ceiling. For purposes of noise reduction, vector post processing was applied by means of a median filter. Vectors were removed if over 2 times the difference of average route mean squared distance (rms) of a neighbouring pixel and iteratively replaced if below 3 times average rms. Dynamic removal and reinsertion of data followed by interpolation allows for smoothing of displacement maps. Artefacts from stitching and any other non-correlated areas have been covered black in the presented DIC strain maps. Lack of software drift correction, and the necessity to remount the samples after each compression step, caused different drift rates between the image sets and resulted in noise towards the bottom and/or corners of single frames.

7.2.3.Slip trace analysis

The theoretical alignment of the slip trace or the twin habit plane on the sample surface was calculated from the grain orientation and compared to the observation from the strain mapping via DIC. The gold film was removed gently by OPS polishing in order to measure grain orientations by EBSD (electron backscattered diffraction). The surface was not flattened entirely to maintain the investigated surface, which resulted in some areas displaying relatively poor indexing, as seen in Fig. 7-3. Orientations maps were recorded using an acceleration voltage of 20kV, 70° sample tilt, Flamenco acquisition software and 0.5µm to 0.8µm stepsize. Euler angles for each grain were read out from the centre of each grain where possible after deformation and used to calculate the angle of the trace of the slip or twin habit plane on the sample surface. Here the "BPW PC Crystal Math tool" from the University of Sheffield was applied to calculate

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the cross product of the slip or twin habit plane and the sample surface for all slip systems, as listed in Tab. 7-2. Additionally, Schmid factors were calculated for each grain assuming uniaxial stress state, which is clearly an oversimplification at a crystal level

Deformation system	Glide plane	Shear direction	Rotation axis	Shear s [1]
Basal (a)	{0002}	1/3 (11 <u>2</u> 0)	$\langle 1\overline{1}00 \rangle$	0.005-0.02
Prismatic (a)	$\{10\overline{1}0\}$	1/3 (11 <u>2</u> 0)	(0001)	0.05-0.07
Pyramidal 1 st (a)	$\{10\overline{1}1\}$	1/3 (11 <u>2</u> 0)	$\langle 0\overline{1}12 \rangle$	
Pyr. $1^{st} \langle c + a \rangle$	$\{10\overline{1}1\}$	1/3 (11 <u>2</u> 3)	<pre>(13.853)</pre>	0.01
Pyr. 2 nd $\langle c + a \rangle$	$\{11\overline{2}2\}$	1/3 (1123)	$\langle 1\overline{1}00\rangle$	

Tab. 7-2: Slip systems used for slip trace analysis and shear strain values for pure Ti [Chun 2005], [Zaefferer 2003], [Yang 2011], [Li 2013]

To compare the imaged slip traces with the theoretical trace angle, the strain map was aligned on the EBSD map for a region of interest. Due to possible slight misalignments between EBSD and strain maps the acceptance angle between expected and measured slip traces was $\pm 3^{\circ}$. In many cases, the 2D slice through the grain only revealed a single slip system, which was then accounted for one per grain. Because pyramidal 1st order slip in <a> and <c+a> direction share the slip trace they could not be distinguished and have been summarised as 1st order pyramidal slip.

7.3. Results

Maps of the maximum shear strain τ_{xy} from the DIC analysis together with the orientation maps (IPF colouring is parallel to the LD) are presented after ~2.5% plastic deformation in Fig. 7-3, showing severe slip band formation, interaction of slip traces with twins and grain boundaries. The macroscopic compression direction LD is horizontal as indicated by the arrow. The complete strain maps for each strain step, as well as more detailed observations on twin formation, are presented in [Smith 2013]. This paper discusses selected grains of the investigated areas only concerning appearance of slip traces and interactions between slip traces and twins.



Fig. 7-3: DIC strain maps of maximum shear τ_{xy} after ~2.5% plastic strain for Ti-0AI, Ti-7AI and Ti-10AI 0n the top and below EBSD mappings after ~5%, ~6.9% and ~ 6.3% macroscopic compressive strain with superimposed DIC strain maps.

7.3.1.Observations of slip traces

The objective here was to compare the relative frequency of basal and prismatic <a>-slip, as well as pyramidal slip systems as function of Al concentration. It should be pointed out that for the Ti-0Al sample only 18 grains could be included in the analysis while in the case of Ti-7Al and Ti-10Al there were 50 and 67 grains respectively. Fig. 7-4 a) shows the activity of basal, prismatic and 2^{nd} order pyramidal slip traces as a function of Schmid factor relative to the total number of observed slip modes (Σ). Due to the ambiguity of exact slip mode when considering 1^{st} order pyramidal slip traces, they were omitted in this plot. Instead the total number and percentage from Σ of observed traces on 1^{st} order pyramidal planes are given in Fig. 7-4 a). Fig. 7-4 b) displays the activity of each type of slip trace in Fig. 7-4a relative to the potential availability per Schmid factor bin for all studied grains as a function of Schmid factor. This type of presentation does in principle take into account the differences in starting texture that results from the different loading directions, but can not be applied for 1^{st} order pyramidal slip.

In general, prismatic slip traces were found to be dominant in all samples. It was noticeable that prismatic slip traces in grains with a comparatively low Schmid factor showed a relatively low shear strain. Multiple variants of prismatic slip traces in the same grain in Ti-OAI were also found, see Fig.7-5. It was observed that there was an increased number of grains that showed only one type of slip in a single grain in Ti-7AI (90%), while shear strain levels within individual slip traces increased slightly. About half of the grains in Ti-10AI showed after about 2.5% plastic strain traces of multiple slip systems, the other half only traces of one slip system. However, the secondary slip traces connected the major slip traces and exhibited usually low shear strain.

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Fig. 7-4: Counts a) and b) Frequency plots from slip trace analysis on DIC strain maps on Ti-0AI, Ti-7AI and Ti-10AI.

Slip traces associated with basal slip were the second most common mode in all alloys, when all potential slip systems in the observed area are considered (Fig. 7-4). In Ti-OAI basal slip traces appeared relatively short, displayed low shear strain and were found together with other type of slip traces in the same grain. Fig. 7-5 shows an example of a grain in Ti-OAI very well aligned for basal slip according to Schmid factor analysis (m_{basal}=0.43) but not for prismatic slip (m_{prism}<0.13), which displays no slip trace at all even though neighbouring grains display slip activity. Basal slip traces of grains with similar orientation and neighbourhood compared to Ti-OAI were strongly developed in the AI containing alloys, traversing across entire grains as shown in Fig. 7-5. To draw attention to this minor contribution to the overall strain the data for basal slip in Ti-OAI in Fig. 7-5 are greyed out. It was noticed that there were slightly fewer but more intense basal slip traces within one grain makes quantification difficult.

In addition to basal and prismatic slip a small number of 1^{st} order pyramidal slip (<a> or <c+a>) and 2^{nd} order pyramidal <c+a> slip traces were identified in all alloys. If one considers the Schmid factor associated with each slip mode, most of the activated pyramidal 1^{st} order slip systems appearing to be of <a> type show similarly high shear strains as the ones observed for basal or prismatic slip and traverse through the full grain. In contrast, the slip traces one might associate with <c+a> type 1^{st} order pyramidal slip based on Schmid factor analysis, displayed only short slip traces with very low shear strains close to grain boundaries or in conjunction with

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other slip traces. Counting the number of different slip traces per grain reveals that Ti-7Al has about 10% of grains with multiple slip systems activated after 2.5% macroscopic strain. In contrast Ti-0Al and Ti-10Al show approximately 37% and 49%, respectively, of grains with multiple active slip systems.

In an attempt to assess the level of shear strain localisation as a function of Aluminium content grains with a similar Schmid factor for prismatic and basal slip were identified within each alloy and presented in Fig. 7-5. The top row illustrates grains likely to deform under prismatic slip, with m_{basal} >0.24 and $m_{prismatic}$ >0.43. The bottom row illustrates grains favourably aligned for basal slip with m_{basal} >0.43 and $m_{prismatic}$ <0.15. This very simplistic approach is only seen as a first step towards comparing strain localisation in the different alloys as the grain neighbourhood might affect the results.



Fig. 7-5: Grains favourably orientated for prismatic <a> slip (top row) and basal <a>-slip (bottom row) for Ti-0Al, Ti-7Al and Ti-10Al. Slip traces for activated system and grain boundaries are indicated for the grains of interest. The small arrow indicates experimental artefacts.

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The grains highlighted in Fig. 7-5 were analysed in terms of shear strain distributions, which are plotted for the case of prismatic slip in Fig.6 a), basal slip in Fig. 6 b) and the average of both grains is given in Fig. 7-6 c). Both types of slip modes show a clear trend of increased levels of maximum shear strain with increasing Aluminium content. Particularly when comparing prismatic shear strain distributions and basal slip strain distributions for Ti-7Al and Ti-10Al, the integrals of the shear strain distributions appear relatively similar indicating that the overall strain in these grains were comparable but shifted to slightly higher strains in Ti-10Al. However, in the case of the grain orientated for basal slip in Ti-0Al almost no strain shear strain was observed.



Fig. 7-6: Normalised frequency of shear strain for grains from Fig. 7-4 favourably orientated for a) prismatic slip, b) basal slip and c) averaged over both grains. Note that the contribution to the shear strain from basal slip from Ti-0AI is diminishable.

7.3.2.Slip-twin interaction

The following section shows examples of shear strain maps that include twins in order to visualise their interaction. In order to distinguish between slip and twinning, black dashed lines highlight the direction of the active slip traces and grey dashed lines indicate twin habit planes. The hcp-unit-cell marked as "P" corresponds to the orientation of the parent grain, while "T" marks the twined orientation. A profile across the twin along the grey drawn line shows the development of maximum shear strain τ_{xy} in matrix and twin as function of applied plastic strain. Grain boundaries are indicated by black dotted lines and the same area is shown as EBSD map with IPF colouring parallel to the LD. Artefacts are covered in black and appear sometimes as black draw line.

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$\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twin

Within the mapped areas, the $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tensile twinning system was identified only in one grain in Ti-OAI (although 5 such twins developed in that sample during deformation to the last strain increment), in 18 grains in Ti-7AI and in 6 grains in Ti-10AI. In all instances, the twin formation was accompanied by slip traces on prismatic planes in the same grain and hence no $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tensile twinning was observed in grains, which deformed without prismatic slip being active. Generally, the strain maps revealed that in many occasions twins emerged from grain boundaries with high local strains, but equally from barely strained boundaries towards grains with intense slip bands. It was also noticed that intense shear traces towards grain boundaries and twin tip in the neighbouring grain did not match up exactly. In other instances, the $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ twins seemed to emerge without the influence of any significant shear strain in neighbouring grains. In any case, the relatively large macroscopic strain steps did not allow conclusions if slip traces do indeed initiate twin formation or vice versa.

A first example of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ twin formation is given for Ti-10Al in Fig. 7-7, marked as area 1 in Fig. 7-3. Fig. 7-7 shows strain maps after 1.2%, 2.6% and 6.3% strain as well as an incremental strain map of $\Delta\epsilon$ =3.7% between 2.6% and 6.3% strain and an EBSD map from the area after



Fig. 7-7: Example for $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tension twinning in Ti-10AI

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compression. It can be seen that after 1.2% compressive strain only prismatic slip bands of low intensity exist and $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ twins have emerged across these slip bands during further compression (2.6% and 6.3%). Although it is not entirely clear, the intense slip bands of a neighbouring grain (indicated by the red circle) suggest that in this case the twins have formed as a result of the stress concentrations generated at the grain boundary.

The max. shear strain maps also reveal the strain associated with twin formation and growth. For demonstration τ_{xy} is plot as line profile along the grey line across a single twin, but not over the slip lines within the twin. The appearance of slip bands within the twin after 6.3% compression is a signature of the strain history during deformation. The incremental strain map ($\Delta \epsilon$ =3.7%) also reveals shear bands within a particularly wide twin that only propagated through the grain in the last strain step (bottom right), which are not observed in thinner twins, which propagated already after 2.6% through the grain. Excluding those slip traces within the twin, τ_{xy} seems to plateau out at about 8%, while the width is growing significantly during compression.

An example of $\{10\overline{1}2\}$ ($10\overline{1}1$) twin propagation in Ti-7Al is marked in Fig. 7-3 as area 2 and presented in detail in Fig. 7-8. Here, twins (in grain 21) seem to be triggered by strain concentrations on the grain boundary from the grain below (grain 29). After 1.5% macroscopic deformation a first twin has propagated few micrometers into the grain being surrounded by prismatic slip bands in a 45° angle. The slip bands are irregularly spaced and exhibit various intensities, while each slip band seems to have homogeneous intensity throughout the grain. Another 1% strain results in the propagation of two more twins, as seen at a total strain of ϵ =2.5% and in the incremental map $\Delta \epsilon$ =1%. The initially seen twin, marked by the grey dashed lines, broadened and propagated further, through an intense band of prismatic slip but stopped shortly after. No significant further strain development can be seen within the initial twin in the incremental map $\Delta \epsilon = 1.0\%$, as it can be seen by comparison of the profiles τ_{xy} in blue ($\epsilon = 1.5\%$) and green (ϵ =2.5%) across the twin, indicated by the drawn grey line. The differential strain map $\Delta \epsilon$ =1% reveals no new slip bands in the area between the three twins, while slip bands in the rest of the grain broaden and intensify in an irregular manner. The propagation of the twins seems impeded by intense slip bands, as the twins stop closely before or after. Not even after another 4.4% strain, at a total strain of 6.9%, any of the previously existing twins exhibited significant strain increase in the differential map $\Delta\epsilon$ =4.4%, as shown by the profile of τ_{xy} across the twin (red line). Instead the twins propagated further into the grain and thickened considerably. The thickening seems faster where slip bands are less intense and the typical twin tips develop towards an area of more intense slip bands, without reaching the other grain boundary yet. Now also the strain localisation to the neighbouring grain towards the top (grain 2) triggers a twin into the discussed grain (grain 21). The severe twin activity in this region after 6.9% compression does not allow the image correlation to work in respect to the undeformed state, but to the previous strain step. In order to plot the profile of τ_{xy} for the last strain step anyway, the sum over all increments $\Sigma\Delta\epsilon$ is utilised. The integral strain suggests a maximum

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value of $\tau_{xy of}$ about 6.5%, which is similar to values measured in Ti-0AI and Ti-10AI. The suggests a value $\Sigma\Delta\epsilon$ is with 8-9% strain slighly higher, which may be down to the different method of calculation.



Fig. 7-8: Example for $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tension twin propagation in Ti-7AI

$\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twin

The far more seldom $\{11\overline{2}1\}\langle\overline{1126}\rangle$ tension twin was identified in one occasion for Ti-7Al and Ti-10Al. Region 3 in Fig. 7-3 marks the $\{11\overline{2}1\}\langle\overline{1126}\rangle$ twin in Ti-7Al and Fig. 7-9 shows the example detailed with the twin being already present after the first strain increment. The twin shows a very high shear strain of ~30% (see profile), which is substantially higher than the shear strain observed for the $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twins. Basal slip is active on one side (bottom right) of the grain, while 2^{nd} order pyramidal <c+a> slip was identified at the other end of the twin (top left), as indicated in the figure with back dashed and dash-dotted lines respectively. Thickening takes place with further plastic deformation while the twin interior does not pick up any more shear strain (see $\Delta\epsilon$ =4.4% and strain profile). During thickening of the $\{11\overline{2}1\}\langle\overline{1126}\rangle$ twin prismatic and basal slip traces arise in the surrounding area during the last strain increment, and a diffuse region of intense strain develops.

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Fig. 7-9: Example for $\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twinning in Ti-7AI

$\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ compression twin

Area 4 in Fig. 7-3 in Ti-OAI (grain 9) displays two $\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ compression twins that have formed across the entire grain after the last strain step. Fig. 7-10 shows a part of the twin, which already emerged after the first strain step in detail. Only very faint slip traces can be seen around the large compression twin, which is significantly different to the observations around the described tension twins. The compression twin in the strain map possesses steps on the twin interface with 1st order pyramidal orientation. The growth of the twin during further plastic deformation resulted in faint prismatic slip traces, which can be seen at the twin tip (bottom), but those may be caused by the more complicated stress conditions close to the grain boundary.

Even though the twin orientates in a crystallographic softer orientation, no further strain accumulation via slip can be seen in the observed plastic strain increment of just $\Delta\epsilon$ =1%, as visualised in the strain profile. The maximum shear strain in the compression twin has a value of almost 10%.

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Fig. 7-10: Example for $\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ compression twinning in Ti-0AI with indications for slip traces on pyramidal planes of 1st order

7.4. Discussion

7.4.1.Slip

It has been shown previously that deformation in many metals is highly localised [Efstathiou 2010, Di Gioacchino 2012] and that strain patterns establish at the beginning of plasticity, which develop with more slip systems becoming active during further plastic deformation [Littlewood 2012]. Strain patterns and the likelihood of activating certain slip modes in an hcp crystal structure is strongly influenced by the loading direction relative to the basal texture of the material [Littlewood 2012]. Therefore, in order to investigate the effect of AI on slip mode

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activity, one has to compare Ti-7AI and Ti-10AI, which were both loaded at a 45° angle to RD. Keeping this in mind, Fig. 7-4 suggests an increased level of basal slip with higher AI content. This is in agreement with observations by [Williams 2002] who undertook compression experiments on single crystal Ti-AI alloys (2.5 to 11.1 at.%) and found basal slip to be promoted relative to prismatic slip in Ti-11.1at.% (Ti-6.6wt%). The current results further support the increased likelihood for basal slip in Ti5AI2.5Sn compared to pure Ti during tension as discussed in [Li 2003]. While the number of observed 2nd order pyramidal slip is relatively small overall, comparing Ti-7AI and Ti-10AI in Fig. 7-4 suggests that a high level of AI does promote <c+a> slip, which could be related to the decreased twin activity at such AI content [Fitzner 2013 a&b].

When considering the level of strain localisation, one might consider all three Ti-alloys even though Ti-0Al was loaded along ND and not at a 45° angle to it. Fig. 7-3 does show that the level of shear strain within slip bands does increase very noticeably with increasing AI content. Fig. 7-5 further emphasis this observation giving examples of grains well aligned for basal and prismatic slip and a more quantitative comparison is presented in Fig. 7-6. In principle, there are two possible factors that can explain these observations, AI lowering of stacking fault energy (SFE) [Metzbower 1977, Guo 2006, Ghosh 2008] and ordering of Al [Van De Walle 2002]. For the case of Ti₃Al formation, Van De Walle et al. estimated from first principle calculations that once a dislocation moved on a prismatic plane, a trailing dislocation has lower resistance and will consequently follow to reorder the Ti₃Al structure. The motion of paired dislocations is known to consume less energy than separate motion of dislocations in ordered structures [Van De Walle 2002] and such arrangements will result in strain localisation. Previous work to identify ordering in the present material using neutron diffraction and TEM analysis showed no indication of ordering for Ti-7AI (note, the material was not aged) and only short range ordering for Ti-10Al (see chapter 6). As there is already a noticeable increase of slip localisation between Ti-0AI and Ti-7AI, it seems to be a result of reduction in SFE. In the case of Ti-10AI, one would expect the reported SRO to contribute to strain localisation but further reduction in SFE from the increased AI content is also expected.

7.4.2.Twinning

It is noticeable from the strain maps that the $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ tension twins only propagates through the grain once the compressive load generates some prismatic slip bands of moderate intensity. This may be understood as prismatic slip is generating a tensile stress component perpendicular to the loading direction, which is parallel to the c-axis. Consequently, the $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ twins form resulting in a reorientation that makes the twinned region favourably aligned for hard pyramidal <c+a> slip [Capolungo-a 2009]. The observation that no significant strain builds up in a tension twin with further straining can therefore be explained by the orientation effect, even though further (Basinski) hardening [Salem 2006] may result from a transition of glissile dislocations in the parent to sessile dislocations in the twin. At higher Arnas Fitzner, PhD Thesis, 2014

plasticity levels the strain maps also suggest that very intense slip bands can impede sideways growth and the development of the typical lenticular twin shape. The shear strain within $\{10\overline{1}2\}$ twins varies between 6-9% within the alloys.

The observations from the two { $11\overline{2}1$ }($\overline{1126}$) tensions twins were in conjunction with basal and pyramidal 2nd order slip. Modelling results by Morris et al. [Morris 2000] suggest that the 2nd order pyramidal slip may cause the { $11\overline{2}1$ } tension twin to form. They argue that pyramidal slip on the { $11\overline{2}2$ } plane (2nd order) can dissociates into a <a> partial dislocation on the basal plane and a twin nucleus on the { $11\overline{2}1$ }-plane remains with lowest energy. Hence, the partial dislocations can move on the basal plane and the { $11\overline{2}1$ }-twin plane, being highly sensitive to the stacking fault energy, and support the formation of the { $11\overline{2}1$ }($\overline{1126}$) tension twin [Morris 2000].

In the case of the { $11\overline{2}2$ }($11\overline{2}3$) **compression twin**, 1st order pyramidal slip was identified in the vicinity of the twin. Because the slip trace analysis does not allow to distinguish between <a> and <c+a> pyramidal slip, it is worth pointing out that a grain orientated for { $11\overline{2}2$ }($11\overline{2}3$) compression twinning is well orientated for 1st order pyramidal <c+a> but not <a> slip. Previous work by Paton and Backofen as well as theoretical work by Yoo and co-workers [Paton 1970, Yoo 2002] also suggested that pyramidal <c+a> slip is most likely to assist the formation of { $11\overline{2}2$ }($11\overline{2}3$) compression twinning. Calculations by Serra et al. [Serra 2002] report that a basal dislocation cannot pass a compression twin boundary in the same fashion as a tensile twin boundary. According to their work, a partial dislocation on the boundary has to combine with a twinning dislocation already existing in the boundary at sufficiently high stress. These are somewhat more complex shuffles than for the { $10\overline{1}2$ } twin and result in slower thickening rates of compression twins and may explain the serrated twin-grain interface in Fig. 7-9.

As pointed out earlier, with increasing Aluminium content the level of shear strain within individual slip bands increases for a given macroscopic strain. Regarding the effect of slip localisation on twin activity, it is important to point out that twin activity was shown in chapter 6 to remain constant or slightly increase between 0 and 7 at.% Al but drops dramatically once short range ordering is observed, independent from the loading direction [Fitzner-a 2013, Fitzner-b 2013]. It seems therefore unlikely that the twin activity is affected by the slip localisation itself, but rather by the introduced ordering making atomic shuffle more difficult.

7.5. Summary

DIC strain mapping was successfully employed to visualise slip traces and their interactions with deformation twins during compression of binary Ti-Al alloys. Distinct differences were found between the three different alloys despite many experimental artefacts and mechanistic observations concerning twin nucleation and growth can be made as follows:

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- Prismatic slip is the dominant slip system in polycrystalline, pure Ti. Basal slip occurs during compression only with minor activity.
- Aluminium addition to Ti leads to significant basal slip activity and strain localisation on basal as well as prismatic planes.
- Slip on 1st pyramidal planes occurs in all three alloys locally with minor strain intensity when rather with <c+a> burgers vector but also with moderate to high intensity when rather with <a> burgers vector, judged on an Schmid factor criterion.
- 2nd order pyramidal slip occurs in all alloys with low shear strain locally.
- Prismatic slip traces are present in the vicinity of the 25 observed {1012}(1011) tension twins within the same grain. No {1012} twin was active without prismatic slip in the same grain, but whole grains deform by prismatic slip without any twinning.
- Stress concentration along grain boundaries or from slip traces of the neighbouring grain were though to promote nucleation of {1012}(1011) tension twins. However, due to relatively coarse macroscopic strain steps and a lag of identified stress concentration in few cases no conclusion on twin nucleation can be made.
- Propagation and thickening of {1012}(1011) tension twins seem impeded from intense prismatic slip bands.
- Basal slip and pyramidal 2^{nd} order slip were identified together with the formation of $\{11\overline{2}1\}\langle\overline{11}26\rangle$ tension twinning in two cases.
- 1st order pyramidal slip could be identified in the vicinity of one {1122}(1123) compression twin, literature and a Schmid factor criterion indicate it to be pyramidal <c+a> slip.
- The measured maximum shear strain is lowest within {1012}(1011) twins (~7-8%), higher in the {1122}(1123) twin (~9%) and by far highest in {1121}(1126) twins (~30%) independent from alloy and macroscopic applied strain level. No significant strain accumulated in twins with further deformaiton.

8. The relationship between nanohardness and the flow stress of Ti alloys: Effect of straining and solute content

Abstract

The anisotropy of hcp-metals influences the ductility and yield strength of materials and is a combination of crystal anisotropy and crystallographic texture. This manuscript discusses the anisotropy of polycrystalline compression samples in connection to the nanohardness of the hcp unit cell for a range of binary Ti-Al alloys with up to 13at.%Al. It is shown experimentally that the work hardening of commercially pure Ti is partly based on the crystal-reorientation by deformation twinning but dislocation hardening only plays a minor role. In example, grains deformed by deformation slip have only slightly increased nanohardness compared to their parents, while twins appear harder than grains of comparable orientation, which is thought to be based on residual stresses in the twinned volume rather than dislocation reactions. More important, $\{10\overline{1}2\}<10\overline{1}1>$ tension twins are significantly harder than their parent grains, while $\{11\overline{2}2\}<\overline{11}23>$ compression twins are softer than their parent grains due to the reorientation.

8.1. Introduction

The plastic deformation of α -titanium at room temperature is characterized by high anisotropy at the single crystal level, with straining along the <c> axis being considerably more difficult than along the <a> axis, especially in compression. This is a direct consequence of its h.c.p. crystal structure, which deforms by a number of different slip systems, often in non-closed packed planes and by deformation twinning, which can also occur in a number of different modes. In addition, many of these deformation modes are directionally dependent and interact with each other. For example, twinning causes significant lattice rotation that significantly modifies slip activity but since twinning is directional, this effect will depend on the deformation mode. The large number of possible deformation modes and their interdependence makes it very difficult to infer their relative activity from the macroscopic stress-strain curve alone, especially after yield.

Unlike the initial slip and twin resistances, which can be determined reasonably well by mechanical tests on single crystals and to some extent via in-situ diffraction experiments coupled with crystal plasticity modelling, the many possible interactions between deformation modes make determining the changes in slip and twinning resistance with deformation much more difficult to ascertain.

Is therefore unsurprising that the hardening behaviour of α -titanium is rather unusual. The rate of hardening is stronger in compression than in tension during uniaxial deformation irrespective

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the loading direction [Nixon 2010, Hama 2015]. In plane strain compression, the hardening behaviour depends on loading direction [Battaini 2007] and a characteristic increase in work hardening rate is seen at effective strains of about 0.04 in uniaxial compression along ND and slightly later (0.05) in plane strain [Salem 2003].

In their work exploring the high strain rate behaviour, [Chichili 1998] found that work hardening rate increased with strain rate but also that the flow stress on reloading after deformation at 77K, was lower than for an equivalent sample deformed at room temperature.

Several mechanisms have been proposed to explain the change in work hardening observed, mostly concentrating on the microstructural changes introduced by twinning. In the comprehensive work by Salem and co-workers [Salem 2003, 2006], twinning is said to contribute to hardening by changing the free slip length (in a kind of Hall-Petch effect) and by the Basinsky effect whereby dislocations are rendered sessile by twinning [Salem 2006]. However in their latter work, Battainni and co workers [Battaini 2007] compared results from plane strain compression tests along different directions and suggested that the difference in hardening behaviour could be explained simply by reorientation hardening caused by tensile twinning and that compressive twinning also contributed to hardening, even though it should cause reorientation softening. Chichili et al [Chichili 1998] explain their results in terms of reorientation induced softening as do Kaschner et al. [Kaschner 2006] in work on Zr. More recently, a mechanism by which dislocations that are incorporated in the twin volume during twin growth lead to very strong latent hardening in the twin has also been suggested [El Kadiri 2010]. Temperature jump experiments suggest hardening due to dislocation multiplication is much less significant than the effects of twinning [Capolungo 2009]. These details are important because they will determine which mechanisms should be considered in crystal plasticity models. For example, in [Salem 2005] the mechanisms proposed in their earlier work are used to justify changing the slip resistance with twinning but reorientation due to twinning is not considered explicitly and hence the corresponding hardening (or softening) effects are not considered.

On the other hand the model in [Proust 2007] accounts for reorientation but also includes a Hall-Petch term to account for a decrease in slip length. However, [Oppedal 2012] showed that the Hall-Petch contribution could be ignored provided the latent hardening in the twinned volumes was made significantly higher than that in the parent grain. This has been explained by the mechanism proposed by El Kadiri and Oppedal [El Kadiri 2010].

Recent work has used crystal plasticity modelling to try to explain and infer mechanisms. However this presents important difficulties, since there are inherent assumptions in the different modelling approaches that will limit their applicability. On the other hand, the only direct measurement of the hardness inside twins is that in [Salem 2006]. In their work nanoindentation

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was used to demonstrate that the twins are harder however they did not consider the wellknown dependence of indentation orientation on nanohardness (NH) e.g. [Britton 2010 b].

In this paper, nanoindentation was used to investigate origins of work hardening on the change in flow stress due to pre-straining (strain or work hardening) and by solute addition. The aim is to confirm whether the twins are indeed harder than the parent grains and also to quantify this difference by comparing it with hardening caused by solid solution strengthening (AI) and accounting for the effect of crystal orientation.

Uniaxial compression tests along multiple directions were carried out on Ti-alloys with different AI contents and different states of short-range order (SRO). The nanohardness of the alloys was determined for different grain orientations, which were determined by EBSD. Commercially pure Ti (CP-Ti) was also indented after compression to 4% and 8% to distinguish the nanohardness between twins and parent grains, as determined by EBSD.

8.2. Experimental methods

8.2.1.Materials

Coarse grain high purity Titanium and fine grain binary Ti-Al alloys with Al concentrations from 0 to 13at.% were produced at the Timet research facilities in Witton, UK. 200g buttons were double melted in a tungsten arc furnace under argon shield followed by β -forging at 1100°C and α -cross-rolling in bar shape (14× 14× 260mm) on a 2-high Robertson mill (WHA Robertson & Co Ltd) at a temperature dictated by composition, and subsequently recrystallized in the alphaphase. Metallic elements were analysed on halved compression samples by Timet – Savoie on a HORIBA Ultima2, C on a HORIBA EMIA 820V combustion analyser, O and N on a LECO EF-400. The compositions are given in Tab. 8-1Tab. 9-1.

Alloy	Al	Al C		Ν	0	Ti	GS
	wt%	at.%	ppm	ppm	ppm		μm
CP-Ti	0.00	0.0	53	31	507	bal.	180
Ti-0Al	0.00	0.0	55	13	474	bal.	94
Ti-3Al	2.00	3.49	72	39	413	bal.	82
Ti-7Al	3.90	6.67	50	23	592	bal.	73
Ti-10Al	5.88	10.01	76	53	756	bal.	71
Ti-10Al ^a	5.88	9.99	76	53	567	bal.	77
Ti-13Al	7.85	13.13	55	94	377	bal.	78

Tab. 8-1: Chemical compositions and grain sizes measured by the linear intercept method of the model alloys in this study.

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8.2.2. Characterisation of micro and macro textures

Grain sizes were estimated from optical polarised light micrographs using the linear intercept method on more than 100 grains. EBSD orientation maps of recrystallized and deformed samples were taken using step sizes of 1-3µm on a FEI Quanta 650 FEG-SEM with the AZtec software package from Oxford instruments. Macro-texture orientation measurements were acquired with a 40µm step size on a CAMSCAN and a FEI Sirion FEG-SEM using the software Flamenco (Oxford instruments) on areas larger than 16mm².

8.2.3. Mechanical testing and macroscopic anisotropy

Cylindrical samples of 6x9mm and additionally of 8x12mm were machined with compression direction along the former rolling direction (RD) and normal direction (ND), as well as 45° between both directions (45°) as indicated in Fig. 8-1. Uniaxial compression tests were conducted on an Instron 5569 and a MTS RT 100 to 3.7% and 8.7% plastic strain at room temperature and a strain rate of $1*10^{-3}$ 1/s.



Fig. 8-1: Schematic of sample geometry in respect to the cross-rolled bar.

8.2.4. Nanoindentation

Recrystallized samples were cross-sectioned and mechanically ground and polished with combined etching attack from Kroll's reagent and oxide particle suspension with the former RD or ND as surface normal. Compression samples were cross-sectioned and polished with the LD (loading direction) as surface normal. Nanoindentations were carried out on samples embedded in Bakelite or glued on Bakelite in a Nanoindenter XP from MTS equipped with a diamond Berkovich indenter head. Indentations were made according to the Oliver and Pharr method [Oliver 2004], typically in arrays with more than 20µm spacing between indents and only below a drift rate between sample and indenter head of 0.15nm/s to minimise vibrations with a constant indentation rate of 0.055⁻¹ to a depth of 500nm. The indenter was held for 10s time at peak load for every measurement. The nanohardness was then calculated independent from the modulus, by relating the maximum force to the projected contact area using the Nanosuite software package and the modulus by stiffness measurements during the unloading to 50% of the maximum force, according to the Oliver and Pharr method [Oliver 2004]. The modulus was only used to ensure the validity of the hardness values, which can be undermined by a loosely held sample, for example. The indentation results were related to individual orientation measurements using EBSD. Indentations of parent grains within 5µm to grain or twin Arnas Fitzner, PhD Thesis, 2014

boundaries have been dismissed. However, due to the experimental difficulty to indent twins more than 5µm from the boundary indentations fully within twins but close to twin boundaries were considered.

8.3. Results

8.3.1.Yield stress and stress-strain behaviour

The yield stress of the different alloys was determined by uniaxial compression testing. The stress strain curves of the high purity Ti are shown in Fig. 8-2 a) up to 9% plastic strain for RD, ND and 45°. The compressive yield strength of the coarse grain Ti in the RD and at 45° is identical at 200MPa, and lower than the yield stress along the ND (230MPa). The work hardening rate is similar for all samples, although it is highest for the 45° sample and lowest for ND, seen in Fig. 8-2 b).



Fig. 8-2: a) Macroscopic stress-strain curves for large grained CP-Ti with LD parallel to ND, RD and 45° in between and b) the corresponding work hardening rate.

All binary alloys tested showed the highest yield stress for ND loading and the lowest for RD loading, as shown in Fig. 8-3 a). This anisotropy can be explained by the texture of the samples and the single crystal anisotropy of Ti. During loading along RD most grains will have high Arnas Fitzner, PhD Thesis, 2014

Schmid factor for prismatic slip, whereas for ND most grains will have a low value. However, the ratio, plotted in Fig. 8-3b), increases from Ti-0AI to Ti-3AI, but decreases subsequently with further AI addition. Similarly, while Ti-0AI has only a small difference between loading in RD and ND, this difference increases with AI content up to Ti-7AI after which it decreases.



Fig. 8-3: Yield anisotropy as function of the Al concentration: a) Yield point in RD, 45° and ND, b) ratio between yield in ND to RD and 45° to RD, c) difference between yield in ND to RD and 45° to RD.

8.3.2. Texture and Microstructural evolution

The evolution of the macrotexture with deformation is shown in Fig. 8-4. Initially the material has a clockwork texture, in which the 0001 pole aligns roughly perpendicular with the rolling direction, without clear preference between ND_1 and ND_{11} , as expected for clock rolled material Arnas Fitzner, PhD Thesis, 2014

(see Fig. 8-4 a) and b). The prismatic $10\overline{1}0$ pole has a slightly higher intensity along RD, which is a consequence of dominant prismatic slip [Philippe 1988]. After 8% compression along ND (Fig. 8-4 c) the texture barely changes, although it is very slightly weaker. On the other hand, 8% compression along RD (Fig. 8-4 d) leads to a high intensity of the basal pole in the LD//RD and a reduced intensity of the prismatic pole along RD.

The high purity Ti material has a mean grain size of approximately 180µm with equiaxed morphology, as shown in Fig. 8-5 a). The EBSD micro map reveals orientation gradients below 2° within one of the recrystallized grains along a line. Fig. 8-5 b) shows an EBSD micromap after 8% compression along ND.



Fig. 8-4: Basal and prismatic pole figures from macro texture measurements after recrystallisation (RX) along the ND a) and b) RD as well as at compressive strains of 0.09 along the ND c) and RD d).

Misorientation profiles in grains only deforming by slip revealed rotations up to 5° along a line. In most grains, deformation twinning also occurred giving rise to new grains with misorientation angles of around 85°, 35° or 65° for the twinning systems $\{10\overline{1}2\}<10\overline{1}1>$, $\{11\overline{2}1\}<\overline{11}26>$ and $\{11\overline{2}2\}<\overline{11}23>$ respectively. The $\{10\overline{1}2\}$ tension twins are indicated by black twin boundaries and have typically lenticular shape. Many grains exhibit multiple $\{10\overline{1}2\}$ twin variants within one parent grain and consume considerable fractions of the parent grain, which makes them

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appropriate for nanoindentation of only twinned volume. One example where the parent grain is nearly fully consumed is labelled as "A" in Fig. 8-5 b), showing also secondary compression twins in the primary tension twin (marked with white boundaries). Hard grains, with their c-axis closer to the LD, exhibit lenticular or needle shaped compression twins as primary twins, partly with secondary { $10\overline{1}2$ } twins (example labelled as "B") and occasionally even with tertiary compression twins forming within the secondary tension twins of the primary compression twin. There are only a few { $11\overline{2}1$ } tension twins, which are usually thinner than 1µm. They are indicated by grey twin boundaries, as in grain "C" in Fig. 8-5 b).



Fig. 8-5: Schematic of methodology: EBSD mappings in IPF-Z colouring from large grained CP-Ti after a) RX treatment and b) 8% compression with indications for nanoindents (sizes not to scale) and the inclination angle between c-axis of the crystal and indentation direction. For illustration full and dashed grey lines distinguish parent grains and twins, respectively.

Careful twin fraction analyses of orientation maps on more than 1mm^2 with $3\mu\text{m}$ stepsize revealed that following 8% compression along RD there is a total twin area fraction of 30%, with 28% { $10\overline{1}2$ } twins, 2.3% { $11\overline{2}2$ } twins and less than 0.5% { $11\overline{2}1$ } twins. The large numbers of { $10\overline{1}2$ } tension twins are responsible for the increase in basal pole intensity shown in Fig. 8-4 d). Loading along the former ND results in dramatically reduced fraction of the { $10\overline{1}2$ } twin but therefore increased { $11\overline{2}2$ } twin fraction, both to approximately 10%. Secondary twinning occurs in about 1% area fraction. The frequency of { $11\overline{2}1$ } twins is not significantly affected from the loading direction. The combination of { $10\overline{1}2$ } tension twinning and { $11\overline{2}2$ } compression twinning results overall in little textural change, as demonstrated with macro texture scans in Fig. 8-4 c).

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8.3.3.Nanohardness

Nanoindentation was carried out in undeformed samples for all alloys and at two deformation levels for the CP-Ti sample. The arrays used for nanoindentation are shown schematically in Fig. 8-5 with enlarged indents for visualisation. The orientation of the material under the indent was determined by overlapping the EBSD map with optical micrographs of the indented area. White points in the Fig. 8-5 a) mark indents which would have been disregarded for analysis because they lie within 5µm of a grain boundary. This condition, makes the thin $\{11\overline{2}2\}$ compression twins in the deformed samples challenging to measure without boundary effects, but reproducible results were possible by considering only measurements in the centre of the wider twins. The $\{11\overline{2}1\}$ tension twins, however were too thin to measure. Previous work showed that nanohardness depends almost exclusively on the angle between the indentation direction and the <c> and therefore this angle is used to represent grain orientation.

8.3.4. Effect of AI content

The nanohardness of the different alloys is plotted as function of the angle between crystallographic c-axis and indentation direction in Fig. 8-6. All samples showed a similar variation of hardness with indentation angle, with <c> axis indentation being significantly harder than <a> axis indentation. For the Ti-OAI sample, for example, the hardness along <a>-direction is about 1.4GPa, about 1GPa lower than for indentations closer to the <c>-axis, at low angles, which is about 2.5GPa. This corresponds to values of maximum forces per indent ranging from 10mN to 20mN respectively. Interestingly, although the prescribed indentation depth was 500nm, indentation depths varied between 510nm to 550nm due to software control.

The plot shows that adding of AI to Ti increases the nanohardness but has only a small effect on its variation with indentation direction. To show this more clearly, the nanohardness values have been averaged for each alloy between 0° and 15° to represent the average hardness near the <c> direction and between 80° to 90° for the <a> direction, as indicated in Fig. 8-6. These averages are plotted in Fig. 8-7 a) as function of the AI concentration. The error bars in Fig. 8-7 a) reflect the range of data in the described angular regimes for <a> and <c>, according to standard error propagation to emphasise the high scatter of the nanoindentation measurements. Values in the soft <a>-direction increase almost linearly from approximately 1.4GPa in Ti-0AI to 3.5GPa in Ti-13AI, while the nanohardness in the hard <c>-direction increases from 2.5GPa to 5GPa with an s-shaped curve. Therefore, nanohardness is directly proportional to AI content, although the effect is slightly smaller from 0 to 3at.% and from 10 to 13at.%, especially along <c>.

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Fig. 8-6: Nanohardness for several binary Ti-Al alloys as function of the <c>-axis orientation. Angular ranges for averaging values in <c> and <a> direction are indicated.

The hardness ratio between <a> and <c> indentations decreases with AI addition as shown in Fig. 8-7 b). This reflects the fact that the difference between <a> and <c> hardness increases with AI content only within the uncertainty (see Fig. 8-7 c), but the mean value increases significantly. Despite the strong effect of alloying on hardness, a grain close to the soft <a>- direction in an alloy of high AI concentration can be softer than a hard grain of an alloy containing less AI. For instance Ti-13AI exhibits softer nanohardness in <a>-direction (3.5GPa) than the c-direction in Ti-7AI (3.8GPa).



Fig. 8-7: Crystal anisotropy as function of the Al concentration: a) Nanohardness (NH) after recrystallization treatment (RX) along crystallographic <a> and <c>-direction (as indicated in Fig. 8-5) and b) the ratio of NH in <c> to <a> as well as the difference between NH in <c> and <a>.

8.3.5.Effect of strain hardening

To investigate the effect of deformation on nanohardness, CP-Ti was tested at two levels of strain: 4%, and approximately 8% (8.7 in RD, 7.7% in ND and 9.2% at 45°). This corresponds to increase in flow stress due to work hardening of approximately 60 MPa each time, as indicated by the grey circles in Fig. 8-2. The results are shown alongside those for the recrystallized material in Fig. 8-8, from which it can be seen that the strained material is slightly harder than the undeformed material and that there is also a noticeable increase in measurement scatter with straining. The mean increase in hardness with straining is small and less than the variation in hardness with orientation. For instance even the highest hardness close to the soft a-axis, measured in compression twins, is at 1.85GPa significantly softer than recrystallized or deformed grains in the hard c-axis and even up to an inclination angle of 40°.

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Despite the scatter, the data reward careful study. The plot in 8-8 shows indents from twinned regions in filled symbols and indents from non-twin regions in open symbols. It is difficult to fit a line to this relatively sparse and scattered data but guiding lines have been drawn to show these trends better. If one considers the non-twin regions alone, then the increase in hardness at 4% is only about 0.15 GPa and it stays constant with further straining to 8%. On the other hand, most indents within twins show a higher nanohardness than indents in non-twinned grains of comparable orientation. The twins at higher angles can have a hardness, which is 0.5GPa higher that the deformed grains and 0.8 GPa higher than undeformed grains, although the difference between average hardness is 0.3 and 0.4 respectively. The twins at lower angles also show higher hardness than the deformed untwined grains, although the difference in hardness is slightly smaller. The measurements in the twins also show much more scatter due to the small dimensions. However, there is no clear difference in the hardness values of the twins at 4% strain and the twins at 8%.



Fig. 8-8: Nanohardness as function of the inclination of the c-axis in respect to indenter direction for CP-Ti after recrystallization, 4% and 8% compression. Open symbols mark parent grains, and filled symbols twins.

8.4. Discussion

8.4.1. Orientation dependence of hardness

The absolute values of hardness obtained show good agreement with other measurements on CP-Ti [Mante 1999, Viswanathan 2005, Merson 2008, Zambaldi 2012] and Al-rich alpha-Ti [Viswanathan 2005, Kwon 2013]. The work by Salem et al. results in similar numbers of the NH to CP-Ti but in MPa instead of GPa, letting one expect a unit confusion in this paper [Salem 2006]. There is one study where the absolute values of hardness are much higher [Britton b 2010], although the difference in hardness between the highest and lowest is similar at 1GPa.

Interpreting the variation in hardness with orientation in terms of relative slip activity is not straightforward since several slip systems are activated during indentation along all orientations nanohardness and indentation depth depending on each other. Work by Kwon et al. on Ti-7wt%Al (~Ti-11.5at.%Al) with a spherical nanoindenter and Viswanathan et al. with a Berkovich indenter on Ti6Al4V showed that indentation along the soft $<10\overline{10}>$ and $<11\overline{2}0>$ directions can in principle activate <a> slip on basal, prismatic and pyramidal planes but also give rise to pyramidal <c+a> slip and twinning. Using a spherical indenter, Kwon et al. also detected evidence of activity on all slip systems for hard indentations (within 5° to the c-axis) although prismatic slip activity was much lower that for the softer orientations. Viswanathan et al. [Viswanathan 2005] also found <c+a> and <a> type dislocations during indentation of Ti6Al4V 15° from the c-axis with a Berkovich indenter. Crystal plasticity finite element simulations of indentation depth and pile-up also suggest that all slip systems are activated to some extent for all directions but that prismatic slip dominates in the soft orientations, whereas all slip systems are activated for the hard orientation [Zambaldi et al. 2011]. In this article, the authors use indentation depth to calculate relative CRSS of the different slip systems although they urge caution because the hardening model used are very limited. Nevertheless, it is clear that indentation direction has a significant effect on the hardness measured.

8.4.2. The effect of Al addition

Increasing the AI content increases both the flow stress and the nanohardness in very similar ways, both showing smaller increases between 0 and 3at.% and between 10at.% and 13at.% than those at intermediate AI contents. Fig. 8-9 shows linear dependence of nanohardness and yield stress, the slope of which depends slightly on which directions are used for the comparison. For indentation along <a> and RD compression the slope is 3.8, whereas for indentation along <c> and ND compression it is about 4.3. In other words, a 100 MPa increment in flow stress corresponds to a change in nanohardness of about 0.4 GPa.

The decreasing ratio of nanohardness NH<c>/NH<a> shows that the hardness becomes more isotropic with increasing AI content. It is tempting to explain this decrease in anisotropy to

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changes in the slip anisotropy. This would be in agreement with the results of Williams et al. [Williams 2002], where AI addition makes basal slip relatively easier compared to prism slip and <c+a> slip relatively easier to <a> slip, even though all slip systems become absolutely more difficult. However, since all slip systems are active for all loading directions this decrease in anisotropy could simply be due to the increase in strength caused by AI addition. Since the increase in strength from AI is an additional term, increasing the slip resistance of all slip systems by the same amount will have the effect of decreasing the anisotropy as defined by the ratio of slip resistances. This is supported by the fact that the ratio of yield strength for the 45° case to that of the RD case decreases from 3at.% AI with increasing AI addition, as would be expected from the overall higher strength levels with similar differences between both directions.

It is then surprising that the yield stress of the Ti-OAI sample is the most isotropic. The yield stress when compressed in RD and 45° is identical and the yield stress along ND is only slightly higher than along RD even though the texture is not different from that in the binary alloys and the nanohardness values show identical variation with indentation direction. The reason for this is likely to be the very low initial slip resistance in the Ti-OAI material and a significant contribution of hardening to the yield stress values measured. As discussed by Hutchinson and Barnett [Hutchinson 2010], if the initial slip resistance is very low then a small absolute increment in hardening with straining has a disproportionate effect on the slip resistance. It is plausible that the yield stress measurement in this material is affected by a high rate of initial work hardening and that since this effect is strongest for RD and 45°, it acts to reduce the measured anisotropy.



Fig. 8-9: Nanohardness along <c> and <a> as function of the yield stress in ND and RD, respectively for various Ti-Al alloys.

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8.4.3. Strain hardening

The hardening behaviour observed during compression testing to just under 10% is similar to that observed by others and is almost independent of direction (see Fig. 8-2b). At 3% the flow stress has increased by 60 MPa and at 9% by about 120MPa for all loading directions.

This change in flow stress is accompanied by a change in nanohardness in untwined material, but this is only detectable for the first strain increment. This suggests that the increase in flow stress observed during compression testing is only partly caused by a change in the local flow stress, and that this hardening occurs in the early stages of deformation. Using the relationship between nanohardness and flow stress developed for the Al containing alloys, the 0.15 GPa change in hardness observed translates to a 35 MPa change in flow stress, just over half of the change in flow stress at 4% and less than a quarter of the flow stress measured at \sim 8%.

The twinned regions however, show a higher hardness than both the undeformed grains and the deformed, untwined regions. However this hardness increase is smaller than the change in hardness with orientation, in contradiction to the results by Salem et al. [Salem 2006]. Nevertheless, it is clear that twins are harder than undeformed grains or deformed parent grains of comparable orientation. The mean difference in hardness is about 0.4 GPa, which corresponds to 100 MPa in equivalent flow stress. Although this increase in hardness is higher than that in the untwined regions, it is still less than that observed in the compression test.

Since the indentation direction is always parallel to the compression direction, the results from $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ tension twins can be easily separated from those of $\{11\overline{2}2\}\langle 11\overline{2}3\rangle$ compression twins. Tensile twinning causes a rotation of the <c>-axis towards the LD, whereas compression twinning causes the <c>-axis to rotate away from the LD. Therefore, all twins at low indentation angles (0-30°) will be tensile twins, whereas the twins at high angles will be compression twins.

Before discussing the origin of the higher hardness in the twinned regions it is worth pointing out that the scatter in the nanoindentation measurements is higher in the twins than in the deformed grains, that the hardness in the twins is identical after 4% and after 9% of strain and that the increase in hardness appears to be higher for the compression twins that the tensile twins. Three possible hardening mechanisms that might explain the higher twin hardness will be considered: change in slip length (Hall-Petch effect), the Basinsky mechanism and residual twinning stresses.

The slip length mechanism is difficult to test since the origin of the Hall-Petch effect is not fully understood. However, it is difficult to see how slip length effects could be detected by nanoindentation, given the small volume of material deformed in the test. So although slip length might be important in explaining the change in flow stress, it cannot explain the higher twin hardness measurement.

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The Basinsky mechanism, by which dislocations are made sessile by twinning, could offer an explanation for the increased hardness measure. In their paper, Salem et al. [Salem 2006] propose that the higher hardness of the twins is experimental evidence of this mechanism. However, comparing their results with ours, it would appear that, in their work, measurements made on twins at low angles were compared to parent grains at high angles. Leaving aside the details of how twinning affects dislocation in hcp metals, which will be very different from those in fcc metals for which the mechanism was proposed, the results presented here cast significant doubts on the relevance of this mechanism. If the increase in hardness arises from the generation of an array of sessile dislocations during twinning, then this effect should be more pronounced for grains containing more mobile dislocations before twinning. Since, for uniaxial compression, compression twins occur primarily in hard grains, they should show almost no increase in hardness, whereas tensile twins, which appear in grains ideally aligned for easy prismatic slip, should show a large increase in hardness. Furthermore, one would expect that the hardness in the twins would be higher at higher strains, since they will be more likely to contain a larger number of dislocations. However, the results clearly show that there is no difference in the hardness at difference strain levels and that the difference in hardness is larger for the compression twins than for the tensile twins.

Significant local residual stresses are generated during twinning, as the twinning shear introduces a misfit in the parent grain. These stresses are the reason why twins are lenticular and they have been studied experimentally and numerically. In a recent numerical study by Arul Kumar et al. [Kumar 2015] it was shown that the twin is constrained by parent grain, which acts to reduce the shear stress in the twinning plane inside the twin. The magnitude of the stresses in the twins depends on the ability of the parent grain, and to some extent the neighbouring grains, to accommodate the misfit strain by plastic deformation but is mostly determined by the twinning transformation. There is also direct experimental evidence for this local stress reduction (sometimes called reversal) [Aydiner 2009]. Such stresses will of course also affect the resolved shear stresses for slip inside the twin during deformation. In the unloaded condition and at a polished surface, these stresses will remain as residual compressive stresses, which are well known to cause an increase in the measured hardness [Tsui 1996]. If the stresses are mostly determined by the transformation shear, then they should be higher in the compression twins (shear strain of 0.225) than in the tension twins (shear strain of 0.167). This agrees with the results in Fig. 8-8, where it is clear that the increase in hardness in the compression twins is higher than in the tension twins. The residual stress argument also explains why the twin hardness is the same after 3% and 8% straining, since the stresses are dominated by the twinning shear strain. It also helps explain why the scatter in the twins is higher than that in parent grains, since the stresses within a twin vary significantly with position [Kumar 2015], and hence will cause the measured hardness to vary with indentation location.

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In summary, these new detailed nanoindentation measurements confirm that the nanohardness of the twins is higher than that in the parent grains. However this difference is small, and much smaller than the total variation with orientation. Furthermore, these results suggest that the higher hardness of the twins is caused by residual stresses and not a Basinski type mechanism.

8.4.4.Implications for work hardening behaviour

These new results have significant implications for the origins of the work hardening behaviour of CP-Ti. Nanoindentation results cannot test the potential Hall-Petch strengthening effect. However, since tension twins in CP-Ti grow to consume the entire grain, this mechanism is probably more relevant for compressive twins and only of significance at high stresses, since compression twins are formed primarily in grains where prismatic slip is difficult at the start of deformation. In addition the results of temperature reversal experiments also suggest that grain refinement by twinning does not necessarily increase the flow stress [Chichili 1998], Kaschner 2006].

Although the nanoindentation results showed that the twins are indeed slightly harder than matrix grains of comparable orientation, consideration of lattice orientation, twin type scatter and magnitude suggests that this increase in hardness is probably caused by the presence of residual stresses induced by the twinning strain and not by a Basinski type mechanism.

What these new nanoindentation results do highlight is the strong plastic anisotropy of Ti. This anisotropy implies that, especially at smaller strains (and low applied stresses), deformation will be very heterogeneous, occurring predominantly on soft oriented grains deforming around hard oriented grains. The hard grains raise the mean flow stress due to their low Schmid factor for prismatic slip and in addition the misfit between hard and soft grains will give rise to back stresses, which will contribute to work hardening. These stresses are probably responsible for the strong Bauschinger effect observed in CP-Ti [Hama 2015].

Twinning causes dramatic changes in orientation during straining, changing the relative fractions of hard and soft orientations to change during deformation and hence it can potentially be a potent hardening mechanism. However since there are two main twinning modes in CP-Ti, the compression and tension twinning mode, twinning should cause either texture softening or hardening, respectively. Reorientation caused by tensile twinning therefore explains the peak in hardening rate observed for compression along soft directions, like RD. However, strong hardening is also observed when loading along hard directions, such as ND, where compression twinning is in balance with tension twinning, and the net texture hardening is close to zero.

Of course if the texture is not very strong, as in the case of the material studied here, primary tensile twinning will also take place and primary compression twins readily form secondary tension twins. But even for stronger textures and at low temperatures, hardening is observed. Arnas Fitzner, PhD Thesis, 2014

For compression loading, the evidence is that both tensile and compressive twinning contribute to the work hardening of the material [Battani 2007]. This implies that reorientation softening from compression twinning is less effective than reorientation hardening from tensile twinning.

To try to explain this difference, the differences between the two twinning modes must be considered. The first is the reorientation angle: tensile twinning reorients the lattice by about 85° whereas the reorientation from compressive twinning is only 65°. Thus the reorientation effect will be stronger for tensile twins, especially when prismatic slip is dominant like in Ti. The other difference is that, in compression loading, tensile twinning usually occurs in grains well oriented for prismatic slip, whereas compression twins appear in hard grains, where prismatic slip is difficult. This means that the potential for relieving the twinning induced misfit stresses inside and near the twins is easier for the tensile case. Since these stresses act to hinder twin growth [Kumar 2015], this could explain why tensile twins grow to cover entire grains, whilst compressive twins usually remain thin. It is also likely to be the reason for the work hardening observed for compression along hard directions like ND and at low temperatures. Since these stresses cannot be relieved, twins cannot grow and instead multiple variants are generated in each grain which becomes increasingly difficult with deformation, with each twin contributing less to the macroscopic strain, giving rise to work hardening. The presence of these thin compression twins and many twin intersections make the idea that reduced slip length could contribute to hardening via a Hall-Petch type effect very compelling. However, it is important to remember that the parent grains are hard and do not deform much if at all before twinning and therefore the creation of new boundaries should not change the macroscopic flow stress even if the slip length is reduced. Instead, the main effect of compressive twinning is probably the generation of high local stresses which will act to lower the shear stress in the reoriented twinned volume, making it appear harder than its orientation alone would suggest. These stresses are strongly directional which is consistent with the finding that the slip length effect can be better represented by change in latent hardening in crystal plasticity models [Oppedal 2012]. This is a simpler explanation than that put forward by El Kadiri and Oppedal [El Kadiri 2010] based on dislocation transmutation. The difficulty in relaxing the twinning stress in the compressive case explains why reorientation softening by compressive twinning is not as significant as expected. So if compressive twinning is dominant, the material will work harden as twinning becomes more difficult and whilst the softening induced by reorientation is prevented by the twinning induced local stresses, the same stresses that cause the nanohardness to increase.

This leaves unexplained results from the temperature reversal experiments by Chichili et al. on Ti and Kaschern et al. on Zr where samples deformed at 77 K have a lower yield stress on reloading than the samples deformed at room temperature, suggesting a strong softening effect induced by compression twinning. In these papers, low temperatures were used to promote twinning at the expense of slip but the experimenters have neglected the strong thermal

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anisotropy of these materials and the associated thermal residual stress relaxation that will occur on reheating to room temperature. Ti has been shown to have an unusually large thermal anisotropy at liquid nitrogen temperatures, partly as a result of an anomalous thermal expansion behaviour, where the thermal expansion along the <c> axis becomes negative below 170 K, whilst along <a> it remains constant at about 9×10^{-6} K [Souvatzi 2007]. This means than, on reheating, the stresses induced by compressive twinning will be relaxed by the differential thermal expansion, hence reducing the back stresses on the reoriented twin volumes, and decreasing the overall flow stress. This is likely to be the reason for the need to add recovery on reheating when modelling this behaviour [Capolungo 2009]. Of course, on reloading, further twinning will induce new stresses, which explains why the original flow stress and work hardening rate are eventually recovered. Therefore, the temperature reversal experiments further strengthen the argument that the local stresses induced by twinning are an important part of understanding how twinning affects work hardening.

8.5. Conclusion

Careful nanoindentation measurements have shown that although the nanohardness of CP-Ti does increase slightly with deformation, the change in nanohardness in the parent grains is only equivalent to a 35 MPa increase in equivalent flow stress as determined by measurement in Ti-Al alloys, and is unchanged from 3% to 9%.

The twinned volume is significantly harder, showing hardness increases equivalent to flow stresses of 100 MPa, but they show large scatter and are also unchanged with deformation. This implies this increase in hardness in not due to a Basinsky type mechanism. Instead it is in all likelihood caused by residual compressive stresses that were generated during twinning. The small increases in local hardness and the fact that they do not change significantly with increasing deformation from 3% to 9% imply that these changes can only explain a small part of the work hardening of these materials. Instead, the work hardening probably arises from back stresses generated by the incompatibility between soft and hard oriented grains, i.e. grains favourably and unfavourably oriented for prismatic slip. Therefore, during compressive straining along soft directions, like RD, the main contribution of twinning to hardening is by reorientation induced hardening, through tensile twinning. Since tensile twinning occurs in grains well oriented for prismatic slip, the twinning stresses can be relaxed by slip during deformation and twins can consume entire parent grains.

Along hard directions, where the contribution of tensile twinning is small, it is suggested that work hardening is caused by the saturation of twinning and strong latent hardening in the twinned volumes, both of which are a direct consequence of the difficulty in relaxing the twinning induced stresses. Thus although compressive twinning does lead to reorientation softening, it does not manifest itself due to the presence of twinning strain induced stresses.

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These can be relieved by exploiting the strong thermal anisotropy of these materials to relieve these stresses, as demonstrated by temperature reversal experiments.

Until recently, the majority of the work on understanding the work hardening in Ti has focused on dislocation mechanisms and changes in slip length caused by twinning. In contrast, the development of internal stresses at the microstructural scale has mostly been ignored. This is somewhat surprising, since the role of these stresses as been recognized in other materials like TWIP steels. These new results suggest that internal stresses play a very important role in the work hardening behaviour of Ti, both during slip, through the development of back stresses between hard and soft oriented grains, and during twinning in determining to what extent twinning and reorientation hardening and softening occur.

9. The effect of Tin on deformation by twinning in α titanium

Abstract

The deformation mechanisms of recrystallised binary Ti-Sn model alloys (0-3.5at.% Sn) have been investigated in respect to nucleation and growth of deformation twins using in-situ loading in combination with neutron diffraction as well as detailed post mortem EBSD analysis. A consistent starting microstructure and texture was generated for all alloys and quasi-static compression were accomplished at ambient temperature along the former rolling direction, promoting tensile twinning. No signs of ordering towards Ti₃Sn were identified by TEM diffraction analysis nor by large d-spacing neutron diffraction analysis. However, Sn does increase the c/a ratio of the hcp-unit cell by only increasing the c lattice parameter. It was found that raising the Sn content to 1at.% increases the 0.2% proof stress significantly while further Sn additions have no significant effect on the 0.2% proof stress but the work hardening rate. The increase in work hardening rate can be explained by a facilitated nucleation of $\{10\overline{1}2\}<10\overline{1}\}$ twins with Sn addition, revealed by analysis of the residual intergranular strains of the twinning grain family. Furthermore, Sn seems to impede twin growth, revealed by analysis of microscopic EBSD maps at strains of 0.09. In that way the overall twin fraction barely changes as function of Sn but the grain refinement due to twinning increases and can be related to the increased work hardening. Frequency and size of $\{11\overline{2}1\} < \overline{11}26$ tensile twins significantly increased with Sn, while $\{11\overline{2}2\}<\overline{11}23>$ compression twins became extremely rare and thin.

9.1. Introduction

In view of the complex alloy chemistry in modern two-phase Ti alloys there is an interest in understanding the role of individual alloying elements on deformation mechanisms and particularly twin activity. As elements like AI, Sn and Zr affect c/a ratio, stacking fault energy/probability and potentially cause short or long range ordering in Ti, it is of great interest to evaluate their role on twin nucleation and growth. From an application point of view adding Sn is of interest due to its strengthening effect in α -Ti [Donachi 2000, Hsu 2009] and improvement in high temperature performance, particularly creep resistance [Kornilov 1963]. Early phase diagrams and Thermocalc calculations suggest that Sn is a slight α stabiliser [Handbook 1992], while more recent publications suggest it has a slight tendency to stabilise β phase [Liu 2005, Yin 2007, Okamoto 2010]. In most cases Sn is classified as neutral element [Luetjering 2007].

The strengthening effect of Sn in Ti alloys were reported for binary Ti-Sn alloys to only show benefits in bending strength until 0.5at.% (1.3wt%), while further addition to 16at.% (32wt%) did Arnas Fitzner, PhD Thesis, 2014

not improve the strength [Hsu 2009]. This is somewhat surprising as experimental phase diagrams and calculations using first principles, DFT or CALPHAD suggest the potential of increasing solid solution strengthening to 9at.% (20wt%) before Ti₃Sn precipitates with a DO₁₉ structure [Liu 2005, Yin 2007, Colinet 2009, Okamotto 2010, Wang 2011]. Coinciding with the solubility limit, Hsu et al. reported embrittlement even though no signs of Ti₃Sn were noticeable in their X-ray diffraction patterns at 31wt% Sn (16at.%) [Hsu 2009]. This might be due to a lack of low temperature aging that would promote formation of an ordering phase. The ordered phase Ti₃Sn is known to be brittle and deformation twinning has not been observed in stoichiometric compositions [Jones 1973, Hashimoto 1990] but in under-stoichiometric compositions [Wong 1994]. Further, short-range ordering has not been reported in the binary Ti-Sn system unlike for the binary Ti-Al system [Namboodhiri 1973].

Observations by X-ray diffraction have shown that Sn increases the c/a ratio less than Al would do per wt% [Teer 1977], but more per at.%, which is mainly caused by a *c*-axis extension with eventually reaching a value suitable for Ti₃Sn [Banumathy 2011]. According to Yoo, this decreases the twin shear associated with the $\{10\overline{1}2\}<10\overline{1}1>$ tension twin, which in principle should enhance twin formation although the energy to reshuffle atoms is also likely to play an important role [Yoo 1981]. Basal slip is expected to be more prominent with increasing Sn addition due to the increase in c/a ratio [Rosi 1953] and may affect the atomic shuffle described by Yoo in an unknown manner. It has been suggested that a decrease in stacking fault energy (SFE) also increases the likelihood for basal slip in Ti-Al alloys [Metzbower 1977], which should also be true for binary Ti-Sn alloys. X-ray diffraction analysis suggests slightly increased stacking faulting probability (SFP) per at.% Sn compared to Al, although in this case ternary Ti-Al-Sn alloys were studied [Shishmakov 1972].

The effect of Sn on SFP does not only suggest the possibility of increased basal slip activity but potentially also enhanced twin activity since decreased SFE enables twin formation but slower twin growth in fcc materials [Meyers 2001, Zhang 2009]. However, it remains unclear if this relation is also valid for hcp materials as strictly speaking, SFE is associated with basal planes while twinning grains usually display slip activity on the prismatic plane as demonstrated in chapter 7. In the case of AI additions to binary Ti-alloys a decreasing twin activity was found with solute content [Biswas 1973, Williams 2002]. However, more recent studies of binary Ti-alloys have noted that AI contents of up to 7at.% result in a minor increase in twin activity [Fitzner 2013 a&b], while further additions and aging treatments result in short range ordering and a dramatic loss of twin activity (see chapter 6). In order to evaluate the importance of SFE on twin activity, it is important to study a system that has less a tendency to ordering than the Ti-AI system.

In the present study, binary Ti-Sn alloys were produced with up to of 3.5at.% (8.2wt%) Sn. Great care was taken to generate alloys with comparable grain size and textures in comparison to detailed deformation studies on binary Ti-Al alloys in chapter 6. The microstructure of the Arnas Fitzner, PhD Thesis, 2014

binary Ti-Sn alloys was first characterised by SEM/EBSD, TEM and neutron diffraction to determine starting texture, grain size, lattice spacing and the state of ordering. Subsequently, insitu neutron diffraction compression experiments were carried out to quantify twin activity and measure the residual elastic strains in the parent grains, which were complemented by detailed post-mortem EBSD analysis for identification and quantification of deformation twinning.

9.2. Materials and Methods

9.2.1. Material preparation

For the purpose of this research 200g ingots with contents of 1at.% and 3.4at.% Sn, 2.4 and 8.1wt% Sn respectively, were double melted in a tungsten arc furnace under argon atmosphere at the TIMET research facility in Witton, UK. As a baseline, an ingot of high purity Ti was produced in the same manner as already used in chapter 6 for the comparison of binary Ti-Al alloys but named Ti-0Sn in the following. The alloys are named according to their atomic Sn concentration. All ingots were subsequently forged at 1100°C, in the β -phase field, and crossrolled high in the α -phase field. The cross rolling was carried out on a "2 high Robertson mill" (WHA Robertson & Co Ltd) at 750°C for Ti-0Sn and at 820°C for the binary Ti-Sn allovs. The cross-rolling resulted in an axis-symmetric bar of 14× 14× 260mm³ with the transverse and normal direction being equivalent and here labelled as ND₁ and ND₁₁. Ti-0Sn was recrystallised (RX) at 750°C, 130°C below the β transus temperature, in a tube furnace under Argon shield for 5 hours followed by air-cooling, while recrystallisation treatments for the Sn containing bars were carried out just below the β -transus at 860°C followed again by air cooling. The β -transus temperatures were determined using Thermocalc. Annealing times for the Ti-1Sn and Ti-3Sn were increased to 8hrs and 25hrs respectively to achieve a similar mean grain size in all alloys, as summarised in Tab. 9-1.

Alloy	Т	t	GS	
	°C	h	μm	
Ti-0Sn	750	5	95	
Ti-1Sn	860	8	96	
Ti-3Sn	860	25	71	

Tab. 9-1: Recrystallisation treatments of binary 1	Ti-Sn model alloys in this stud	У
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Chemical analyses were performed by TIMET - Savoie, France, on halved compression samples using inductively coupled plasma mass spectrometry on a HORIBA Ultima2 for metallic elements, on a HORIBA EIMA 820V for C and on a LECO EF-400 for O and N. Tab. 9-2 shows that C and N contents were kept below 60ppm while oxygen is below 600 ppm for Ti-0Sn and Ti-3Sn but above 1200 ppm for Ti-1Sn.

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9.2.2. Microstructure analysis

Cross sections were prepared from the mid-section of non-deformed and deformed samples with the plane normal parallel to the former rolling direction (RD) followed by mechanical grinding down to P4000 paper and polishing with oxide particle suspension (OPS) on a semiautomatic polishing apparatus with 5N pressure and intermediate etching with Kroll's reagent for 10s until a crisp optical micrographs could be recorded using a differential interference filter (DIC), as shown in Fig. 9-1 a). The presented textures were measured on areas bigger than 4×4 mm² with 40µm stepsize using a CamScan Maxim 2500FEG SEM equipped with NordLYS detector and Flamenco acquisition software. The CamScan was operated at 20 kV using an aperture of 100µm and a spot size of 6.25 resulting in 6.8nA probe current. Detailed orientation maps were also recorded on a FEI Sirion FEG SEM using Flamenco acquisition software. 100µm aperture and spot size 4, resulting in 5.06nA probe current and on a FEI Quanta 650 with a similar setup but using AZTEC acquisition software. Both microscopes are equipped with a NordLYS detector. Orientation maps were recorded using a step size of 1µm and scans covered typically more than 2mm². Data were cleaned and analysed using the HKL software package. Twin boundary criteria, as given by Bozzolo et al. [Bozzolo 2010], were used to identify twins and quantify manually relative area fractions for each system.

Thin foils for transmission electron microscopy (TEM) were ground with P1200 paper to about 100µm thickness and perforated by electro polishing (6% perchloric acid (60%) and 94% methanol) at -30°C at 15V using a Tenupol 5 with an attached cooling unit. Selected area diffraction patterns were recorded on a FEI Tecnai G20 with a LaB₆ filament at 200 kV, equipped with Ditabis image plates. Furthermore, long wavelength powder diffraction type measurements were carried out at the time-of-flight beamline WISH, based at the neutron spallation source ISIS, UK, to assess the state of ordering. For this measurement, two cylindrical bulk samples of 8mm diameter and 12mm length were loaded in one of two Vanadium cans of 0.3mm wall thickness and mounted on an Al candlestick. Boron nitride shielding was used to avoid scattering from the Al holder. The sample was aligned in the centre of the beam gauge volume (20x80mm) and measurements were taken below pressures of 0.05 bar up to 40µA. Background subtracted spectra from bank 3, which provided the highest flux in the d-spacing range of interest, were smoothed with moving average over 20 points.

9.2.3.Mechanical testing

Cylindrical compression samples of 6mm diameter and 9mm length were machined for ex-situ compression analysis while cylindrical samples of 8mm diameter and 12mm length were more appropriate for in-situ loading using neutron diffraction. Standard compression tests were conducted on an Instron 5569 at room temperature and an initial strain rate of 10⁻³ 1/s with the loading direction (LD) being parallel to the original rolling direction (RD). The use of Lubriplate grease minimized barrelling of the sample and helps to maintain a uniaxial stress state during Arnas Fitzner, PhD Thesis, 2014

deformation. Samples for microstructural and texture observation were monotonically strained parallel to the RD up to strain of to ~0.02, 0.04 and 0.09.

9.2.4.In-situ loading using neutron diffraction

In-situ compression experiments using neutron diffraction were carried out on beam line Engin-X, ISIS, UK using equal procedures as presented in chapter 6. The axial detector covers approximately $\pm 10^{\circ}$ to LD and the transverse detector covers a similar range, as shown in Fig. 9-4 of chapter 6 or Fig. 9-1 in [Malamud 2014]. The samples were incrementally loaded and diffraction patterns were obtained at several increments until 75% of the yield stress was reached according to the ex-situ compression tests. These data were used for the determination of the diffraction elastic constants. Beyond 75% of the yield stress, the measurements were carried out in the unloaded condition, i.e. after some plastic deformation, to avoid significant cold creep during neutron diffraction measurements. A further 14 measurements were carried out up to a plastic strain of 0.09. A current of 30 µA was collected for each data point to ensure a good signal-noise ratio, which took 24 minutes under optimal beam conditions. Single peaks were fitted using the in-house ISIS software Open Genie to calculate the lattice strain evolution as described by Warwick et al. [Warwick-b 2012]. The initial lattice spacing of each alloy was determined by Rietveld analysis of the spectra. The *a*- and *c*-parameter as well as the c/a ratio are listed in Tab. 9-2.

9.3. Results

9.3.1.Starting Material

Tab. 9-2 shows no significant change in the *a* lattice parameter with increasing Sn content while the *c* lattice parameter increases with Sn concentration. The corresponding c/a ratio increases and agrees with previously reported values [Teer 1977, Leyens 2003]. The current data show a non-linear relationship between Sn concentration and *c*-parameter or c/a ratio.

Alloy	Sn	Sn	С	Ν	0	Ti	<a>	<c></c>	c/a
	wt%	at.%	ppm	ppm	ppm		nm	nm	
Ti-0Sn	0.00	0.0	55	13	507	bal.	2.949	4.681	1.587
Ti-1Sn	2.41	0.99	38	56	1227	bal.	2.949	4.679	1.590
Ti-3Sn	8.08	3.42	42	25	589	bal.	2.949	4.700	1.594

Tab. 9-2: Chemical composition of the model alloys in this study (by TIMET Savoie) and lattice parameters from neutron diffraction at EnginX, ISIS. Other impuriteis are below 60ppm (wt%).

Fig. 9-1 a) shows differential interference contrast (DIC) optical micrographs of the starting microstructures for the three alloys. The micrographs suggest a fairly uni-modal grain size (GS) distribution for all alloys but a slightly smaller grain size of Ti-3Sn compared to the other two alloys. The average grain size for each alloy is presented in Tab. 9-1. Fig. 9-1 b) shows 0002 Arnas Fitzner, PhD Thesis, 2014

and $10\overline{10}$ pole figures for the three compositions recorded by EBSD macro texture scans. The basal pole is preferentially distributed fairly homogenously perpendicular to RD in all alloys although the strength of this clock texture strengthens noticeably with increasing Sn content. It has to be noted that the texture map of the pole figures of Ti-3Sn was of poor quality and may have caused artefacts. The $10\overline{10}$ pole figures show a slight fibre texture along RD. The ratio of $10\overline{10}$ pole intensity to $11\overline{20}$ pole intensity in the axial detector of Engin-X describes the strength of the fibre. The ratio decreases linearly from 0.57 in Ti-0Sn to 0.42 in Ti-1Sn and only 0.35 in Ti-3Sn and indicates a stronger $11\overline{20}$ fibre with Sn addition.



Fig. 9-1: a) Optical micrographs using DIC filter and b) textures of the starting material.

The diffraction patterns recorded on the long-wavelength WISH beamline is presented in Fig. 9-2. The focus here was on the large d-spacing range in order to identify any possible indications of ordering. Both Sn containing alloys show similar levels of incoherent scattering, which is significantly above the level of Ti-0Sn. No patterns show any evidence of a superlattice reflection at around 3Å that would correspond to Ti_3Sn or a diffuse scattering hump that might be interpreted as an indication of short range ordering. The absence of any superlattice reflection was also confirmed by selected area electron diffraction pattern analyses imaging along the [1010] zone axis.



Fig. 9-2: WISH spectra from ISIS, showing only the root of the major hcp-alpha peaks and increased diffuse background when Sn is added without significant difference between both Sn alloys apart from peak positions

9.3.2.Flow curves

The flow curves for uniaxial compression along the former RD are presented in Fig. 9-3 a). The 0.2% yield strength increases dramatically with the addition of 1at.% Sn but only slightly with a further addition of 2.4at.% Sn. This apparent non-linear solid solution strengthening behaviour of Sn might be caused by the comparably high O content measured in Ti-1Sn.

The work hardening rate θ as function of compressive strain is shown in Fig. 9-3 b), which shows a substantial increase of the hardening rate for Ti-3Sn while Ti-1Sn shows only a slight increase of θ compared to the Sn free alloy.



Fig. 9-3: a) True stress-strain curves under quasi-static compression in RD for binary Ti-Sn alloys in solution treatment and after ageing. b) Work hardening rate θ as function of the true strain (data averaged and smoothed).

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9.3.3.Diffraction analysis from in-situ experiment

A particular focus was placed on the evolution of the integrated intensity of the 0002 reflection measured in the loading direction during the in-situ compression experiment on Engin-X as the common $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning mode results in the <c> axis rotating into the loading direction, hence increasing the basal pole intensity [Phillipe 1988]. The change of the integrated intensity of the 0002 peak is given in Fig. 9-4 a) as a function of true strain providing an indication of twin activity during compression. All three alloys show very similar linear intensity evolutions below 0.04 true strain. The true strain at which the first intensity increase of the basal reflection can be noted is at about 0.01 for all alloys. Beyond 0.04 true strain the twin activity increases most notably for Ti-0Sn while the Sn containing alloys continue to show a more linear behaviour.

Fig. 9-4 b) displays the evolution of the residual 0002 lattice strain recorded in the transverse direction, i.e. for a grain family that is likely to twin. It should be kept in mind that most of the grains in the present starting texture are favourably orientated for $\{10\overline{1}2\}<10\overline{1}1>$ twinning, but the recorded 0002 diffraction peak along the transverse direction only origins from a fraction of those gains. The residual lattice strain increases in the tensile regime up to the point where twinning starts, which is indicated by grey glowing data points in Fig. 9-4 b) and can be inferred from the initial intensity increase in Fig. 9-4 a). The maximum residual lattice strain associated with the onset of twinning decreases with Sn addition. After the onset of deformation twinning the residual lattice strain decreases steadily with increasing twin fraction.



Fig. 9-4: a) Axial intensity evolution of {0002}-plane $\Delta I_{(0002)}$ related to 85° tensile twinning as function of true strain derived from neutron diffraction at EnginX and b) evolution of transverse lattice strain on {0002}-plane $\mu \epsilon_{(0002)}$ as function of true strain for recrystallised material. The onset point of twinning is marked in grey.

9.3.4. Deformation microstructures and textures

EBSD orientation maps recorded after different stages of plastic deformation during uniaxial compression testing can be used to follow the development of all twin types. Fig. 9-5 a) and b) show band contrast maps after 0.04 and 0.09 true strain, respectively, with twin boundaries colored in red for the $\{10\overline{1}2\}<10\overline{1}1>$ tension twin, in green for the $\{11\overline{2}1\}<\overline{11}26>$ tension twin and in aqua for $\{11\overline{2}2\}<\overline{11}23>$ compression twins. The measurements reveal that volumes of $\{10\overline{1}2\}<10\overline{1}1>$ tension twins are dominant in all three alloys, which demonstrates that the evolution of the 0002 integrated intensity measured in the loading direction (Fig. 9-4 a) does indeed represent well the twin evolution in the material. Compression $\{11\overline{2}2\}<\overline{11}23>$ twins in Ti-0Sn grow to similar sizes to $\{10\overline{1}2\}<10\overline{1}1>$ tension twins but are far less frequent. Such wide compression twins are not evident in the Sn containing alloys; instead $\{11\overline{2}1\}<\overline{11}26>$ tension Arnas Fitzner, PhD Thesis, 2014

twins become more frequent. A closer analysis of Fig. 9-5 b) reveals that the $\{10\overline{1}2\}<10\overline{1}1>$ tension twins in Ti-3Sn are narrower and do not coalesce as readily observed in Ti-1Sn or Ti-0Sn, but occur as many parallel lamella.



Fig. 9-5: Deformation microstructures. Bandcontrast maps after a) compression to strains of 0.04 and b) to 0.09 with highlighting twin types by different boundary colours as Red= $\{10\overline{1}2\}<10\overline{1}1>$, Green= $\{11\overline{2}1\}<\overline{11}26>$, Aqua= $\{11\overline{2}2\}<\overline{11}23>$. c) Textures after compression to a strain of 0.09 parallel to RD.

While the overall twin area fraction barely changes between Ti-1Sn and Ti-3Sn, the grains are more refined by the twin lamellas in Ti-3Sn. At this strain level the frequency of $\{11\overline{2}1\}<\overline{11}26>$ tension twinning clearly increases with Sn addition from less than 0.5% in Ti-0Sn up to about 4% in Ti-3Sn. The decrease in the $\{10\overline{1}2\}<10\overline{1}1>$ twin area fraction after 0.09 true strain can also be seen from the basal pole figures presented in Fig. 9-5 c). The basal pole along the loading direction is clearly strongest for the Sn free alloy, which again reflects the rotation of the <<c> axis into the loading direction as a result of $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning.

9.4. Discussion

Within the limited range of binary Ti-Sn alloys studied here, Sn shows a significant impact on the flow stress behaviour, almost doubling the 0.2% proof stress by relatively small additions of Sn, while further Sn barely increases the proof stress and the twin area fraction, as a function of Arnas Fitzner, PhD Thesis, 2014

plastic deformation, is not greatly affected by the Sn content. It can also be noted that Sn does increase the ability of the alloy to work harden. It should be kept in mind that about twice as much O is cointained in Ti-1Sn compared to the other two alloys, which partially explains the relatively small effect towards the highest Sn content. A further important observation is that, in contrast to the Ti-Al system, no indications of short or long range ordering (Ti₃Sn) were identified in the present study at similar increasing c/a ratio. Some of the experimental observations are summarised in Fig. 9-6.

The central interest in the present study is the role of Sn on twin activity. The results in Fig. 9-4 a), 9-5 and 9-6 b) and d) demonstrate that it is difficult to determine if Sn enhances or reduces $\{10\overline{1}2\}<10\overline{1}1>$ twin activity. While there are slight twin activity variations with Sn content regarding the minor twin modes, in example $\{11\overline{2}1\}<\overline{11}26>$ tension twinning and $\{11\overline{2}2\}<\overline{11}23>$ compression twinning, the overall activity of the dominant $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning mode seems to be hardly affected by the Sn content. The increased O content in Ti-1Sn, likely to reduce twin activity, may explain the slighly reduced twin activy compared to Ti-0Sn. However, Fig. 9-5 b) suggests that, while the overall $\{10\overline{1}2\}<10\overline{1}1>$ twin fraction does not increase, the twins become significantly thinner with increasing Sn content, especially at the higher Sn content. Therefore, Sn seems to facilitate twin nucleation but to impede twin growth. This observation is supported by Fig. 9-3 b) showing stronger work hardening with rising Sn content. Wu et al. showed that tension twinning results in very significant work hardening in Ti [Wu 2008]. The rotation of the <c> axis in the loading direction leads to texture hardening and grain refinement by twin formation gives rise to additional hardening. The latter factor seems to be enhanced by the addition of Sn. Further support for a facilitated twin growth is the decreased residual lattice strain along the c-axis for twin nucleation, summarised in Fig. 9-6 e). However, after extrapolation to lattice strain values at full stress Ti-1Sn exhibits higher values than Ti-0Sn, as shown in Fig. 9-6 f) but further Sn addition decreases the value despite almost identical stress levels at which twinning occurs.

The EBSD maps show an increase in area fraction of $\{11\overline{2}1\}<\overline{11}26>$ tension twins with Sn addition from less than 0.5% in Ti-0Sn to over 4% in Ti-3Sn, indicated by diamonds in Fig. 9-6 c). Samples of high Sn content develop wide $\{11\overline{2}1\}<\overline{11}26>$ tensions twins and multiple parallel twin lamellae occur frequently. At the same time, an increase in Sn reduces the likelihood $\{11\overline{2}2\}<\overline{11}23>$ compression twinning.

The latter two observations agree with the shear argument proposed by Yoo [Yoo 1981], since Sn increases the c/a ratio, the twin shear for $\{11\overline{2}1\}<\overline{11}26>$ twinning is reduced and the twin shear for $\{11\overline{2}2\}<\overline{11}23>$ twinning is increased. But despite decreasing twin shear for the $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning system the overall fraction barely changes as a function of Sn content. The changing occurrence of twin morphology with increasing Sn content can be explained with argumentations of the decreasing SFE.

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According to ab-initio simulations by Wang and co workers, the nucleation of a $\{10\overline{1}2\}<10\overline{1}1>$ tensile twin in Mg must involve simultaneous formation of the zonal dislocation with a partial and a set of twinning dislocations [Wang-b 2009]. Dislocation dissociation can in principal occur easier at lower SFE and hence form a wider twin nucleus easier, as shown experimentally on hcp Zr–Sn alloys by Sastry et al. [Sastry 1974]. Consequently, a reduced SFE should facilitate the formation of the initial stacking fault and the glide of twinning dislocations to form the critical size of the twin. Similar relations were reported for Cu-Al alloys with fcc structure [Zhang 2009] and in principle a decreasing SFE should make twin nucleation in Ti more probable as well. Zhang et al. further proposed that twin growth is impeded due to more difficult cross-slip in Cu-Al alloys. Metzbower connected a decreasing SFE in binary Ti-Al alloys to a reduced propensity for cross-slip in the absence of ordering [Metzbower 1971], which may explain the observed change towards thinner twins at higher Sn contents.



Fig. 9-6: Summary of results as function of Sn concentration a) 0.2% proof strength $\sigma_{0.2}$; b) Fractions of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ -twin TT₁; c) Fractions of $\{11\overline{2}1\}\langle\overline{11}26\rangle$ -twin TT₂ and $\{10\overline{1}1\}\langle10\overline{1}2\rangle$ -twin CT; d) Twin activity $\delta\Delta I/\delta\epsilon$, as the rate at which the axial {0002}-intensity changes with true plastic strain ϵ for plastic strains below 0.4 and above for Ti-0Sn only; e) Residual microstrain on <c> axis $\epsilon\mu_{nuc\{0002\}}$ at the onset of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ -twinning from favourably orientated grain family; f) Extrapolated microstrain on <c> axis $\epsilon\mu_{nuc\{0002\}}$ at the onset of $\{10\overline{1}2\}\langle10\overline{1}1\rangle$ -twinning from favourably orientated grain family.

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Another important aspect of twinning is the ability of the neighbouring grains to accommodate the generated twin shear. Chapter 7 demonstrated that prismatic slip accommodates the twinning shear of $\{10\overline{1}2\}<10\overline{1}1>$ tensile twins and basal slip the twin shear of $\{11\overline{2}1\}<\overline{11}26>$ tension twins. This emphasises the importance of relative strengthening of the different slip systems. The increasing c/a ratio favours basal slip from a theoretical viewpoint. According to arguments of Metzbower also the decreasing SFE affects basal slip more than prismatic slip. Even though direct measurements on the slip activity in the Sn containing Ti alloys were unsuccessful (and therefore not presented), the much wider $\{11\overline{2}1\}<\overline{11}26>$ tension twins in Ti-3Sn suggest increased basal slip activity experimentally. In turn, one may interpret the thinner $\{10\overline{1}2\}<10\overline{1}1>$ tensile twins in Ti-3Sn as a consequence of more difficult prismatic slip relative to basal slip.

9.5. Conclusion

Binary Ti-Sn alloys containing 0, 1 and 3.4 at.% Sn were produced with comparable grain size distribution and basal texture. Compression tests along the original RD showed dramatic increase in compressive yield strength with 1at.% Sn but only shallow increase with further Sn addition. Sn was shown to increase the work hardening rate even though the overall $\{10\overline{1}2\}<10\overline{1}1>$ twin fraction barely changed. Combination of in-situ compression using neutron diffraction and post mortem EBSD analysis showed that Sn facilitates the onset of $\{10\overline{1}2\}<10\overline{1}1>$ twinning but hinders the growth, leading to increased grain refinement during compression at higher Sn content. The grain refinement is thought to increases the work hardening rate. An increasing fraction of $\{11\overline{2}1\}<\overline{11}26>$ twin but suppression of the $\{11\overline{2}2\}<\overline{11}23>$ was also observed with increasing Sn content by EBSD micro mapping.

While an increasing c/a ratio with Sn can explain the formation and growth behaviour of $\{11\overline{2}1\}<\overline{11}26>$ and $\{11\overline{2}2\}<\overline{11}23>$ twins, it only holds for the nucleation of $\{10\overline{1}2\}<10\overline{1}1>$ twins. Further research is required to determine if the SFE reduction with Sn is the dominant factor concerning $\{10\overline{1}2\}<10\overline{1}1>$ twin nucleation and growth or a possible change in slip character.

10. The effect of Zirconium and grain size on deformation by twinning in α titanium

Abstract

The twin activity of binary Ti-Zr model alloys (0-10at.% Zr) in recrystallized condition was investigated in respect to nucleation and growth of deformation twins using in-situ loading in combination with neutron diffraction as well as detailed post mortem EBSD analysis. The binary Ti-Zr system allows evaluating the influence of stacking fault probability or energy on twin activity in pure Ti at almost constant c/a ratio and without superimposed effects of ordering phenomena. Almost identical starting microstructures and textures were generated for alloys of 0 and 3.6at.% Zr, at a grain size level of approximately 80µm. Comparisons to higher Zr contents are made between 3.6 and 10at.% Zr on a grain size level of 25µm, allowing additionally to investigate the influence of the grain size on twinning.

It was found that raising the Zr content increases the 0.2% proof stress linearly and causes a significant load drop after the yield point, becoming more pronounced with Zr addition and bigger grain size. This was connected to an earlier and facilitated onset of $\{10\overline{1}2\}<10\overline{1}1>$ twinning, revealed by analysis of the residual intergranular strains of the twinning grain family using in-situ neutron diffraction. The increased work hardening rate with Zr addition or grain size reduction at moderate plastic strains between 0.04 and 0.09 is rationalised by enhanced grain refinement induced by more, but smaller $\{10\overline{1}2\}<10\overline{1}1>$ twins at overall similar twin fractions. Facilitated nucleation and impeded growth of $\{10\overline{1}2\}<10\overline{1}1>$ twins may be related to the decreasing stacking fault energy (SFE) with Zr addition. However, the likelihood and appearance of $\{11\overline{2}1\}<\overline{11}26>$ tension twins is barely changed by Zr addition or the grain size. Considering the starting texture $\{11\overline{2}2\}<\overline{11}23>$ compression twin activity is similar at the observed grain sizes and solute contents, just as the c/a ratio.

10.1. Introduction

It is of fundamental interest to explore the effect of alloying on deformation twinning in alloys with an hcp structure by evaluating parameters like the c/a ratio, ordering or the stacking fault energy (SFE). Alloying always changes more than one of those parameters and makes it inherently difficult to investigate systematically the effect of one parameter on twin formation and growth. While it is recognised that addition of more than 10at.% (6wt%) Al to Ti supresses the activity of twinning during deformation [Williams 2002, Fitzner 2013 a&b], which seems to be closely related to the formation of short and long range ordering as described in chapter 6, the role of other typical alloying elements in Ti alloys on twin formation is far less known.

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Zirconium (Zr) is an alloying element used for example in common aeroengine alloys such as Ti-6242 and Ti-6246 as it strengthens α -Ti significantly and yet allows excellent cold workability [Dochachi 2000]. Binary Ti-10wt%Zr (5.5at.%) even exhibits improved ductility and strength over CP-Ti after more than 70% cold work [Nakasuji 1996]. Furthermore Zr addition improves grindability, polishing properties and elastic recovery and Zr addition maintains the biocompatibility of Ti [Donachi 2000, Kobayashi 1995&1998, Nakasuji 1996, Ho 2008] making it a universal alloying element for intermediate-strength Ti products.

Zr is fully soluble in Ti in both, α and β phase [Handbook 1992, Hari Kumar 1994]. Even though Zr is classified as neutral element regarding phase stability [Luetjering 2007], it stabilises slightly the β phase in the binary Ti-Zr system although the exact temperature of the β transus varies between different phase diagrams and estimations from Thermocalc [Handbook 1992, Hari Kumar 1994]. Sen et al. have shown from X-ray diffraction Fourier analysis that Zr increases both *c* and *a*-lattice parameter, without significant effect on the c/a ratio and notice a particularly high faulting probability compared against complex Al rich Ti-alloys, like Ti-6Al-4V [Sen 1998]. Consequently, binary Ti-Zr alloys can be used to evaluate the effect of stacking fault probability (SFP), or the inversely related SFE [Metzbower 1971], on twin activity of Ti without significant influence of the c/a ratio or ordering.

Experiments on alloying systems with a fcc crystal structure related decreasing SFE to twin nucleation but reduced twin growth [Zhang 2009]. However, such clear trends have not been observed in metals with an hcp crystal structure such as Ti and Zr alloys. In fact, increasing levels of N, C, O and Fe or the substitutional AI in Ti suppress twinning despite an increase in SFP [Biswas 1973, Williams 2002, Fitzner 2013-a].

In the present study, binary Ti-Zr alloys were produced with 3.6at.% (6.5wt%) and 10at.% (17.5wt%) Zr. In the case of Ti-3Zr it was possible to produce a grain size and texture that makes the material comparable to the binary Ti-AI and Ti-Sn alloys of chapter 6 to 9. The addition of 10at.% Zr to Ti only allowed growing grains to a mean diameter of 20µm. Therefore, Ti-3Zr was also produced with such small grain size allowing a comparison of the two binary alloys.

The material was characterised by optical and electron microscopy (SEM, TEM) as well as neutron diffraction to determine starting texture, grain size, lattice spacing and the state of ordering. In-situ compression experiments using neutron diffraction were carried out to quantify the twin activity and measure the elastic lattice strains in grains orientated favourably for twinning, which where subsequently complemented by detailed post-mortem EBSD analysis for identification and quantification of deformation twinning.

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10.2. Materials and Methods

10.2.1. Material preparation

For the purpose of this research, batches of 200g, with contents of 0, 3.6at.% and 10at.% Ziconium, were double melted from high purity Ti sponge and Zr swarf in a tungsten arc furnace under argon atmosphere at the TIMET research facility in Witton, UK. The alloys are named according to their atomic percentage of solute. The subsequent thermo-mechanical processing included β forging at 1100°C and cross-rolling on a "2 high Robertson mill" (WHA Robertson & Co Ltd) at 750°C. The rolling resulted in a square bar $(14 \times 14 \times 260 \text{ mm})$ with the transverse and normal direction being equivalent and here labelled as ND_I and ND_I. Finally, equiaxed grains were formed during recrystallisation treatment in the α phase. Ti-0Zr was recrystallised (RX) at 750°C for 5 hours in a tube furnace under argon shield followed by air-cooling, as accomplished in chapter 6. The RX temperatures for Zr containing alloys were chosen about 15°C below the β -transus temperatures, determined using Thermocalc. A RX treatment on Ti-3Zr at 824°C for 25hrs yielded a similar mean grain size to Ti-0Zr, but annealing trials to achieve a comparable grain size at higher Zr content were not successful [Ji 2013]. The maximum grain size was only 20µm after annealing for 25hrs at 750°C, labelled as Ti-10Zr SG (small grain). A shorter heat treatment of 5hrs at 824°C was introduced for Ti-3Zr in order to match the grain size of Ti-10Zr SG, labelled as Ti-3Zr SG. All alloys, heat treatments and the corresponding grain sizes are summarised in Tab. 10-1.

Alloy	T	t	GS
	°C	h	μm
Ti-0Zr	750	5	93
Ti-3Zr	824	25	65
Ti-3Zr SG	824	5	33
Ti-10Zr SG	750	25	20

Tab. 10-1: Heat treatments of the model alloys in this study

Chemical analyses were performed on halved compression samples by TIMET, Savoie, France, using inductively coupled plasma mass spectrometry on a HORIBA Ultima2 for metallic elements, on a HORIBA EIMA 820V for C and on a LECO EF-400 for O and N. All three alloys showed C, N concentrations below 90ppm while O contents varied between 900 ppm and 1800 ppm, as listed in Tab. 10-2.

10.2.2. Microstructure analysis

Samples for microstructural observations were prepared from the middle sections of recrystallised and deformed material. Cross sections with the plane normal parallel $(\pm 2^{\circ})$ to the former rolling direction (RD) were cut using abrasive Al₂O wheels and subsequently prepared

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by mechanical grinding to P4000 paper. The finely ground surfaces were etched with Kroll's reagent for 10s and afterwards polished with oxide particle suspension (OPS) on a semi-automatic polishing apparatus with 5N pressure for 1h. Optical micrographs were recorded after three times etching and OPS-polishing using a differential interference filter (DIC), as shown in Fig. 10-1. The presented textures were measured on those surfaces covering areas bigger than $4 \times 4mm^2$ with 40µm step size on a CamScan Maxim 2500 FEG SEM with NordLYS detector. The CamScan was operated at 20 kV using an aperture of 100µm and a spot size of 6.25 resulting in 6.8nA probe current. Detailed orientation maps were recorded on a FEI Sirion FEG SEM using 100µm aperture and spot size 4, resulting in 5.06nA probe current and on a FEI Quanta 650 FEG SEM with a similar setup. Both microscopes are equipped with a NordLYS detector but the former with acquisition software Flamenco and the latter with ACTEC. Typically, more than $1mm^2$ was scanned using a step size of 1µm. The data were cleaned and analysed using the HKL software package. Twin boundary criteria, as given by Bozzolo et al. [Bozzolo 2010], were used to identify twins and quantify relative area fractions for each system.

Thin foils for transmission electron microscopy (TEM) were produced by first grinding samples with P1200 paper to about 100 μ m thickness followed by electro polishing (6% perchloric acid (60%) and 94% methanol) at -30°C at 15V using a Tenupol 5. The foils were investigated by selected area diffraction on a FEI Tecnai G20 with a LaB₆ filament at 200 kV, equipped with Ditabis image plates.

Furthermore, long wavelength powder diffraction type measurements were carried out to assess the state of ordering at the time-of-flight beamline WISH, ISIS. Two cylindrical bulk samples of 8mm diameter and 12mm length were loaded in one of two vanadium cans of 0.3mm wall thickness and mounted on an AI candlestick. Boron nitride shielding was used to avoid scattering from the AI holder. The sample was aligned in the centre of the beam gauge volume (20x80mm) and measurements taken below pressures of 0.05 bar for more than 30μ A. Background subtracted spectra from bank 3, which provided the highest flux at 90° from the incident beam, were smoothed with moving average over 20 points.

10.2.3. Mechanical testing

Cylindrical compression samples of 6mm diameter and 9mm length were machined for ex-situ compression testing. In-situ loading using neutron diffraction was performed using cylindrical samples with the same ratio of height to diameter of 1.5, but with diameters of 8mm to achieve faster counting rates on bigger sampled volumes. Due to material shortage Ti-3Zr SG was only available with 6mm diameter and 9mm length. Standard compression tests were conducted on an Instron 5569 at room temperature and an initial strain rate of 10^{-3} 1/s with the loading direction (LD) parallel to the original RD. The use of Lubriplate grease minimized barrelling of the sample and ensured a uniaxial stress state during deformation. Samples for metallography were strained monotonically to $\varepsilon_{pl} = 0.02$, 0.04 and 0.09 parallel to RD.

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10.2.4. In-situ loading using neutron diffraction

In-situ compression experiments using neutron diffraction were carried out at beam line Engin-X, ISIS, UK, using the same procedures as described in chapter 6. The samples were loaded in increments up to 75% of the expected yield stress, according to the ex-situ compression tests, to determine diffraction elastic constants (DEC_{hkl}). Beyond 75% of the yield stress, the measurements were carried out in the unloaded condition, i.e. after some plastic deformation, to avoid significant cold creep during neutron diffraction measurements. A current of 30 μ A was collected for data points in Ti-0Zr and of 25 μ A for the Ti-Zr binary alloys to ensure a good signal-noise ratio. Single peaks were fitted using the in-house ISIS software Open Genie to calculate the residual lattice strains $\varepsilon_{hkl-residual}$ as described by Warwick et al. [Warwick-b 2012]. Equation 10-1 describes the relation between DEC_{hkl} and the stress difference between measurement and maxumum stress $\Delta\sigma$, allowing extrapolation of $\varepsilon_{hkl-residual}$ to lattice strain values at stress $\varepsilon_{hkl-\sigma}$.

$$\varepsilon_{hkl-\sigma} = \frac{\Delta\sigma}{DEC_{hkl}} + \varepsilon_{hkl-residual}$$
 equation 10-1

The initial *a* and *c* lattice parameter of each alloy were determined by Rietveld analysis of the spectra and are listed in Ta. 10-2.

The experimentally measured and fitted integrated intensity of a diffraction peak I_E depends not only dramatically on the texture, but on sample size. The diffraction peaks of a smaller sample have a by the gauge volume ratio reduced intensity, but an increased intensity due to missing absorption. Measurements of the integrated intensity in axial direction of the 0002 peak I_E on Ti-3Zr SG were corrected to I_C according to the averaged intensity ratio of the neighbouring peaks in both materials in axial direction, as described by equation 10-2 with I_{Ti-3Zr} 1010_{axial} as integrated intensity of the 1010 peak of Ti-3Zr, I_{Ti-3Zr} SG1010_{axial} as integrated intensity of the 1010 peak of Ti-3Zr SG, I_{Ti-3Zr}1011_{axial} as integrated intensity of the 1011 peak of Ti-3Zr and I_{Ti-3Zr} SG1011_{axial} as integrated intensity of the 1011 peak of Ti-3Zr SG. This simple correction can be used due to the very similar starting texture of Ti-3Zr and Ti-3Zr SG, seen on almost identical ratios of intensity of the 1010 and 1011 peak in both materials of 0.44 and 0.47, respectively. By choosing peaks either side of the peak of interest (0002 in axial direction), the dependence of absorption on the wavelength can be neglected.

$$I_{C} = [(I_{Ti-3Zr}10\overline{1}0/I_{Ti-3Zr}_{SG}10\overline{1}0) + (I_{Ti-3Zr}10\overline{1}1/I_{Ti-3Zr}_{SG}10\overline{1}1)]/2 \quad \text{equation 10-2}$$

The integrated intensity of the 0002 diffraction peak in the axial detector was close to zero and insufficient for the fitting procedure before the onset of twinning and therefore checked visually. If no peak was present values have been set to 0 manually and the fitting results were only used when peaks amendable for fitting were present, indicating twinning being active.

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Alloy	Zr	Zr	С	Ν	0	Ti	<a>	<c></c>	c/a
	wt%	at.%	ppm	ppm	ppm		nm	nm	
Ti-0Zr	0.00	0.0	55	13	507	bal.	2.949	4.681	1.587
Ti-3Zr	6.6	3.58	74	33	636	bal.	2.960	4.699	1.587
Ti-3Zr SG	6.6	3.58	74	33	534	bal.	2.962	4.706	1.585
Ti-10Zr SG	17.5	10.02	70	33	580	bal.	2.981	4.728	1.586

Tab. 10-2: Chemical composition of the model alloys in this study and lattice parameters from neutron diffraction at Engin-X, ISIS. Other impurities are below 90ppm.

10.3. Results

10.3.1. Starting Material

Neutron diffraction results presented in Tab. 10-2 show almost linear increase of the *a* and *c* lattice parameter with Zr content, with almost constant c/a ratio of 1.586±0.001, in agreement with previously reported values [Sen 1998, Lutjering 2007] and Vegards law [Denton 1991]. According to Tab. 10-1, despite various heat treatment trials, Ti-3.6Zr does display a smaller grain size than Ti-0Zr, sitting somewhere between Ti-0Zr and the small grain version of Ti-3.6Zr.



Fig. 10-1: a) Optical DIC micrographs with 5x and 20x magnification for the small grained (SG) materials and b) pole figures of the starting microstructure for each alloy. Arnas Fitzner, PhD Thesis, 2014

Comparing Ti-3Zr SG and Ti-10Zr SG, it is apparent that Ti-10Zr SG has a 50% smaller grain size than Ti-3Zr SG. Representative microstructural images can be found in Fig. 10-1a). Fig. 10-1 b) shows 0002 pole figures from EBSD macro texture scans with varying intensity distribution in the ND-ND plane but very low intensity along the former RD in all alloys. While Ti-0Zr and Ti-3Zr exhibit a $10\overline{10}$ fibre along the former RD, Ti-3Zr SG and Ti-10Zr SG exhibit more an $11\overline{20}$ fibre as evident from the two distinct intensities in the $10\overline{10}$ pole figures.

The diffraction spectra recorded on the neutron powder diffractometer WISH are shown in Fig. 10-2 and exhibit increasing background levels from incoherent scattering with Zr addition, especially from 1.8Å to 2.4Å, which is related to the opposite sign of the coherent scattering length of Zr and Ti. Bragg reflections cancel out when the coherent scattering length approaches 0 at a Zr concentration of approximately 33%at.% [Sidhu 1956, Bellissent-Funel 1995]. Relatively high background levels around 2Å can be inferred from Fig. 10-3 c) in reference [Bellissent-Funel 1995]. Due to a lack of material, Ti-3Zr was only measured on the larger grain size level. A weak peak at 2.9Å is rather unusual to appear in the α structure, but could even be found in the larger sample of pure Ti used in chapter 6. Apart from those artefacts none of the diffraction patterns shows clear evidence of an ordered structure. TEM analysis using selected area electron diffraction patterns with the zone axis along [1010] did not show any indication of ordered structures either. In summary, the alloys form random solid solutions with increasing cell volume and SFP [Sen 1998], but constant c/a ratio.



Fig. 10-2: WISH spectra from ISIS, showing only the root of the major hcp-alpha peaks and increased diffuse background with Zr addition, especially between 1.5-2.5Å.

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10.3.2. Macro and micromechanical behaviour

Fig. 10-3 a) presents flow curves from uniaxial compression tests along the former RD. The 0.2% yield strength increases dramatically with Zr addition but only little with grain size reduction in Ti-3Zr. The flow curves of the Zr containing binary alloys exhibit a stress drop after initial yielding, which is best seen in the work hardening plot in Fig. 10-3 b). This stress drop increases with Zr addition, decreases with grain size reduction and is absent in Ti-0Zr. Fig. 10-3 b) also shows that the work hardening above strains of 0.04 increases significantly with Zr content but decreases with a reduction in grain size to a lesser extend.



Fig. 10-3: a) True stress-strain curves under quasi-static compression in RD for binary Ti-Zr alloys in solution treatment at two grain size levels. b) Work hardening rate θ as function of the true strain (data averaged and smoothed).

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10.3.3. Diffraction peak evolution

As the {1012}<1011> tension twin induces a lattice reorientation of the twinned volume with the c-axis close to LD, following the evolution of the 0002 integrated intensity indicates the {1012}<1011> twin activity [Phillippe 1988, Preuss 2010]. As the starting texture of the different alloys showed slight variations, the change of 0002 integrated intensity is presented in Fig. 10-4 a) as a function of true strain. Linear fits of the intensity change $\delta\Delta I/\delta\epsilon$ until plastic strains of 0.04 show no significant changes with Zr concentration or grain size. The plastic strain ϵ_{nuc} at which the first sign of a basal diffraction peak in the pattern of the axial detector was noted visually indicates the onset strain of {1012} twinning. Careful observation of the data reveals that with decreasing Zr the plastic strain at which twinning nucleates, ϵ_{nuc} , is reduced, while a grain size reduction delays the onset of twinning more noticeably.

In contrast to lowering the starting strains, Zr seems to impede twin activity at strains above 0.04. This state has to be judged carefully and is based on only few data points due to beam loss and time constrictions during the experimentation. The intensity change of Ti-3Zr SG was additionally scaled up by a factor of 1.27, according to Equation 10-2 to correct for the variation in sample dimension. The data do not suggest any significant effect of the grain size on the integrated intensity evolution while the intensity increases slower at higher Zr content. Under the assumption that the majority of twins is captured by the axial detector this suggests that Zr decreases twinning activity at higher strains.



Fig. 10-4: a) Axial intensity evolution of {0002}-plane $\Delta I_{(0002)}$ related to 85° tensile twinning as function of true strain derived from neutron diffraction at Engin-X and b) Evolution of transverse lattice strain on {0002}-plane $\mu \epsilon_{(0002)}$ as function of true strain. The onset point of twinning is marked in grey.

The residual strain evolution associated with the basal plane along the transverse direction, i.e. the grain family favourably orientated for $\{10\overline{1}2\}<10\overline{1}1>$ twinning, is presented in Fig. 10-4 b). It can be seen that significant residual tensile lattice strains build up transverse to the compression direction, which are released when twinning starts as indicated by the grey marker. As the data combine, it can be seen that Zr lowers not only the true plastic strain ε_{nuc} but also the residual lattice strain for twin initiation $\varepsilon \mu_{res\{0002\}}$. The grain size decrease dramatically increases both $\varepsilon \mu_{res\{0002\}}$ and ε_{nuc} , suggesting more difficult twin nucleation.

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10.3.4. Deformation microstructures and textures

EBSD band contrast maps of deformation microstructures are shown at a compressive strain of 0.04 in Fig. 10-5 a) and at a strain of 0.09 in Fig. 10-5 b). The maps highlight twin boundaries of the $\{10\overline{1}2\}<10\overline{1}1>$ tension twins in red, in green for $\{11\overline{2}1\}<\overline{11}26>$ tension twins and in aqua for $\{11\overline{2}2\}<\overline{11}23>$ compression twins. Sections of the maps after the intermediate applied strain are presented in Fig. 10-5 a) and show more twin boundaries in the Zr rich alloys. The increased twin boundary density with Zr becomes more pronounced at higher strain, as seen in Fig. 10-5 b). Here, it can also be seen that a grain size reduction decreases the twin boundary density. Twin fraction analysis on more than two times bigger maps than presented in Fig. 10-5 b) reveal approximately 27% of $\{10\overline{1}2\}<10\overline{1}1>$ tension twins and less than 3% of the other two twin systems together in Ti-0Zr. The dominant $\{10\overline{1}2\}<10\overline{1}1>$ twin originates usually from soft grains with the $\{0002\}$ plane perpendicular to LD. The fraction of this twin mode increases with Zr addition to almost 40% in Ti-3Zr at a strain of 0.09. The measured twin fraction in the small grained Ti-3Zr SG is about 10% below Ti-3Zr with the bigger grain size. The twin fraction increases slightly with further Zr addition in Ti-10Zr SG despite the small grain size.

The {0002} plane within most of the { $10\overline{1}2$ } twins is orientated within 30° to LD, indicated by yellow circles in Fig. 10-5 c), and consequently the intensity around the former RD rises, as seen in comparison of Fig. 10-1 b) and Fig. 10-5 c) and only few twins appear beyond 30° from LD (outside the yellow circle). Analysis of the intensity increase within 30° to LD on pole figures from macro texture scans before and after deformation, as described in detail in [Fazal 2013], confirms the increasing { $10\overline{1}2$ }< $10\overline{1}1$ > twin activity with increased grain size and Zr content as observed during analysis of microscopic orientation maps. Additionally, analyses of optical micrographs using a point count technique confirmed both trends [Fazal 2013].

Of interest for the interpretation of the neutron diffraction data is that the intensity maximum of the 0002 pole lies only for Ti-0Zr within 7x10° to LD, corresponding to the reception area of the axial detector at Engin-X [Malamud 2014]. Consequently, the 0002 intensity maximum lay outside the yellow marked region in Fig. 10-5 c) and the majority of twins of the Zr containing alloys is not captured from the Engin-X setup. The coverage of the transverse detector is also indicated for the sake of completeness.

Analyses of the microscopic orientation maps further revealed that the area fraction of the $\{11\overline{2}2\}<\overline{11}23>$ compression twin is in average only 2% in Ti-0Zr and decreases to 0.5% in the binary Ti-Zr alloys without effect of the grain size on the overall fraction. However, majority of the $\{11\overline{2}2\}<\overline{11}23>$ compression twins in Ti-0Zr occurs in hard grains, which are not as frequent as in the Zr containing alloys. The $\{11\overline{2}1\}<\overline{11}26>$ tension twins become in average slightly more frequent with Zr addition, but they are restricted to only around 0.5% area fraction in the alloys without significant effect of grain size or Zr. The morphology of those twins barely changes with alloying.

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Fig. 10-5: Deformation microstructure. Bandcontrast maps after compression to strains of a) 0.04 and b) 0.09 with highlighted twin types by different boundary colors as Red= $\{10\overline{1}2\}<10\overline{1}1>$, Green= $\{11\overline{2}1\}<\overline{11}26>$, Aqua= $\{11\overline{2}2\}<\overline{11}23>$. c) 0002 and 10 $\overline{10}$ pole figures after compression to strains of 0.09 parallel to RD with indications for the reception area of the axial and transverse detector at Engin-X and a 30° circle in yellow.

10.4. Discussion

The binary Ti-Zr alloys of the present study exhibit significant strengthening of the 0.2% yield stress $\sigma_{0,2}$ with further increase with grain size reduction, as summarised in Fig. 10-6 a). In the absence of precipitation, classic solid solution strengthening theories based on the misfit between solvent and solute can predict such initially almost linear strengthening, which becomes less pronounced with solute concentration [Dieter 1986]. More interesting for this manuscript is the effect of deformation twinning on the work hardening behaviour after yielding. Fig. 10-3 and Fig. 10-6 b) show that the minimum work hardening rate θ_{min} becomes pronounced at the investigated strains once Zr is added and significant work softening after yielding develops at increased Zr content. Such increasing load drops have been connected previously to an increasing ratio of nucleation to propagation stress of twins in fcc materials [Christian 1995]. This initial decrease of θ_{min} , indicating facilitated propagation, does not necessarily contradict the postulate by Sen et al. that Ti-Zr alloys "should show rapid strain hardenability, due to the presence of high dislocation density and increased deformation faulting compared to pure titanium", just as Ti-Al alloys [Sen 1998]. In fact θ increases with Zr addition at higher strains, between 0.04 and 0.09, almost independent of the grain size. The texture hardening and simultaneous grain refinement caused by $\{10\overline{1}2\}$ twins both substantially increase the work hardening rate [Wu 2008]. However, the overall $\{10\overline{1}2\}$ twin area fraction at a plastic strain of 0.09 increases only little with Zr content and grain size (see Fig. 10-6 c) and cannot explain the observed increasing θ at higher strains with Zr addition on its own. Neither $\{11\overline{2}1\}$ nor $\{11\overline{2}2\}$ twins show significant effects of solute content or grain size under consideration of the starting texture.

It is tempting to associate the essentially equal $\{11\overline{2}1\}$ and $\{11\overline{2}2\}$ twin fractions (see Fig. 10-6 d and e) and morphologies (Fig. 10-5 a and b) across the Ti-Zr alloys to the equal c/a ratios and the associated twin shear [Yoo 1981]. In contrast, Ti-based alloying systems with variable c/a ratio (Ti-Al, Ti-Sn) presented in chapter 6 and chapter 9 showed significant variations in fraction and morphology of $\{11\overline{2}1\}$ and $\{11\overline{2}2\}$ twins. However, the morphology of $\{10\overline{1}2\}$ twins varies significantly with Zr content despite constant twin shear and suggests another parameter governing its formation and affecting the work hardening behaviour.

In-situ neutron diffraction experiments were conducted to improve the understanding of the changes in $\{10\overline{1}2\}$ twin formation and to gain insight in the lattice strain evolution during compression at variable solute content. Fig. 10-6 f) summarises the measurements of the $\{10\overline{1}2\}$ twin activity $\delta\Delta I/\delta\epsilon$ from the neutron diffraction experiment at Engin-X for low and intermediate strain levels. The averaged slope of the intensity increase of the 0002 pole in axial direction during compression to strains of 0.04 agrees to a slightly increasing $\{10\overline{1}2\}$ twin fraction with Zr content on the larger grain size level (blue open diamonds) from the orientation maps analyses. But further Zr addition on the lower grain size level seems to decrease the twin

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activity $\delta\Delta I/\delta\epsilon$ for strains to 0.04 (black diamonds) and more pronounced for higher strains between 0.04 and 0.09 (grey triangles), contradicting the weak increasing trend of the orientation map analyses. Especially the decreasing twin activity $\delta\Delta I/\delta\epsilon$ between strains of 0.04 and 0.09 with Zr content on the larger grain size surprises, as the orientation map analysis suggests increased twin fraction. Reason for the discrepancy between the twin activity $\delta\Delta I/\delta\epsilon$ derived from the neutron diffraction experiment and the twin fraction derived from orientation maps can be found in the deformation textures. The basal pole figures of the Zr containing alloys in Fig. 10-5 c) exhibit intensity maxima between 10° and 30° degree to LD instead of $\pm 10^{\circ}$ around LD as in Ti-0Zr. As a result the detectors of Engin-X, covering about 7x10° as indicated in Fig. 10-5 c) with yellow rectangles, do not capture the majority of the twins in the alloys, but in Ti-0Zr. Ergo the twin activity of the alloys measured at Engin-X appears lower than estimates from orientation maps and distorts relative comparisons to Ti-0Zr. Concluding from the orientation maps, the dominant $\{10\overline{1}2\}$ tension twin exhibits a rather subtle increase because the initial grain size actually decreases with Zr content and counteracts the increasing twin activity with Zr addition. The grain size reduction at 3.6at.% Zr lowers the likelihood for twinning. An increasing twin activity with Zr was also confirmed by a point count technique of the twin area fraction on optical micrographs in previous work for multiple loading directions and strain levels [Fazal 2013].

The plastic strains of first intensity increase in the axial Engin-X detector ε_{nuc} , indicating the onset of twin activity, suggests that Zr facilitates the early stages of twin formation as summarised in Fig. 10-6 g). At the big grain size level, Zr clearly reduces the amount of plastic strain to initiate twinning, and less pronounced at the small grain size level. A decrease in grain size delays the onset of twinning dramatically. The ability of Zr to facilitate the onset of twinning in Ti is furthermore supported by the decreasing residual elastic lattice strains on the basal plane from the grain family favourably orientated for twinning at the onset of twinning, marked by a grey glow in Fig. 10-4 b). Extrapolation of those residual lattice strain values $\epsilon \mu_{res(0002)}$ to values at maximum applied stress before twin initiation shows a similar trend, as summarised in Fig. 10-6 h). Increasing Zr content and grain size both reduce $\epsilon \mu_{nuc(0002)}$. One direct result of the facilitated {1012} twin nucleation appears as increased twin boundary density with increasing plastic deformation and Zr content, marked in red in Fig. 10-5 a) & b). As the $\{10\overline{1}2\}$ twin area fraction increases only little with Zr and the twins appear thinner one may conclude that the twin growth is impeded by Zr addition. It is unwise to conclude that from the neutron data due to the described issues. But the nature of twinning to relax the lattice strains of the parent grains along the c-axis together with facilitated twin propagation may explain the pronounced flow softening after yielding at higher Zr contents. Considering that the twins harden the material due to the texture change and the grain refinement it is remarkable to observe 5MPa flow softening after yielding. With twin formation becoming relatively seen to the yield strength easier, more twins form and the twin boundary density increases at an overall similar area fraction at strains of 0.04 and 0.09.

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As the c/a ratio does not suggest any changes in the character of twinning, the solute Zr seems to affect the dislocation mobility to nucleate and propagate twins as well as to accommodate the twin shear in the parent grain and neighbouring grains. Previous research on fcc materials suggested that an decreasing SFE facilitates the separation of partial dislocations, which are required for the formation of a twin nucleus [Christian 1995, Zhang 2009]. Assuming an indirect relation between SFP and SFE, as proposed by Metzbower et al. for the Ti-Al system [Metzbower 1971], one could relate the facilitated twin formation with Zr addition to the dramatically reduced SFP reported by Sen et al. [Sen 1998]. At the same time a decrease in SFE was related to more difficult cross slip [Metzbower 1971], which allows twin growth to happen in fcc materials [Zhang 2009]. Therefore, the decrease in SFE may be related to both facilitated twin formation, especially the propagation, and impeded twin growth. However, one may also argue that twin nucleation and propagation becomes easier than twin growth.

Even though the current results cannot confirm those assumptions directly, they clearly show thinner twins at higher Zr content. The enhanced the grain refinement is thought to increase the work hardening rate at strains above 0.04 for two reasons. Once, it was pointed out in chapter 8 that residual stresses in twins contribute to the hardening and an increased twin boundary fraction may complicate those stress fields, leading to additional hardening. Furthermore, grain refinement reduces the distance of free dislocation motion and leads to the empirical Hall-Petch hardening. That finer grains and hence increased grain boundary fraction increase the strength could also be observed at 3.6at.%Zr on two grain sizes. Despite many efforts during previous researchers to understand why a grain refinement reduces the twin activity in hcp metals, no concrete mechanistic explanation was given [Salinas-Rodrigues 1994, Meyers 2001, Yu 2010, Yu 2012].

Salinas-Rodrigues pointed out that larger grains develop more extensive planar arrays of prismatic slip, which can act as more effective stress concentrations for twin nucleation. However, when slip occurs in cellular structures as in CP-Ti the free slip length is much shorter than the grain size and any stress concentrations would occur on the scale of the pile-ups instead of the grain size, as Meyers et al. alluded correctly. Despite this, some factor depending on the grain size seems to influence twinning as twining possesses a higher Hall-Petch slope than slip [Meyers 2001] supressing twinning at smaller grain size. Surface effects as source for twin nucleation as in micropillar testing [Yu 2010] can be excluded in the present study on bulk samples of similar grain size. But the number of available promoters for twinning, such as screw-dislocation poles, is reported to be less in smaller volumes [Yu-a 2012] and hence twinning becomes more difficult and eventually entirely replaced by <c+a> slip with decreasing grain size.

Following this argument, more plastic strain should be required when the grain size decreases to initiate twin formation by promoting dislocations. The residual lattice strain measurements Arnas Fitzner, PhD Thesis, 2014

along the c-axis of the parent grains are more than 3 times higher in Ti with 3.6at.%Zr when the grain size is halved at the point of twin nucleation. Higher tensile lattice strains along the c-axis before the onset of twin formation and during subsequent formation to strains of 0.09 further suggest that the generation of the necessary dislocations requires more stress at a finer grain size.



Fig. 10-6: Summary of results as function of Zr concentration for grain sizes of 80±15µm and 26±4µm (SG) a) 0.2% proof strength $\sigma_{0.2}$; b) Minimal work hardening rate at the onset of twinning $\theta_{min} c$) Fractions of $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ -twin TT₁; d) Fractions of $\{11\overline{2}1\}\langle \overline{1126}\rangle$ -twin TT₂; e) $\{11\overline{2}2\}\langle \overline{1123}\rangle$ -twin CT; f) Twin activity $\delta\Delta I/\delta\epsilon$, as the rate at which the axial 0002-intensity changes with true plastic strain ϵ for plastic strains below 0.04 and above for Ti-0Zr only; g) Residual plastic strain for onset of $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ -twin ϵ_{nuc} , from the first indication of 0002-intensity in the axial detector; h) Extrapolated microstrain on <c> axis $\epsilon\mu_{nuc\{0002\}}$ at the onset of $\{10\overline{1}2\}\langle 10\overline{1}1\rangle$ -twinning from favourably orientated grain family.

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10.5. Conclusion

Comparisons of deformation twin activity during uniaxial quasi-static compression were conducted on alloys of 0, 3.6 and 10at.%Zr by means of EBSD and neutron diffraction. The results are influenced by a decreasing grain size with Zr addition and a change of the distribution of prismatic planes, but the basal texture and the c/a ratio are almost identical in all alloys.

Zr addition to Ti increases the yield point significantly, but induces increasing flow softening after the yield, followed by increased work hardening rate between strains of 0.04 and 0.09. Zr was shown to facilitate nucleation and propagation of $\{10\overline{1}2\}$ tension twins but to impede the growth rate of those twins, seen by the reduced residual lattice strain development of the twinning grain family and higher twin boundary fractions in EBSD microstructures at only slightly increasing area fraction. The formation and growth behaviour of $\{10\overline{1}2\}$ tension twins is rationalised with the dramatic increase in SFP with Zr addition. The tendency of $\{11\overline{2}1\}$ tension and $\{10\overline{1}1\}$ compression twinning is barely altered, which can be related to the c/a ratio. Previous empirical findings on the Hall-Patch effect on twinning are confirmed.

11. The Effect of Oxygen on twinning in Ti-10AI

ABSTRACT

The deformation mechanisms of model alloys containing 10at.% Aluminium (Al) and either 0.4 or 1.5at.% Oxygen (O) have been investigated in respect to nucleation and growth of twins using in-situ loading in combination with neutron diffraction as well as detailed post mortem EBSD analysis. A consistent starting microstructure and texture was generated for both alloys promoting tensile twinning during compression testing. Large d-spacing neutron diffraction and TEM analyses revealed similar degrees of short range ordering (SRO) in both alloys. It was found that raising the O content increases the 0.2% yield strength to the level of Timetal 6-4 and supresses $\{10\overline{12}\}<10\overline{11}>$ tensile twinning strongly and $\{11\overline{2}1\}<\overline{11}26>$ tensile twinning entirely in Ti-10Al. Analysis of the residual intergranular strains of the twinning grain family during in-situ neutron diffraction revealed that $\{10\overline{12}\}$ twin nucleation was delayed to a compressive strain of 0.03. During twin formation residual intragranular strains reduce with increasing plastic strain but increase when deformation slip is dominant at high O content. The correlation between O content and twin activity might be a simple result of increased slip localisation at higher O content and a lack of the matrix grains to accommodate the rather homogeneous twin shear.

11.1. Introduction

The fundamental impact of either O or Al on strength and deformation slip in pure Ti was explored previously [Biswas 1973, Okazaki 1973, Sakai 1974, Truax 1974, Conrad 1981, Williams 2002] but the impact on $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning was mostly neglected from those studies. Nevertheless, tension and compression twinning both have striking impact on textural and microstructural development during forming and consequently on the strength and work hardening behaviour of a product [Salem 2003&2006, Bache-a 2001]. Ti alloys containing significant parts of AI and minor parts of O are an integral part of modern aircrafts based on their excellent specific strength. Both solutes stabilise the alpha phase [Wahlbeck 1966, Schuster 2006] and have even synergetic effect together, widening the alpha/beta two-phase region [Van Thyne 1954, Schofield 1957]. Wahlbeck and Gillet [Wahlbeck 1966] describe the alpha-Ti field by TiO_{0+x}. Alloying with Al does not only decrease the density but also increases the strength of pure Ti [Truax 1974]. The rather small amounts of Oxygen (O) used for alloying, usually less than 0.4 wt% (1.2at.%), have very little impact on the density but they increase the strength dramatically and consequently the specific strength increases over proportionally when both alloying partners are present in appropriate quantities [Luetjering 2007]. Also the fatigue behaviour of commercially pure Ti improves with addition of interstitials [Conrad 1981]. Major problem with either alloying element is a critical loss in ductility above a certain concentration [Truax 1974, Conrad 1981]. This loss is thought to origin from a transition of slip from a wavy and cellular structure to straight, localised slip bands on well-defined planes and increasingly

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difficult cross slip with increasing concentration of Al or O as well as to dynamic strain ageing [Biswas 1973, Conrad 1981, Truax 1974, Williams 2002]. It is interesting that O, as interstitial element going in the octahedral sites of the Ti lattice [Gupta 1962, Blanter 2004], changes the dislocation patterns similarly to the substitutional element Al. Al and O are reported to have a synergetic effect on that transition [Luetjering 2007]. The reason for that transition is not entirely understood, but it is thought to be a *chemical effect,* coming from an increase in the stacking fault probability (SFP) and the inversely related stacking fault energy (SFE) on basal or prismatic plane [Metzbower 1977]. Metzbowers measurements on the SFP suggest that both elements have a positive synergetic effect on the SFP.

With addition of O ordering phenomena were reported from about 15at.% [Kiowa 1969, Kornilov 1970], much above practical concentrations. But O was also reported to occupy octahedral sites of every second layer of interstice planes over the whole range of solid solution [Yamaguchi 1969], even though only proven from 9at.% by a combination of electron, neutron and X-ray diffraction. Such arrangement of O atoms has an *elastic effect* and expands the unit cell non-spherical and the c-axis much faster than the a-axis, leading to increasing c/a ratio [Yamaguchi 1969, Kratochvil 1970]. Al addition to Ti leads to a contraction of the unit cell [Ghosh-a 2008], with the a-axis shrinking faster than the c-axis and finally increasing the c/a ratio similarly to O per at.%. Al is known to form short-range order domains from concentrations as low as 7at.% (4wt%) [Namboodhiri 1983]. The onset of ordering was related to a hardening effect due to interactions between dislocations and solutes [Conrad 1981] and a suppression of deformation twinning in chapter 6. *Elastic effects* like size and modulus differences predict solid solution hardening somewhat satisfactory [Conrad 1981] but cannot accurately explain the hardening considering short-range interactions between interstitial and the moving dislocation core [Tang 1969].

The contribution of *chemical interactions* in the binary Ti-O system was suggested to strengthen the material [Tyson 1969, Kratochvil 1970]. A surprisingly slow diffusion rate and high resistivity increase with O [Ames 1953] indicate that covalent Ti-O bonds are formed [Sargent 1972]. Sargant and Conrad [Sargent 1972] proposed that covalent bonds cross the basal plane more often than prismatic planes, even when O is randomly distributed. Conrad notes that energies from elastic and chemical effects are of similar order and may be equivalent, both based on electronic interactions between the atoms.

None of those theories has been established yet and physical reasons for the strengthening mechanisms are not entirely clear. Because of the practical relevance of alloys based on the Ti-Al-O system this manuscript aims to populate the experimental database for synergetic effects of Al and O in Ti and explores the sensitivity of deformation twinning. Therefore alloys of Ti-10Al with relatively low and high O content were produced with almost identical texture and microstructure. Investigations of the deformation behaviour focus on twin activity, using a neutron diffraction in-situ lattice-strain scanner and EBSD micro and macro texture mapping. Arnas Fitzner, PhD Thesis, 2014

11.2. Materials and Methods

11.2.1. Material preparation

Two small ingots with a weight of 200g composed of high purity Ti and 10at.% Al were double melted in a tungsten arc furnace under argon atmosphere at the TIMET research facility in Witton, UK. One button was additionally infused with TiO₂ powder to target an O concentration of 4000ppm in weight (1.2at.%). The microstructure was broken down by β forging at 1100°C and afterwards by α -cross-rolling in bar shape (14× 14× 260mm) on a "2 high Robertson mill" (WHA Robertson & Co Ltd) at 870°C. The rolling resulted in a symmetric bar of approximately 26cm in length, with transverse and normal direction being equivalent and here labelled as ND₁ and ND₁₁. Both bars were sectioned and recrystallised (RX) at 968°C for 5 hours in a tube furnace under argon shield followed by air-cooling, as summarised in Tab. 11-1.

Chemical analyses are summarised in

Tab. 11-2 and were performed on halved compression samples by TIMET Savoie, France using inductively coupled plasma mass spectrometry on a HORIBA Ultima2 for metallic elements, on a HORIBA EIMA 820V for C and on a LECO EF-400 for O and N. The results confirm about 10at.% Al and exceptionally low levels of other impurities in both bars below 61ppm. Ti-10AI exhibits relatively low O concentration (0.44at.%) and Ti-10AI-O high concentration (1.53at.%).

Alloy	Т	t	GS
	°C	h	μm
Ti-10Al	986	5	70
Ti-10Al-O	986	5	65

Tab. 11-1: Thermo-dynamical processing of the alloys in this study

11.2.2. Microstructure analysis

Metallographic cross sections with the plane normal parallel to the former rolling direction (RD) were cut and prepared by mechanical grinding down to P4000 paper. This was followed by polishing on a semi-automatic polishing apparatus with 5N pressure with oxide particle suspension (OPS) from STRUERS. After one hour of polishing an intermediate etching with Krolls reagent for 10s was inserted and followed by another hour of OPS polishing. This combined polishing-etching procedure was repeated three times in total. The presented texture measurements origin from such surfaces and capture areas bigger than $4 \times 4mm^2$ with $40\mu m$ stepsize on a CamScan Maxim 2500FEG SEM with NordLYS detector, operated at 20 kV and 6.8nA probe current using Flamenco acquisition software. Detailed orientation maps were recorded on areas bigger than $1mm^2$ on a FEI Sirion FEG SEM using Flamenco and on a FEI Quanta 650 using AZTEC acquisition software with a reduced probe current of approximately 5nA. The detailed orientation maps were cleaned and analysed using the HKL software Arnas Fitzner, PhD Thesis, 2014

package. Twin area fractions were measured manually on the cleaned maps using the twin boundary criteria given by Bozzolo et al. [Bozzolo 2010]. Thin foils for transmission electron microscopy (TEM) were perforated using a Tenupol 5 with attached Julao cooling unit at -30°C and 15V with a solution of 6% perchloric acid (60%) and 94% methanol. The foils were investigated by selected area diffraction on a FEI Tecnai G20 with a LaB₆ filament at 200 kV, equipped with Ditabis image plates. Cylindrical bulk samples of 8mm diameter and 40mm length were used for neutron powder diffraction measurements at the time-of-flight beamline WISH, ISIS, in order to assess the state of ordering. Spectra were collected for counts of 30µA below pressures of 0.05 bar to reduce the background. Data in bank 3 provide the highest flux were α_2 reflections are expected and are presented here. First the background, an empty Vanadium can used as sample holder, was subtracted from the spectra and finally data were smoothed with a moving average over 20 points.

11.2.3. Mechanical testing

Cylindrical compression samples of 6mm diameter and 9mm length were machined for ex-situ compression testing. In-situ loading on Engin-X, ISIS, was performed using cylindrical samples of 8mm diameter and 12mm length for better counting rates. Quasi-static compression tests were conducted on an Instron 5569 at room temperature and an initial strain rate of 10⁻³ 1/s with the loading direction (LD) parallel to the original rolling direction (RD). The use of Lubriplate grease ensures a uniaxial stress state and minimizes barrelling during deformation. Samples for microstructural and textural observations were monotonically compressed to strains of 0.04 and 0.09 parallel to RD, but only deformation microstructures from the step wise strained samples at Engin-X are presented here.

11.2.4. In-situ loading using neutron diffraction

In-situ compression experiments were carried out using neutron diffraction on the lattice strain scanner ENGIN-X, ISIS, UK. The setup and the methodology are identical to previous investigations on the binary Ti-Al system and are described in more detail in chapter 6. It may only be mentioned that the 8x12mm cylindrical samples were loaded in stress increments up to 75% of the expected yield stress from ex-situ compression tests to record diffraction data in the elastic regime for the determination of the diffraction elastic constants. Samples were loaded in position increments above 75% of the yield stress up to 9% plastic strain. Above 75% of the yield spectra were recorded at a stress of -15MPa in order to grip the sample and avoid cold creep during the collection of 30 μ A. The in-house ISIS software Open Genie fitted the six major hcp-peaks separately to calculate the lattice strain evolution as described by Warwick et al. [Stapelton 2008]. Rietveld analysis of the six major peaks before loading gave the lattice spacing to high accuracy, as listed in Tab. 2.

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11.3. Results

11.3.1. Starting Material

A small anisotropic expansion of the unit cell with addition of 1at.% O was found from Rietfeld analysis of neutron diffraction spectra. The results, listed in

Tab. 11-2, suggest the *c* lattice parameter increases about four times more than the a lattice parameter. However, due to the rather small changes the corresponding *c/a* ratio shows negligible increase at a level of 10at.% Al. The starting microstructures are shown along the former RD in Fig. 11-1a) as bandcontrast maps of microscopic EBSD scans. Ti-10Al-O contains more clusters of small grains than Ti-10Al, leading to a reduced mean grain size of 65 compared to 70µm, respectively. Misorientations within grains are usually below 2°. EBSD macro texture measurements did not show pronounced macorzones after recrystallization but a distinct basal ring-texture, presented in Fig. 11-1 b). Very low intensity of basal poles within 45° to RD is present in both alloys. The basal intensity is distributed perpendicular to RD with highest intensity about 45° between ND₁ and ND₁₁. The 1010 pole figures show highest intensity 30° away from RD and relatively low intensity exactly in the RD, especially with higher O content. The intensity ratio of the 1010 reflection to the 1120 reflection in the axial detector of Engin-X decreases from 0.24 to 0.15 with increasing O content and confirms the EBSD texture measurements. Both measurements suggest that O leads to a stronger 1120 fibre after cross-rolling.



Fig. 11-1: Microstructure and texture after recrystallisation. a) Microscopic bandcontrast maps with observation direction along the former RD and b) Basal and prismatic pole figures from macro texture measurements.

Tab. 11-2: Chemical composition of the model alloys in this study and lattice parameters from neutron diffraction at Engin-X, ISIS. Other impurities are below 61ppm.

Alloy	Al	Al	С	Ν	0	0	Ti	<a>	<c></c>	c/a
	wt%	at.%	ppm	ppm	ppm	at.%		nm	nm	
Ti-10Al	5.9	10.0	76	53	620	0.44	bal.	2.928	4.674	1.596

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The diffraction spectra from neutron beamline WISH show no evidence of a clear superlattice reflection corresponding to Ti₃Al (α_2), as indicated by the stars in Fig. 11-2. Instead a broad intensity increase is noticeable at the position of the {1120} reflection of α_2 in both cases, attributed with short-range order towards α_2 . Also, analysis of selective area electron diffraction patterns with the zone axis along 1010 showed no clear indication of an α_2 superlattice reflection in neither of the two alloys, seen in Fig. 11-3. Only strong image enhancement could reveal weakest intensity of such reflections, which is overshadowed by experimental artefacts from the thin foils.



Fig. 11-2: WISH spectra, showing only the root of the major hcp-alpha peaks. Positions of the 5 major α peaks and α_2 peaks are indicated.



a) Ti-10Al RX b) Ti-10Al-O

Fig. 11-3: TEM selected area diffraction patterns on $<10\overline{1}0>$ zone axis with 600mm camera length.

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11.3.2. Flow curves

The addition of O to Ti-10Al results in a significant increase in the compressive 0.2% yield strength along the original RD from -700MPa to -970MPa, as can be inferred from Fig. 11-4 a). Once yielded, the flow stress increases almost linearly for Ti-10Al, as seen on the marginally increasing work-hardening rate until the maximum strain of 0.09 (see Fig. 11-4 b). Ti-10Al goes through a minimum in the work hardening rate θ_{min} of approximately 1800MPa at a strain of 0.02. In contrast, the work hardening rate θ of Ti-10Al-O decreases from 2000MPa with increasing plastic strain.



Fig. 11-4: a) True stress-strain curves under quasi-static compression in RD and b) Work hardening rate θ as function of the true strain (data averaged and smoothed).

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11.3.3. Diffraction peak evolution

The starting texture, shown in Fig. 11-1 b), does not allow neutrons to diffract from basal planes into the axial detector of Engin-X. No deformation slip mode can rotate the 0002 axis with the current starting texture into the coverage of the axial detector (approximately $\pm 10^{\circ}$ to LD) below strains of 0.09. Neither deformation twinning of type {1121} or {1122} does contribute to the increase in integrated intensity $\Delta I_{(0002)}$. Only deformation twinning of type {1012} can increase the intensity $\pm 30^{\circ}$ to RD//LD suddenly by re-orientation of the 0002 pole. The increase in the 0002 integrated intensity $\Delta I_{(0002)}$ as a function of true strain is given in Fig. 11-5 a) and indicates the {1012} twin activity. $\Delta I_{(0002)}$ indicates much higher activity of the {1012} twin in Ti-10AI compared to Ti-10AI-O in general. Furthermore, the first increase in 0002 intensity, indicating the plastic strain for the onset of deformation twinning of type {1012}, increases dramatically with O addition from 0.013 to 0.03.



Fig. 11-5: a) Axial intensity evolution of {0002}-plane $\Delta I_{(0002)}$ related to 85° tensile twinning as function of true strain derived from neutron diffraction at Engin-X and b) evolution of transverse lattice strain on {0002}-plane $\mu \epsilon_{(0002)}$ as function of true strain. The onset point of twinning is marked in grey.

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The little twin activity in Ti-10Al-O results in a fundamentally different evolution of the residual lattice strain of the 0002 peak $\mu\epsilon_{0002}$ in grains favourably orientated for $\{10\bar{1}2\}$ twinning, measured in the transverse detector and plot in Fig. 11-5 b). In Ti-10Al lattice strains increase linearly before the onset of plastic flow. With the onset of twinning in Ti-10Al, marked by a grey glow in Fig. 11-5 b), the residual tensile lattice strain on the c-axis of the potential parent grains decreases. Noteworthy are two observations on the evolution of $\mu\epsilon_{0002}$ in Ti-10Al-O. First, the residual lattice strain barely increases in the elastic regime. Than, much decreased twin activity in Ti-10Al-O does not allow a lattice relaxation with increasing plastic strain as monitored in Ti-10Al, instead the residual lattice strain increases up to a plastic strain of 0.07 gradually before it relaxes little in the last data point. Extrapolation of the similar residual lattice strains at the onset of $\{10\bar{1}2\}$ twinning with 905µm/m for Ti-10Al and 838µm/m for Ti-10Al-O lift the value of the O rich material much higher. The extrapolated lattice strains of 2300µm/m and 3300µm/m suggest that much higher stresses are required to initiate twinning at higher O content.

11.3.4. Deformation microstructures and textures

As already explained on the example of neutron diffraction data, the activity of the $\{10\overline{1}2\}<10\overline{1}1>$ tensile twinning system is indicated by the texture development during uniaxial compression testing. Fig. 11-6 a) shows the 0002 and $10\overline{1}0$ pole figures at a true strain of about 0.09 for comparison against the initial textures, shown in Fig. 11-1b). The intensity of the basal pole figure within 30° to RD//LD of Ti-10Al increases by 12% after compression to a strain of 0.09 but only by 1.3% in Ti-10Al-O. This barely visible intensity increase in Ti-10Al-O confirms the finding of the neutron diffraction experiment that O reduces twin activity. The $10\overline{1}0$ pole figures exhibit now both virtually no intensity within ±10° to LD and look almost identical for both alloys. Just Ti-10Al forms a fully closed ring in the ND-ND. Due to lower twin activity in Ti-10Al-O this ring does not quite close. Orientation maps confirm assumptions of $\{10\overline{1}2\}$ twin activity from the texture development directly and exhibit about 15% twin area fraction in Ti-10Al but only a twenties in Ti-10Al-O (0.7%). Ti-10Al shows with 1.8% area fraction a good amount of $\{11\overline{2}1\}$ tension twinning, but no $\{11\overline{2}1\}$ twins were identified over an area of more than 2mm² in Ti-10Al-O. Few grain boundaries with $\{11\overline{2}1\}$ twin crystallography were identified, highlighted green in Fig. 11-6 b).



Fig. 11-6: Deformation textures and microstructures at a compressive strain of 0.09: a) Textures along the former RD b) Bandcontrast maps of deformed microstructures highlighting twin types by different boundary colours: Red = $\{10\overline{1}2\}<10\overline{1}1$, Green= $\{11\overline{2}1\}<\overline{11}26$, Aqua= $\{11\overline{2}2\}<\overline{11}23$.

Also $\{11\overline{2}2\}$ compression twin boundaries (aqua) are highlighted in Fig. 11-6 b) for both alloys. Those boundaries mark only grain boundaries, which happen to have the twin relationship [Bozzolo 2010] but not the typical twin morphology. Twin boundaries of the $\{10\overline{1}2\}$ were also found on normal grain boundaries in Ti-10Al-O, but reflect mostly twin lamellas.

11.4. Discussion

The dual comparison of this study showed an increase of 270MPa in proof strength of Ti with 10at.%Al by increasing the Oxygen content from 0.44at.% to 1.53at.%, achieving the yield strength level of Timetal 64. Interestingly, the strengthening from grade 1 to grade 4, equivalent to an increase of 0.7at.% O, is similarly powerful per at.% comparing compressive or tensile proof stresses [Wasz 1996, Brandes 2012]. More relevant for the current study is the dramatic effect of O on twin activity in the two Ti-Al-O alloys despite very similar states of ordering towards Ti₃Al, starting microstructures and basal textures which promote prismatic slip and $\{10\overline{12}\}$ tension twinning.

O addition in Ti-10Al distorts the lattice in a similar way as it would do in pure Ti, but the expansion per at.% seems slightly increased along the c-direction in comparison to results by Yamaguchi on CP-Ti [Yamaguchi 1969]. The increased c/a ratio in the O rich alloy suggests after calculations of the twin shear by Yoo [Yoo 1981] a facilitated formation of $\{10\overline{1}2\}$ and $\{11\overline{2}1\}$ tension twins. However, no significant effects are expected due to the marginal changes summarised in Tab. 11-1. Even though the differences in the basal and prismatic pole figures after rolling and recrystallisation treatment do not change the Schmid factors of prismatic slip

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and $\{10\overline{1}2\}$ tension twinning dramatically, they suggest a difference in slip character. The weakened $(10\overline{1}0)$ fibre texture and therefore the strengthened $(11\overline{2}0)$ fibre texture at higher O content indicate increased basal slip activity. Already more than 60 years ago Rosi et al. [Rosi 1953] related an $(11\overline{2}0)$ fibre to dominance of basal slip in Magnesium, Zinc and Cadmium but an $(10\overline{1}0)$ fibre to dominant prismatic slip in Zirconium and Ti, confirming the relation between texture and slip activity. Smallman made the next step and related the SFE to rolling textures of fcc and hcp metals, but excluded the atomic size misfit and valence differences as governing parameter for texture evolution during forming [Smallman 1964, Smallman 1999]. However, the changing likelihood for deformation twinning and the change in slip character with temperature [Nemat-Nasser 1999], make it hard to conclude from the hot-rolling texture to active slip systems at room temperature. Metzbowers results show that O addition in binary Ti-Al alloys increases the SFP, which is most likely related to a decreasing SFE on the basal plane, which should in theory increase basal slip activity [Metzbower 1977], supporting states of both Rosi et al. and Smallman. Indeed the slip trace analyses presented in chapter 7 on binary Ti-Al alloys provide experimental evidence for increased basal slip activity during compression in alloys of more pronounced $(11\overline{2}0)$ fibre texture and increased AI content, backed up by experiments on Ti-Al single crystals [Williams 2002]. The stronger $(11\overline{2}0)$ fibre in Ti-10Al-O suggests therewith increased basal slip activity in comparison to Ti-10AI, and even more so to commercially pure Ti, which would affect the twin formation and growth. Slip localisation does not only occur on basal planes but also on prismatic planes with increased AI content and especially with increased O content [Truax 1974].

If one summarises measurements on the binary Ti-AI system of the state of ordering by neutron diffraction in chapter 6 and by Thirmlalai [Thirumalai 2000], of the slip character by slip trace analysis using TEM [Neeraj 2001] as well as digital image correlation (chapter 7) and first principle calculations [Van De Walle 2002] it becomes obvious that the onset of slip localisation coincides with the onset of SRO and a suppression of twin formation. But TEM and neutron diffraction analyses could not show any differences in the state of SRO towards the DO₁₉ structure between the present alloys making it doubtful if Ti₃AI formation further localises slip at increased O content. If SRO towards Ti₃Al does not change, another parameter has to cause the changed slip character on 0002 and $10\overline{10}$ planes with increasing O content. The slip localisation on 1010 planes may be connected to the preference of Ti-O bonds to cross the basal plane over the prismatic plane, as it was proposed by Sargent and Conrad [Sargent 1972]. Any change of the dominant slip system may not create the right dislocations for twin nucleation and alter the stress and strain states in the grains, so that twin growth is impeded. For instance, the shear of prismatic slip complements the shear of $\{10\overline{1}2\}$ twinning [Capolungo a 2009] and hence reduced prismatic slip activity, or increased basal slip activity, reduces the ability of the parent grains to accommodate $\{10\overline{1}2\}$ twin shear and supresses their growth.

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Even though the present results only allow speculations about the cause of twin suppression, the effects on macroscopic and microscopic stress-strain response is clear. EBSD micro and macro mappings as well as the intensity evolution of the basal pole in the axial detector from the in-situ compression experiments agree on dramatically reduced twin activity and much-delayed onset at increased O concentration. The small twin area fraction at a compressive strain of 0.09 below 2% and the gradual movement from the basal poles towards the LD, seen in a comparison of Fig. 11-1 b) and 11-8 a), both indicate increased slip activity in the O rich alloy. This increase in slip activity with O also affects the residual lattice strain evolution fundamentally. When twinning is active, as in Ti-10AI, the residual lattice strain on the 0002 plane $\mu\epsilon_{0002}$ of the grains favourably orientated for both prismatic slip and twinning decreases. Without significant activity of deformation twinning, dominant deformation slip results in a gradual transition of the residual lattice strains on the c-axis in transverse direction $\mu\epsilon_{0002}$ from the linear elastic regime into the plastic regime at a true strain of nearly 0.02. The very small twin area fraction, below 2% after compression, does not allow a relaxation of $\mu\epsilon_{(0002)}$, instead $\mu\epsilon_{(0002)}$ increases to over 1000µm/m.

The dominace of deformation slip lowers the WH rate with increasing plastic strain, as the contribution of grain refinement and texture hardening to the overall hardening is small. In contrast Ti-10Al exhibits a minimum in the work hardening rate before texture hardening and grain refinement by $\{10\overline{1}2\}$ and $\{11\overline{2}1\}$ twinning increase the work hardening rate steadily after the yield.

11.5. Conclusion

The effect of Oxygen (O) on deformation twinning in Ti with 10at.%Al was observed on O levels of 0.4 and 1.4at.% in model alloys with almost identical microstructure, basal texture and state of ordering. Loading experiments along the original RD were conducted up to a plastic strain of 0.09, favouring the activation of prismatic slip and {1012} twinning. EBSD micro and macro texture analysis, as well as in-situ compression at Engin-X show in Ti-10at.%Al with 1500ppm O {1012} twins readily and {1121} twin rarely, resulting in a relaxiation of residual lattice strains in grains favourably orientated for prismatic slip and {1012} twins are strongly supressed at an O content of 5000ppm {1121} twins disappear entirely as active deformation mode, resulting in increasing residual lattice strains on the basal plane $\mu_{\epsilon_{(0002)}}$ transverse to the loading direction in the plastic regime and a decreasing work hardening rate due to the small contribution of texture hardening and grain refinement. It is proposed that increasing slip activity on basal planes and slip localisation on prismatic planes do not provide dislocations for twin nucleation and that the more heterogeneous stresses and strains in the grains are deleterious for twin growth.

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12. Communications

This chapter outlines accomplished work to confirm the effect of ageing on twin activity in different alloying systems and the effect of alloying on ductility. Results are presented as short communications using the same methodologies described in chapter 4 unless stated otherwise.

12.1. The effect of ageing on twinning in Ti6Al4V

It was shown on the binary Ti-AI system that ageing reduces the twin activity during compression along the former RD. It remained unclear if this is a direct consequence of the transition in the state of ordering towards Ti₃AI itself or just a consequence of more planar slip induced by the onset of ordering [Neeraj 2001]. It is known for long time that Ti6AI4V undergoes small amounts of deformation twinning [Tanaka 1975, Yapici 2006, Prakash 2010]. Practical interest to investigate if ordering supresses twinning in industrial AI rich Ti-alloys is based on the effect of twinning on texture evolution during processing and the related mechanical anisotropy [Bache 2001, Chun 2005]. To investigate the effect of ordering on twin activity a systematic comparison of the twin activity of recrystallised and aged Ti6AI4V was undertaken by means of electron microscopy before and after uniaxial quasi-static compression.

12.1.1. Starting material

Timet, Witton produced a lab-scaled bar of Ti6Al4V by cross rolling. Samples were either recrystallised and air cooled or recrystallised and slowly cooled with 10K/h and aged for one week at 420°C (see Tab. 12-1). The chemistry is given in Tab. 12-2. Rietfeld refinements on neutron diffraction spectra at Engin-X revealed an *a*-lattice parameter of 2.949nm and a *c*-lattice parameter of 4.700nm, resulting in a c/a ratio of 1.594.

Industrial	Alloy	Т	t	Tage	t _{age}	GS
name		°C	h	°C	h	μm
Timetal 6-4 or	Ti6Al4V	860	24	-	-	10
ASTM Grade 5	Ti6Al4V ^a	860	24	420	120	10

Tab. 12-1: Thermo-mechanical processing schedule of Ti6AI-4V

Tab. 12-2: Chemical composition of the model alloys in this study and lattice parameters from neutron diffraction at Engin-X, ISIS. Other impurities are below 60ppm.

	Al	V	Fe	0	Ti
at.%		bal.			
wt%	Corres	bal.			

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The recrystallised and air cooled material shows an a grain sizes of about 10µm, as shown on a microscopic bandcontrast map from EBSD measurements with 20kV acceleration voltage in Fig. 12-1 a) as well as non indexed regions between those grains. The α macroscopic orientation map along the former RD (Fig. 12-1 b) shows mainly green and blue toned regions stretching more than 4mm in width with the basal plane perpendicular to RD. However, red colored regions with the basal plane aligned along the RD stretch over almost 2mm. The Macroscopic orientation map along the former ND (Fig. 12-1 c) exhibits pronounced stripes of up to 1mm in width and more than 2mm in length. Microscopic orientation mapping, shown in Fig. 12-1 d), resolves typical macrozones, clusters of grains with similar orientation, often separated by small angle grain boundaries.

Fig. 12-1: Orientation mapping of recrystallised Ti6Al4V (Ti64). a) fine scaled EBSD bandcontrast map for α from recrystallised material with observation direction //RD. β is marked in pink and twin boundaries are indicated as Red= $\{10\overline{1}2\}$ < $10\overline{1}1$ >, 1}< Green={11 2 11 26>. Aqua= $\{11 \ \overline{2} \ 2\} < \overline{11} \ 23>$. Macroscopic orientation maps along the former b) RD and ND in IPF Z colouring, both showing macrozones.

Microscopic high resolution EBSD, using only 10kV acceleration voltage and simultaneous EDS revealed that the non-indexed regions between the primary α grains of the RX material in Fig. 12-1 a) and d) contain secondary α lamellas. The up to a few 100nm wide lamellas have seemingly random orientation (see Fig. 12-2 a). β phase is only indexed at the boundary between primary and secondary α with one single orientation per island (see Fig. 12-2 b). Aged samples exhibit no secondary α and therefore the EBSD and EDS map were recorded with 20kV acceleration voltage. The regions between the primary α grains in the aged material are filled completely with β -phase of one single orientation.

Fig. 12-3 depicts the EDS mapping for a) Ti, b) Al, c) V and d) Fe of the same areas presented in Fig. 12-2 b) and c) for the RX and aged condition. It can be seen in both conditions that the primary α phase is rich in Ti and Al, but depleted in V. The EDS mapping on the RX state shows in the region of prior β , being β and secondary α at room temperature after air-cooling, clearly increased V content and slightly increased Fe content. No compositional difference can be noticed between β and secondary α phase, possibly due to the small phase dimensions of β . The EDS mapping on the aged state shows clearly V and Fe enriched β phase and suggests that barely any Al is retained in the centre of the β islands. Averaged concentrations of at least three EDS point scans, given in Fig. 12-3, do not reflect the chemistry measured by Timet, Savoie (Tab. 12-2) and show comparably lower Al content and relatively high Fe contents. The β islands are slightly smaller after the ageing treatment compared to the RX state.

The ageing treatment increases the degree of ordering towards Ti_3AI , as can be seen from the increasing intensity of the corresponding superlattice reflection in selected area diffraction patterns along the <1010> zone axis (Fig. 12-4).



Fig. 12-2: Microstructural changes upon slow cooling and ageing of Ti6Al4V. Fine scaled EBSD maps with a) IPF colouring for α band contrast for β and vice versa in b) IPF colouring for β and band contrast for α . The EBSD maps and simultaneous EDX scans on the RX state are taken with 10kV and 0.025µm step size, while the aged sample was scanned with 20kV and 0.05µm stepsize.



Fig. 12-3: Micro segregation during slow cooling and ageing. Simultaneous EDX maps to the EBSD maps from Fig. 7-2 for a) Ti, b) Al, c) V and d) Fe. Elemental compositions are averaged over more than 5 EDX point scans.



Fig. 12-4: TEM selected area diffraction patterns on <10 $\overline{1}$ 0> zone axis with 600mm camera length for RX and aged Ti6Al4V. White arrows indicate Ti₃Al superlattice reflections.

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12.1.2. Mechanical behaviour

Quasi-static uniaxial compression tests to strains of 0.09 showed that the ageing treatment raises the 0.2% proof stress from -970MPa to -1040MPa. The flow curves for samples strained to 0.09 are shown in Fig. 12-5 a) in black for the RX condition and in red for the aged condition, unfortunately tested on different stress-strain rigs. Comparison of the RX sample strained to only 0.04 (grey in Fig. 12-5 a) and the aged sample strained to 0.09, both tested on the same machine, shows clearly a sharper transition from the elastic into the plastic regime for the aged condition. The work hardening rate of the three samples is shown in Fig. 12-5 b). While the work hardening rate of the RX sample compressed to a strain of 0.09 decreases slightly with increasing strain, the aged sample has a rather constant rate. However, the RX sample compressed only to low strain appears to have a higher work hardening rate. However, due to the unfortunate circumstances nothing can be concluded from the work hardening rate.



Fig. 12-5: a) True stress-strain curves of Ti6Al4V under quasi-static compression in RD and b) Work hardening rate θ as function of the true strain (data averaged and smoothed) after solution treatment (RX) and after ageing (aged).

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12.1.3. Deformation textures and microstructures

Fig. 12-6 shows 0002 and $10\overline{10}$ pole figures of the RX condition a) before loading and at strains of b) 0.04 and c) 0.09. Before loading, the main intensity of the 0002 pole is distributed in the ND_I-ND_{II} plane, but a central intensity spot reaching ±15° around the LD is present. The



intensity of this spot increases only little with increasing plastic strain level and the spread exceeds $\pm 20^{\circ}$ around LD at a strain of 0.09. At the same time, the intensity of the four intensity spots about 45° between ND_I and ND_{II} reduces with increasing compressive strain. A crystal compressed perpendicular to the basal plane normal can rotate the basal plane normal into the LD by {1012} tension twinning suddenly [Philippe 1988]. Any other deformation system would change the texture gradually. The prismatic 1010 fibre texture spreads out with increasing compressive strain, which can be caused by deformation twinning or slip.

Fig. 12-6: Texture development during compression of solution treated material along the former RD a) before loading at compressive strains of b) 0.04 c) 0.09.

Fig. 12-7 shows fine scaled EBSD maps at a strain of 0.09 parallel to RD and provides direct evidene of twin activity. Boundaries of $\{10\overline{1}2\}$ twins are highlighted in the bandcontrast maps of Fig. 12-7 a) in red. The RX state exhibits $\{10\overline{1}2\}$ twins throughout the presented section of the map, but not in the bottom right hand corner. The lack of twinning in that corner can be understood under consideration of the starting texture. The grain orientations of the area presented in Fig. 12-7 a) are shown in Fig. 12-7 b) in IPF Z coulouring, highlighting {1012} twin boundaries black. Most grains in the bottom right corner of the RX state are orientated with the 0002 pole into the LD and are therefore unlikely to undergo {1012} twinning, but likely to undergo $\{11\overline{2}2\}$ compression twinning. However, no $\{11\overline{2}2\}$ compression twins or $\{11\overline{2}1\}$ tension twins could be identified by EBSD across the full observation area of 0.4mm². The aged state shows far less twin boudaries (Fig. 12-7 a), but increasing amounts of β phase, as indicated in pink. However, β phase could not be indexeed at the top and bottom of the map and white areas remain between the α grains. The white framed area within a) and b) is shown magnified in Fig. 12-7 c). Here, it can be seen that most $\{10\overline{1}2\}$ twins in the RX state span across entire grains and readily exceed $2\mu m$ in width. $\{10\overline{1}2\}$ twins in the aged condition span only rarely across a full grain and occur rather at the edge of grains as twin nucleus. The size in the aged state exceeds only seldom 1µm in any dimension. Consequently, the twin activity of aged material is reduced in comparison to recrystallised Ti6Al4V.

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Fig. 12-7: Deformation microstructures at a compressive strains of 0.09 parallel to RD: a) Bandcontrast maps highlighting twin types by different boundary colors: Red= $\{10\overline{1}2\}<10\overline{1}1>$, Green= $\{11\overline{2}1\}<\overline{11}26>$, Aqua= $\{11\overline{2}2\}<\overline{11}23>$ and β phase in pink. b) Same area as a) but in IPF coloring with twin boundaries indicated as Black= $\{10\overline{1}2\}<10\overline{1}1>$, Grey= $\{11\overline{2}1\}<\overline{11}26>$. White indicates non-indexed regions and/or β . c) shows the in a) and b) marked section enlarged in the same coloring as b).

12.1.4. Summary and Conclusion

A systematic comparison of recrystallised versus slowly cooled and aged Ti6Al4V showed increased yield strength with ageing during quasi-static compression along the original RD of a cross-rolled bar in lab scale. Post-mortem EBSD analysis showed little twin activity in the RX sample and even less in the aged sample at a compressive strain of 0.09. Investigations on the binary Ti-Al system suggest that the increasing ordering towards Ti_3Al with ageing reduces twin activity. The role of slip localisation and the transformation of secondary alpha to beta need investigating to conclude why twin activity decreases with the applied ageing treatment.





Investigations on the binary Ti-Al system showed that ageing treatments lead to decreased work hardening rate and twin activity. It is of practical interest if this finding is also valid for industrial alloys containing more than 7at.% (4wt%) Al. of Therefore, comparison deformation а behaviour and microstructures of Ti5Al2.5Sn, produced on an industrial forging route, was accomplished after recrystallization (RX) and after ageing treatment (aged). The material was held at 815°C for 15hrs for recrystallization and for ageing additionally cooled with 10K/h to 400°C and held there for 48hrs, as listed in Tab. 4-2. Both treatments created an equiaxed microstructure, with about 66µm mean grain size, shown in Fig. 12-8 a). The distribution of the

Fig. 12-8: EBSD investigation on recrystallized Ti5Al2.5Sn: a) Bandcontrast map b) 0002 and 10-10 pole figures from c) macroscopic orientation map along FD in IPF-Z colouring. Orientation maps perpendicular to FD with d) 40µm and e) 2µm step size in IPF-Z colouring.

0002 pole has a preference in the transverse plane TD_{I} - TD_{II} (Fig. 12-8 b), but the texture is generally more randomised than textures from the laboratory rolling mill at Timet, Witton.

Macro zones were found in macroscopic orientation maps stretching over 4mm in width and more than 4mm in length, as presented in Fig. 12-8 c) and d). Microscopic orientation maps (Fig. 12-8 e) show small misorientations between grains within a macrozone and stripy areas along FD of grains with entirely different orientations.

Fig. 12-9: a) True-stress strain curve on Ti5Al2.5Sn for uniaxial compression along the former FD and b) the work hardening rate.

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Macroscopic compression testing along the original FD showed in RX and aged state a 0.2% yield strength of 750MPa, as it can be inferred from Fig. 12-9 a). The work hardening rate decreases slightly with ageing (see Fig. 12-9 b). However, RX samples loaded along FD to different plastic strains show significant differences in the 0.2% yield stress and the work hardening behaviour. Such variability is caused by macorzones with dimensions more than 2/3 of the sample diameter itself. This textural inhomogeneity may be reason for almost equal yield strength (±5MPa) when samples are compressed along the original FD or TD.



Microstructural observations at a compressive strain of 0.09 show barely any difference in the basal or prismatic pole intensity within 30° to the LD (see Fig. 12-10 a). Microscopic orientation maps of RX material show activity of $\{10\overline{1}2\}$ tension twins, and $\{11\ \overline{2}\ 1\}$ tension twins, as indicated in the bandcontrast maps by red and green twin boundaries, respectively (Fig. 12-10 b). Both twin types are only active in grains favourably orientated for twinning, in example with the c-axis almost perpendicular to the LD, and appear very narrow. No twins can be observed in hard orientated grains. Consequently the patchy texture dominates in which regions twinning occurs. The short ageing treatment

Fig. 12-10: EBSD investigations on material after 9% compression along FD: a) texture of compressed RX sample Band contrast map after compression of b) RX material and c) aged material.

reduced the twin activity dramatically and only $\{10\overline{1}2\}$ twins of few micrometers in size could be identified but $\{11\overline{2}1\}$ and $\{11\overline{2}2\}$ twins were virtually not active, as seen in Fig. 12-10 c).

he intensity increase during in-situ compression of recrystallized material at Engin-X is with -2.3 less pronounced than in Ti-13AI. The onset of twinning was identified at plastic strains of about 0.02, with the residual lattice strain on the c-axis in grain family favorably orientated for twinning from -600µm/m. The very small twin activity did not allow a relaxation of the residual lattice strains on the c-axis in transverse direction with increasing load as observed in the sample Ti-13AI. In order to conclude if ordering or slip localisation causes this decrease in twin activity, TEM or neutron diffraction work has to proof increased ordering with the applied ageing treatment. Investigations on slip localization by means of ECCI or DIC are required to show if the twin activity is suppressed due to slip localization.

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12.3. The effect of ageing on twinning in the Ti-Sn system

It was shown that ageing of Ti-7AI and Ti-10AI promotes SRO and reduces the work hardening capacity during compressive loading compared to solution treated material. This reduction is clearly based on the suppressive effect of ageing on twin formation but it remains unclear if deformation twinning is supressed due to the ordering of the solutes itself or indirectly by increased slip localisation. It is from fundamental interest if the ordering towards the DO₁₉ structure affects the deformation systems similarly in other alloying systems, such as the binary Ti-Sn system. In order to investigate the effect of ageing and possible ordering on the deformation behaviour, binary Ti-Sn alloys containing 1at.% and 3.4at.% Sn were compressed in solution treated and aged state. Aged samples were cooled from the RX temperature with 10K/h to 450°C and held for 5 days at this temperature shielded with argon (see Tab. 4-2), in analogy to ageing treatments on the binary Ti-Al alloys. Fig. 12-11 shows the a) flow curve and b) work hardening rate of RX and aged state. Adding Sn to Ti increases the 0.2% yield stress and the work hardening rate at higher plastic strains, as already discussed in chapter 9. The ageing treatment results in significantly dropping work hardening capacity of Ti-3Sn, to an equivalent level with Ti-1Sn without significant effect on the yield strength. Ti-1Sn seems to work harden similarly from yielding to strains of 0.09 after the ageing treatment, rather than continuously decreasing the work hardening rate with increasing state in the RX state.

A very similar trend was observed upon ageing of Ti-7AI and Ti-10AI and could be rationalised



with a loss in twin activity due to the formation of short-range order. If the fund hanism of twinning are defd identica the Ti-Al and Ti-Sn in expect to find svste eith Itwin nucleation leformed or twi microstruct ordering aged towar n low Sn Ti₃S concern reported ould be befor neutron inter diffraction d state

Tab. 5.6 Texture development of Ti2A

Fig. 12-11: ¹ is the stress strain binary alloys on a) the stress-strain curve, b) the work hardening behaviour

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12.4. Effect of alloying on ductility

Abstract

This chapter presents the tensile properties of cross-rolled binary model alloys containing AI, Sn or Zr as well as more complex alloys with increased V and O content. Additionally, forged bars of CP-Ti and Ti5Al2.5Sn are characterised. It can be seen that substitutional AI has the biggest strengthening potential in Ti at ambient conditions. However, addition of 1at.% Sn is more affective than the addition of 1at.% AI, but further Sn addition has little effect. A concentration of 3.5at.% of Zr, Sn or AI results in very similar yield stresses around 240 MPa-320MPa. Ti strengthens almost linearly with Zr addition, but over proportional between AI contents of 3.5 and 10at.%. Addition of AI and Sn decrease the ductility dramatically, but Zr only little. Interestingly, increased level of ordering coincides with increasing elongation in AI rich alloys. A decreasing likelihood of $\{11\overline{2}2\}$ twinning during compressive loading can be connected to decreasing ductility.

12.4.1. Introduction

Experimental results on tensile tests for CP-Ti [Tanaka 1975, Simbi 1996, Ouchi 1998, Warwick 2012a, Roth 2014] and the industrial alloys Ti6Al4V and Ti5Al2.5Sn [Leguey 2002, Littlewood 2012, Marmy 2001, Stapleton 2008, Li 2012, Kennedy 1982, Tanaka 1975, Warwick 2012b] have been performed in dependence of for instance grain size, oxygen content, processing route and loading direction. The ductility loss in the alloys was related to the loss of twinning as deformation mode, slip planarity, grain size reduction and α_2 formation. With AI as most important substitutional alloying element, major efforts were made on the binary Ti-Al system [Lienert 2009, Gysler 1982, Gysler 1977, Truax 1974]. Truax and McMahon suggest a dramatic decrease in ductility with already 2wt% (3.5at.%) Al addition but increasing ductility above 6wt% (10at.%). Surprisingly, ageing treatments of Ti-6wt%Al and Ti-8wt%Al (10 and 13at.%) improved the elongation to failure. But further Al addition to a concentration of 10wt%Al (16.5at.%) embrittles the material [Gysler 1982].

Oxygen as interstitial element in CP-Ti increases the anisotropy and the strength, but also reduces likelihood for twinning and ductility [Ouchi 1998, Brandes 2012]. The occurrence of twinning was connected to lower work hardening rates but therefore higher yield strength, in comparison of RD and TD tensile samples [Roth 2014]. The substitutional alloying element Zr is commonly used for spectacle frames. Addition of Zr substantially strengthens Ti, accompanied by a moderate ductility loss. When a certain amount of Zr has been added to Ti, the strength increase becomes less pronounced and the ductility improves again [Nakasuji 1996]. Other researcher report more linear behaviour with Zr addition and also dramatic effects of the heat treatment procedure, especially on ductility [Imgram 1962]. Work on binary Ti-Sn alloys only

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considers bending experiments and, just as in the case of Ti-Zr alloys, was only based on practical interests.

More systematic work is required to understand tensile properties in different Ti alloys. The following work focuses on the effect of Al, Zr and Sn on strength and ductility development, but also explores the effect of multiple alloying elements in Ti6Al4V, Ti-6Al-O and Ti5Al2.5Sn. The influence of grain size and starting texture are discussed.

12.4.2. Results of tensile tests

Initial state

The initial state of the alloys is described detailed for all alloys in chapter 5 and here only described briefly. Most alloys can be compared on an equiaxed grain size of approximately 80µm, but Ti-3Zr SG, Ti-10Zr SG and Ti6Al4V exhibit significantly smaller grain size. Furthermore, the investigated binary alloys show mostly very comparable starting textures, as seen on the low basal pole intensity along the former RD in the pole figures of Fig. 5-9 and on the basal intensity in the axial detector of Engin-X. Only the industrial alloys Ti6Al4V and Ti5Al2.5Sn exhibit basal intensity in the axial detector of Engin-X. Only minor distribution differences of the prismatic poles are present between the alloys, seen on the ratio of integrated intensity of $\{10\overline{1}0\}$ to $\{11\overline{2}0\}$ pole in the axial detector of Engin-X (Fig. 5-10). Schmid factors for the present basal ring texture have been calculated for uniaxial tension using Hexaschmid [Stark 2010]. The calculations suggest a high probability for prismatic slip (mprism<a>>0.4) in the majority of grains, but a low likelihood for basal slip (m_{basal<a>}<0.1). Pyramidal <a> slip has a rather low Schmid factor of m_{pyramidal<a>}~0.29 and is less likely to occur. Pyramidal slip systems with c-component have generally high Schmid factors $m_{\text{pyramidal} < +a} > 0.3$. $\{10\overline{1}2\}\langle\overline{1}011\rangle$ tension twins are not favoured due to the polar nature of twinning [Christian 1995], instead the $\{10\overline{1}1\}$ ($\overline{1}012$) compression twin is easy to activate. Due to the initially different starting texture in Ti6Al4V and Ti5Al2.5Sn basal slip and tensile twinning are more likely deformation mechanisms during uniaxial tension. However, as commonly accepted the relative CRSS values of the slip systems play an important role for their activation as well. The effect of grain size on the CRSS can be widely neglected as most alloys have 80µm grain size, but in Ti-10Zr and Ti6Al4V, which have only an α grain size of 30µm and 10µm, respectively. To cover this case tests on CP-Ti with different grain sizes have been conducted.

Tensile properties of binary Ti-Al alloys

Fig. 12-12 shows flow curves of Hounsfield tension samples of the alloys Ti-3AI, Ti-7AI and Ti-10AI in recrystallised state. It can be seen that AI addition increases the flow stress significantly and reduces ductility, most pronounced in Ti-10AI. Ti-7AI shows the highest work hardening rate. Fig. 12-12 also shows the flow curves of sheet tension samples for Ti-0AI, Ti-7AI, and Ti-10AI in RX state. Unfortunately no sheet sample of Ti-3AI was available due to material Arnas Fitzner, PhD Thesis, 2014

shortage. To implement Ti-3AI in the comparison of tensile properties of the sheet samples, tensile tests on both geometries are compared initially. Afterwards, the sheet samples are compared as function of alloying and grain size to finally evaluate compositional effects on strength and ductility.

The Hounsfield geometry shows higher stresses and lower elongation to failure than the sheet samples during tensile testing with constant initial strain rate (see Fig. 12-12). Both effects may be caused by the increases surface to volume ratio in the sheet samples, enabling the material to change shape in the gauge section easier, and the influence of the elastic spring back of the grips in both sample geometries. However relative comparisons reveal same trends in the alloys Ti-7AI and Ti-10AI: AI addition strengthens but decreases ductility. The yield stress of the sheet samples within one alloy batch is reproducible, but elongation values scatter by ±3% of the average value. Differences between batches of the same alloy can be significant. Tensile samples of "Ti-10Al low Oxygen" (red dashed line in Fig. 12-13 a)) show 30MPa higher flow stress compared to the second batch "Ti-10AI II" (red drawn line in Fig. 12-13 a). A by 800ppm higher O level in "Ti-10Al low Oxygen" (1800ppm instead of 1000ppm) may explain the slightly increased strength. Comparisons across both sample geometries cannot be made directly but results of the sheet samples can be studied confidently. Truax and McMahon as well as Blackburn and Williams evaluated the tensile properties of Ti with 2wt%Al (3.5at.%) in context with CP-Ti and AI contents to 8wt% (13at.%) [Blackburn 1969, Truax 1974]. Their data match reasonably well with the current datasets on the sheet samples. Therefore, lines in Fig. 12-13 b) to e) of the sheet samples were adjusted in accordance to the previous literature results and the Hounsfield geometry at 3.5at.%.



Fig. 12-12: True tensile stress-strain curves for Hounsfield and sheet sample geometry on binary Ti-Al alloys after recrystallization treatment.

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Fig. 12-13: Summary of tensile data of AI containing samples a) Yield point: b) Ultimate stress; c) Elongation to failure; d) Reduction in area

Significant increase in yield strength can be found until 10at.% AI addition and only a little increase to 13at.% AI (Fig. 12-13b). The initial strengthening with addition of 3.5at.% AI is little but a much more pronounced effect can be noted from 3at.% onwards up to 10at.%AI, followed by a little strength increase to 13at.% AI. Neither yield strength nor upper strength are Arnas Fitzner, PhD Thesis, 2014

significantly affected by the ageing treatment in Ti-7AI, but both properties increase by ageing Ti-10AI (only one sample tested). The ultimate strength develops generally similarly to the yield strength, showing little increase with initial AI addition, more pronounced increase from 3.5 to 10at.% Al and again only little increase from 10 to 13at.% Al. But Al affects the ductility detrimentally up to 10at.% and surprisingly positive comparing Ti-13Al and Ti-10Al (Fig. 12-13 d). Ageing of Ti-7AI has no significant effect on ductility, but the aged Ti-10AI sample exhibits improved elongation to failure and a lowest R_A . Values of R_A are summarised in Fig. 12-13 e) and decrease strictly monotonic with AI concentration, with Ti-10AI and Ti-13AI on a similar level. Careful examination of the stress strain curves (Fig. 12-13 a) suggests that the stable elongation is improved in Ti-13AI, compared to Ti-10AI but the ductility after the ultimate strength is reduced. The work hardening rate θ , shown in Fig. 12-14, equals 0 when the ultimate stress is reached and facilitates comparisons of the end of uniform elongation. Significantly later neck formation is found in aged Ti-10AI and CP-Ti, while the other Ti-AI alloys show very similar work hardening behaviour. The alloys work-harden more rapid than CP-Ti after the yield point, with Ti-7Al work-harden fastest initially, but θ decreases with plastic strain rapidly. CP-Ti exhibits almost constant θ and therefore overall highest work hardening capacity. The ageing treatment of Ti-10AI stabilised the work hardening behaviour, suggesting that the same deformation mode is active to higher strains. However, the fluctuations of the calculated work hardening rate is too big to come to conclusions between the RX alloys.



Fig. 12-14: Work hardening rate θ for the binary Ti-Al system for the full test a) and for the plastic region only b) as function of true stress.

Micrographs of RX state, the grip section and sections corresponding to strains of 0.01, 0.04 and 0.09 of the tested Hounssfield tensile sample are presented in Fig. 12-15. The grip section of Ti-3AI exhibits single twins, but no twin can be found in Ti-7AI and Ti-10AI. The RX state is twin free. All sections of the tensile sample show an increasing amount of pores with increasing AI content, which is not as pronounced in the RX state. While twins are present in all sections of the tested Ti-3AI Hounsfield sample and span across a grain, only few twins are present in Ti-7AI. Ti-10AI exhibits only singled twins near the neck, where stress states become increasingly complicated. The voids near the neck in Ti-10AI can be up to 100µm long, but only several tenth Arnas Fitzner, PhD Thesis, 2014



of μ m in Ti-7AI, while Ti-3AI shows no evidence of voids near the necked region. This indicates that the twin activity decreases with increasing AI content and void formation may cause failure in Ti-7AI and Ti-10AI.

Fig. 12-15: DIC micrographs of RX state and sections corresponding to strain values of 0, 0.01, 0.04 and 0.09 of Hounsfield tensile samples of Ti-3AI, Ti-7AI and Ti-10AI tested along RD to failure.

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Before the Ti-Zr binary system and Ti6Al4V can be understood, the effect of grain size on tensile propertied has to be evaluated. Therefore, high purity Ti was tested on three grain sises in uniaxial tension and all flow curves are plot in Fig. 12-16 a). CP-Ti 870 exhibits the biggest grains with approximately 180µm in diameter, CP-Ti 750 exhibits about half of that grain size and CP-Ti forge with about 30µm the smallest grain size. Yield and ultimate strength (Fig. 12-16 b) increase with grain size reduction linearly on the Hall Petch plot between the three batches of material, in accordance to the literature [Fishburn 1976]. The forged, small grained CP-Ti bar shows biggest scatter between the two samples in yield and ultimate strength. This scatter may indicate texture inhomogeneity in the forged bar across the radius. However, a good linear fit with R^2 =0.973 for the Hall-Petch slope k=0.9MN/mm^{3/2} of the yield strength confirms the Hall-Petch relation.



Fig. 12-16: Tensile curves a), yield and ultimate stress b) and elongation ϵ_F and reduction in area R_A c) for grade 1 CP-Ti in different grain sizes and textures.

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The ductility values (Fig. 12-16c) do not follow a clear trend but the reduction in area R_A improves linearly with decreasing grain size. The initial improvement of elongation ϵ_F with grain size reduction in the cross-rolled bars of CP-Ti is followed by lowest elongation values in the forged CP-Ti with the smallest grain size. The big-grained and cross-rolled CP-Ti samples show a third more elongation and a higher work hardening rate in comparison to the forged bar. The ductility drop in the forged bar indicates a dramatic effect of the starting texture on ductility.

Fig. 5-9 shows the basal and prismatic textures of all three materials and it can be seen that the cross-rolling resulted in almost homogeneous distribution of the basal poles in the ND-ND plane but forging in intensity maxima with almost no intensity in between. The prismatic pole is consequently less homogenously distributed in the forged material. Therefore, it is inappropriate to compare effects of alloying addition across different processing routes and the effect of Zr addition can only be studied on the cross-rolled bars.

Ti-Zr

Two tensile tests were successfully performed on Ti-3Zr with approximately 80µm grain size, and on Ti-10Zr SG with only around 30µm grain size. No samples of Ti-3Zr SG were available due to material shortage. All flow curves are presented in Fig. 12-17 a). The yield strength of samples summarised in Fig. 12-17 b) increases less than linear with Zr addition. The smaller grain size in Ti-10Zr suggests, according to the Hall Petch relationship decreased strength for comparable grain size to Ti-3Zr. Results of cross-rolled CP-Ti confirm the relationship between grain size and yield strength for the present starting texture for grain sizes of 180µm and 80µm, as described above. Therefore, the strengthening is expected to be almost linear with Zr addition, as also suggested by Nakasuji and Okada [Nakasuji 1996]. The work hardening rate of Ti-3Zr is substantially above CP-Ti 750, but similar to Ti-10Zr. Despite the smaller grains size in Ti-10Zr, which suggests a reduced work hardening rate according to investigations by Del Valle and co workers on Mg alloys [Del Valle 2006], Ti-10Zr still work hardens substantially. Consequently, the present results suggest that Zr addition increases the work hardenability of Ti significantly and counteracting the grain size difference. The combination of uniform elongation and work hardening behaviour leads to comparably high ultimate strength in Ti-3Zr and the biggest difference to the yield strength, as can be inferred from Fig. 12-17 c). Fig. 12-17 d) suggests a linear reduction of the elongation to failure with Zr addition. Both, CP-Ti 750 and Ti-3Zr offer excellent ductility, but Ti-10Zr SG only about 25%. The reduction in area decreases linearly with Zr addition, shown in Fig. 12-17 e). The present results confirm the proposal by Sen et al., that the increasing SFP with Zr leads to more work hardening.

Ti-Sn

Sn addition impacts the yield strength, ultimate strength, elongation to failure and reduction in area very pronounced with addition of 1at.% Sn, but further Sn addition has little effect, as

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shown in Fig. 12-17 a)-e) together with data on the Ti-Zr system. While the data points in the Ti-Zr system depend almost linearly on the Zr content, a power law fit captures the behaviour of the yield stress, the ultimate strength and the elongation to failure best as function of the Sn content. The initial increase in yield and ultimate strength is connected to a fatal ductility loss in Ti-1Sn, but the strength levels increase only little to Ti-3Sn. The elongation to failure and the reduction in area are almost identical at both Sn concentrations and approximately reduced by factor two in comparison to CP-Ti 750.



Fig. 12-17: Tensile curves of Ti-Sn and Ti-Zr system a); Yield point b); Ultimate stress c); Elongation to failure d) and Reduction in area e). Arnas Fitzner, PhD Thesis, 2014

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Al rich alloys

Compositions of multiple elements can show overall better properties than the binary compositions. As a reference, flow curves of Ti-10Al are presented in Fig. 12-18 a) containing ~1000ppm O (Ti-10Al II) and ~1800ppm O (Ti-10Al low O). O addition to Ti-10Al leads to significantly strengthening (see Fig. 12-18 b). While no effect on the ductility can be observed between ~1000ppm and ~1800ppm O, at ~5000ppm a reduction of the elongation to failure and reduction in area is prominent (Fig. 12-18 c). Previous work suggests that increased slip planarity and increased risk of grain boundary cracking reduce the work hardening capacity and stable elongation [Truax 1974, Williams 2002]. The reduction in uniform elongation can only be confirmed for one of the two tested samples. However, both samples show almost constant work hardening rate until the necking occurs. But both samples of Ti-10Al-O elongate less than 2% after necking before a brittle fracture, resulting in low R_A .

The yield and ultimate strength of Ti6Al4V are about 50MPa above values of Ti-10Al-O (Fig. 12-18 a) and b). Furthermore, Ti6Al4V exhibits more homogeneous elongation to failure at a similar (or higher) level compared to Ti-10Al and Ti-10Al-O and improved reduction in area. The work hardening behaviour is nearly constant throughout the stable elongation in Ti-10Al-O, while Ti6Al4V shows a gradual decrease in the work hardening. Therefore less slip localisation is expected in Ti6Al4V.

A fair comparison between Ti6Al4V and Ti-10Al with high and low O content requires consideration of the starting texture, as described by Fundenberger et al. and Roth et al. on Ti6Al4V and CP-Ti [Fundenberger 1997, Roth 2014]. While Ti-10Al and Ti-10Al-O were pulled along the former RD with barely any basal poles aligned in tension axis, Ti6Al4V exhibits more than 10% of the basal pole orientated in RD//LD. The more heterogeneous α -texture and a more complex microstructure with primary alpha, 5% secondary α lamellas and approximately 1% β phase make it difficult to compare the cross-rolled alloys directly. Comparing these results to the industrial alloy Ti5Al2.5Sn is even more difficult in the present case.

The tension direction of Ti5Al2.5Sn is perpendicular to the former FD, instead of parallel, due to material availability. With LD//TD a much higher fraction of the c-axis is aligned in the tensile axis, though leading to higher initial yield but lower elongation to failure and work hardening capacity [Fundenberger 1997, Roth 2014]. The very patchy texture, full of macro zones with more than 1mm in diameter, does not guarantee comparable textures in both tested samples and may cause the experienced scatter in yield and elongation. A macrozone could fill the entire gauge section. The yield strength of Ti5Al2.5Sn lies just above the strength of Ti5Al2.5Sn lies even below the values of Ti-10Al caused by a low work hardening rate. By similar reduction in area R_A with the Ti-10Al with high and low O concentrations, Ti5Al2.5Sn exhibits decreased

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elongation (Fig. 12-18c). The low elongation also impacts the total work hardening negative until the ultimate strength is reached.

However, macro zones in Ti6Al4V and especially in Ti5Al2.5Sn with width and thickness above 1mm can change the texture of the tested volume significantly. A direct comparison to the binary model alloys is therefore not possible. In order to compare the industrial alloys with the model alloys either comparable starting textures need to be present or the anisotropy evaluated carefully. Apart from those concerns, the industrial workhorse Ti6Al4V shows highest strength values without sacrifices in ductility during tension tests at ambient temperature.



Fig. 12-18: Tensile curves for AI rich Ti alloys a); Yield and Ultimate stress b); Elongation (triangles) and Reduction in area (crosses) c).

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Results summary and discussion

For better overview across the data only one representative tensile curve per tested alloy is plotted in Fig. 12-19. The three different substitutional alloying elements impact the properties in fundamentally different ways (See Fig. 12-20). Prismatic slip was reported as dominant deformation mechanism during tension of CP-Ti in varying conditions [Rosi 1953, Li 2012], resulting in cellular dislocation structures towards higher strains [Lederich 1978] and only little slip localisation in bands [Li 2013]. Tanaka and Horiuchi identified deformation twinning on rolled plate of large grained CP-Ti as active deformation mechanism by acoustic emission measurements and optical microscopy, but not at a grain size of only 10µm [Tanaka 1975]. The comparison of the forged and cross-rolled bar with different grain sizes is further complicated by the influence of the processing route on ductility and strength. Xu and Zhu [Xu 2012] suggested higher strength and lower ductility values for forged CP-Ti bars compared to rolled plate, rationalised by twins in the forged structure. Tensile tests on Mg alloys processed on different routes indicate reduced elongation with sharper basal textures [Del Valle 2006]. Despite the low O content in the forged CP-Ti bar, the elongation is below the cross rolled bar, suggesting a very strong effect of the processing route and/or the basal texture. Consequently, it is unwise to include the results of the forged CP-Ti in the comparison of the cross-rolled Ti-Zr alloys with similar grain size and the effect of Zr is evaluated on two grain sizes. Fig. 12-20 a) shows that Zr strengthens Ti slightly less than linear and reduces the ductility linearly with concentration as well, accounting for the grain size reduction. Solid solution strengthening laws considering misfit and solute concentration [Dieter 1986] describe such behaviour. Al addition strengthens Ti initially similarly to Zr, but becomes much more effective from 7at.% until 10at.%. This over proportional strengthening of AI is connected to SRO formation, as already described by Truax and McMahon [Truax 1974] and in chapter 6. Completion of short range ordering and formation of the long range ordered Ti₃AI at higher AI concentrations increases the strength moderately, similarly to the initial strengthening with AI or Zr addition. Increased slip planarity is a direct consequence of the ordering [Van de Walle 2002] and leads to strain localisation but surprisingly not to earlier neck formation. But slip planarity and shear bands formation can also be associated with a lowering in work hardening rate [Truax 1974].

While basal slip becomes more likely with increasing AI content due to a smaller CRSS ratio to prismatic slip [Williams 2002], basal slip is reported [Leguey 2002] as dominant deformation mechanism in Ti5Al2.5Sn and Ti6Al4V. Prismatic and pyramidal <a> as well as pyramidal <c+a> slip and deformation twinning are activated to smaller extend [Tanaka 1975, Kennedy 1982, Li 2012, Li 2013]. Prismatic slip leads to small rotations around the <c>-axis but basal slip rotates the crystal around the <a>-axis [Chun 2010] and changes the Schmid factor for all deformation system much more than prismatic slip does. The transition from prismatic to basal slip may therefore explain the increased work hardening rate and the ductility loss with increasing AI content.

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Addition of Sn to Ti shows a very strong effect on yield strength and ductility with the first at.%, but no major property changes with further Sn addition, similarly to behaviour in bending of as cast Ti-Sn alloys [Hsu 2009]. The dramatic drop in ductility may be connected to either increased void formation or dramatically increased basal slip activity.

In analogy, the low ductility of pure Mg or Be at room temperature compared against pure Ti or Zr can be rationalised with basal slip as dominant mechanism in Mg and Be, but prism slip in Ti and Zr [Rosi 1953, Walsh 2009].



Fig. 12-19: Representatives curves of sheets tensile samples for a) binary Ti-Al system, b) complex alloys, c) binary Ti-Sn and Ti-Zr system, d) CP-Ti produced by different manufacturing routes.

Grain refinement and texture changes by twinning are strongly limited but subgrain form by slip during deformation of Ti5Al2.5Sn and Ti6Al4V [Leguey 2002] can lead to Hall-Petch strengthening with increasing deformation. However, the reduced ductility of Ti5Al2.5Sn in comparison to Ti-10Al, or any other binary alloy, may be caused by the forging texture. Oxygen addition to Ti-10Al was associated with pronounced shear band formation [Truax 1974] and results in a lowered work hardening rate and ductility, as also observed with increasing A content in the binary Ti-Al system. The fine grained duplex microstructure of Ti6Al4V shows excellent strength and ductility values. The role of the beta-phase during deformation remains unclear, but it could allow the grain rotation by basal slip.

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Fig. 12-20: Mechanical properties of sheet samples a) Yield stress; b) Ultimate stress; c) Elongation to failure; d) Reduction in area.

12.5. Fe segregation in Ti-Zr system

Heat treatments in the Ti-Zr system lead to segregations on grain boundaries and triple points on optical micrographs above the β -transus, as it would be expected from the phase diagram. Optical micrographs for documentation are presented in an undergraduate project [Ji 2012]. Interesting was that traces of Fe were found after prolonged annealing in or close to the beta phase on grain boundaries and triple points by high resolution EDX, as shown in Fig. 12-22. EDX point scans indicate contents above 0.5at.%Zr in those triple points and less than 0.1at.% in the grain centre. This suggests that Fe diffuses into the β phase at high temperature. Similar behaviour was observed in Ti6Al4V during this work, where Fe traces gathered in the V rich β phase. Perez et al. already describe Fe enhances the diffusion of elements like AI and Ta [Perez 2003]. The role of Fe on diffusion enhancement of V and Zr on the recrystallisation behaviour is poorly understood and required further investigation.



Fig. 12-21: Backscattered electron images (BSE) and EDX maps of Ti-10Zr alloy with OPS finish after a) 24h at 750°C, b) 24h at 800°C and c) 65h at 800°C.



Fig. 12-22: BSE image and high resolution EDX on Ti-10Zr after 65hrs at 800°C showing Fe segregation at triple points and grain boundaries.

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13. Summary

Improved knowledge about deformation twinning in Ti and its alloys as well as in other hcp metals is of practical relevance as twinning affects the texture evolution during forming and surface treatments like shot peening or machining. Textural differences dictate the mechanical anisotropy of a product and impact its lifetime in service for various reasons. This raises fundamental interest on the mechanism by which the addition of Al and O reduce the twin activity of Ti. This dissertation project explores the activity of deformation twinning in a range of binary model alpha-Ti alloys containing AI, Sn or Zr as well as in more complex AI-rich model Tialloys and industrial forgings. Microstructures with equiaxed grains of about 80µm in size and basal ring textures were created by laboratory cross-rolling in most binary model alloys to evaluate the effect of the solute on $\{10\overline{1}2\}<10\overline{1}1>$ twinning independent of grain size, texture and loading condition. Only the grain size of an alloy containing 10at.% Zr did not exceed 30µm, which is believed to origin from grain boundary segregations. In approach to evaluate the effect of Zr independent of the grain size from 0 to 10at.%, cross-rolled material containing 3.6at.%Zr and forged CP-Ti were investigated on a smaller grain size additionally. Despite similar microstructures in the forged and cross-rolled material, textural differences between both manufacturing routes affect the local grain neighbourhood and the ease of slip transfer across grain boundaries. Differences in crystallographic texture, microstructure and local neighbourhood affect the micro- and macro-mechanical behaviour and derogate from evaluations of solute effects on deformation mechanisms. Consequently, the industrially forged CP-Ti and Ti5Al2.5Sn as well as laboratory cross-rolled Ti6Al4V require separate evaluation. Therefore this dissertation focuses on the effect of alloying on $\{10\overline{1}2\}<10\overline{1}1>$ twin formation solely in the model alloy systems. The effect of grain size variation, at almost identical neighbourhood, is evaluated on Ti-3at.%Zr towards smaller grains and additionally on CP-Ti towards larger grains. Quasi-static compression at ambient temperature to small and moderate plastic strains along the original RD promotes $\{10\overline{1}2\}<10\overline{1}1>$ tension twinning with the current starting texture.

It was found that addition of up to 10at.% Zr increases the 0.2% proof stress of Ti almost linearly, typical for solid solution strengthening. The effect of grain size is comparably small. Addition of 1at.%Sn strengthens Ti very pronounced, but further addition to a maximum of 3.4at.%Sn has limited effect. The strengthening of 3.5at.%Al addition is moderate and similar to the effect of Zr but lower than Tins effect. However, further Al addition to 10at.% increases the yield strength over proportionally, attributed to the presence of SRO towards Ti₃Al as found by TEM and neutron diffraction analyses. The onset of fully ordered Ti₃Al in Ti-13Al has only moderate effect on the yield strength due to the semi-coherent nature of Ti₃Al and lacking solid solution strengthening. While random substitutional solid solution strengthening by Al, Zr or Sn not only increases the strength but also the work hardening capacity, the onset of ordering reduces the work hardening capacity. This reduction is already present in recrystallised Ti-10Al Arnas Fitzner, PhD Thesis, 2014

but more pronounced in Ti-13AI or after ageing treatments, promoting ordering from as little as 7at.%AI as seen on long d-spacing neutron diffraction spectra of WISH, ISIS.

The change in work hardening behaviour is related to the nature of deformation by slip and twinning. Nanoindentation on recrystallised and deformed samples revealed that slip work hardens the material only little but the lattice rotation induced by $\{10\overline{1}2\}<10\overline{1}1>$ tension twins hardens the material significantly, which is thought to be enhanced by residual stresses in the twin. High-resolution strain mapping by digital image correlation further supports a pronounced effect of texture hardening and residual stresses, as no significant shear strain accumulates within a formed twin below strains of 0.08.

The role of $\{10\overline{1}2\}<10\overline{1}1>$ twinning on work hardening was further estimated by EBSD orientation map analyses at strains of 0.01, 0.04 and 0.09 and continuously by in-situ neutron diffraction measurements at Engin-X, ISIS. Considering both techniques, alloying barely changes the overall twin fraction at strains of 0.09 when the solute is in random solution. While the texture hardening is expected to be approximately constant in those alloys (CP-Ti, Ti-1Sn, Ti-3Sn, Ti-3Zr, Ti-10Zr, Ti-3Al, Ti-7Al) the work hardening rate increases nevertheless with increasing deformation. Those increasing work hardening rates are rationalised with an increased twin boundary density in all three binary systems as seen in orientation maps. Neutron diffraction data suggest that twinning starts at lower plastic strains and lower residual lattice strains with increasing solute content, leading to thinner twins at overall similar fraction. The resulting grain refinement is thought to impede dislocation glide during deformation and increase the work hardening rate. Facilitated twin nucleation as well as impeded twin growth in fcc materials were previously connected to a decrease in stacking fault energy with alloying, and current results suggest this to be also valid for Ti-based hcp alloys in random solution. In principle lowering the SFE facilitates dislocation dissociation, which was described as essential for twin nucleation, and impedes cross-slip, required for twin growth in fcc metals. Binary Ti-Zr alloys were reported to exhibit higher SFP, or lower SFE, compared to the binary Ti-Al and Ti-Sn systems and exhibit most pronounced grain refinement during deformation. The binary Ti-Zr alloys even exhibit flow softening, which is thought to result from pronounced $\{10\overline{1}2\}<10\overline{1}1>$ twin nucleation and easy propagation.

However, formation of short range ordering towards Ti_3AI in the Ti-AI system decreases the overall $\{10\overline{1}2\}<10\overline{1}1>$ twin activity significantly despite continuously increasing SFP with solute content. The reduced twin activity lowers the work hardening capacity in comparison to random solid solutions, especially noticeable after ageing. While ageing treatments to promote ordering towards the DO₁₉ structure reduced the overall twin activity in the industrial composition of Ti6AI4V and in industrially forged Ti5AI2.5Sn, the work hardening rate is barely affected due to the small twin activity in the recrystallised states. Ageing treatments in the binary Ti-3Sn model alloy indicated reduced twin activity by a dramatic loss in work hardening capacity during uniaxial compression.

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It is difficult to judge if the ordering itself or the changes it imposes on the slip character supresses the twin activity. Experiments and first-principles calculations conducted previously established that the formation of ordering towards Ti₃Al leads to slip localisation. Strain mapping in sub-micrometer resolution using digital image correlation (DIC) confirmed the dominance of prismatic slip in CP-Ti and slip localisation on basal and prismatic planes with Al. In addition, the DIC strain maps confirmed that basal and prismatic slip are almost as likely in Ti-10Al and showed for the first time substantial activity of prismatic slip prior to $\{10\overline{12}\}<10\overline{11}>$ twinning and activity of basal slip prior to $\{11\overline{2}1\}<\overline{11}26>$ twinning.

The transition of the slip character towards basal slip and slip localisation on prismatic planes with increasing AI content may therefore be responsible for increased likelihood of $\{11\overline{2}1\}<\overline{11}26>$ twinning and declining $\{10\overline{1}2\}<10\overline{1}1>$ twin activity with increased AI or Sn content. The increasing c/a ratio in those two alloying systems seems of minor importance compared to the changing slip character as only $\{11\overline{2}1\}<\overline{11}26>$ twins are affected but not $\{10\overline{1}2\}<10\overline{1}1>$ twins. Slip localisation leads to more than 50 times of the applied compressive strain in single slip bands in Ti-10AI and surrounding areas of low strain. This changes character and distribution of dislocations, which are required for twin nucleation. The much more heterogeneous stress and strain states possibly reduce the ability of the matrix to accommodate the rather homogenous shear strain of a twin.

It is proposed that twinning is supressed because of the slip localisation instead of the ordering itself. This proposal is further supported by a comparison of Ti-10AI at high and low Oxygen content, where O strongly supresses twin activity. This suppression cannot be explained with the similar states of ordering towards Ti₃AI in both alloys but with reported substantial slip localisation with either addition of O to Ti or ordering towards Ti₃AI.

The nature of $\{10\overline{1}2\}<10\overline{1}1>$ twinning is important for the texture evolution during forming. However, $\{10\overline{1}2\}<10\overline{1}1>$ tension twinning is an unlikely deformation mechanism during tensile loading along the RD and barely affects the tensile properties. Tension along the RD promotes $\{11\overline{2}2\}<\overline{11}23>$ compression twins instead. The barely altered likelihood of $\{11\overline{2}2\}<\overline{11}23>$ compression twinning in the binary Ti-Zr alloys during compressive loading correlates with a moderate ductility loss during tension. The suppression of $\{11\overline{2}2\}<\overline{11}23>$ compression twins during compressive loading with increasing Al or Sn content can be related to the ductility decrease.

The activity of $\{10\overline{1}2\}<10\overline{1}1>$ tension twinning is of minor importance for practical applications which require ductility but may be interesting for living predictions of machined parts. Active $\{11\overline{2}2\}<\overline{11}23>$ compression twins improve the tensile properties.

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14. Future work

To confirm the suppressive effect of ordering on twin formation and work hardening in the binary Ti-Sn system and in Ti5Al2.5Sn further diffraction work is required to access the state of ordering in those materials and the twin activity in the aged Ti-Sn alloys. Furthermore, it needs to be established that not ordering itself but the change ordering imposes on the character of deformation slip reduces twin activity. Therefore, the relative activity of slip systems in the binary Ti-Sn and Ti-Zr alloys may reveal new insight in the role of slip, the c/a ratio and the stacking fault energy on twin formation. Further microstructural work is required to explain how increased ordering in Ti-13Al and in aged Ti-10Al increases the elongation to failure and if void formation is the dominating failure mechanism during tensile testing in the binary Ti-Al alloys or the transition from dominant prismatic slip in CP-Ti to pronounced basal slip in Al rich alloys. The binary Ti-Sn and Ti-Zr systems can be used as a reference to keep parameters such as the c/a ratio or the degree of ordering constant.

Method of choice for characterising slip is high-resolution digital image correlation. However, the strain mapping as accomplished in this study is too time consuming and not practical. The development of in-situ compression-tension rigs allowing working distances below 5mm and much improved alignment procedures between the DIC strain maps and the corresponding EBSD map are vital for a wider success of this technique. The correlation of whole stitched image maps would facilitate high-resolution strain mapping significantly and allow overnight jobs with small plastic strain increments. Repetition of the DIC strain mapping experiments on compression samples showing compression twinning is required to analyse slip-twin interactions more comprehensively and to observe if prismatic slip in compression twins is required to form secondary tension twins. Using finer macroscopic strain increments would allow better understanding of the interactions between slip and twins. Ultimately, modelling neighbourhood effects using finite element methods is admirable to analyse the strain accumulation before twin formation and during twin growth. Furthermore, a quantitative analysis of strains accommodated by each slip system would enhance the power of high-resolution strain mapping by DIC tremendously, compared to the qualitative analysis as performed in the present study. Another huge challenge is the application of DIC strain mapping during in-situ deformation in a TEM. With TEM images in lattice resolution, DIC strain maps could theoretically have a sub-lattice resolution in the strain map due to the interpolation of single pixle during the correlation algorithm. Once experimental difficulties can be resolved, this approach should reveal strains in atomic scale and give new insights into dislocation migration, which may help to simulate deformation by physical laws and quantum mechanics.

Apart form the rather fundamental quests set by this work, it as from practical interest to make use of the acquired data. One example is the machining of Ti alloys where twins form readiliy on the machined surface and may initate cracks and accelerate the oxidation behaviour at elevated

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temperatures during the life of the part. The lifetime of machined Ti parts could be improved if cutting stresses during the machining process could be kept below the critical stress for twin initiation. Fig. 14-1 a) summarises the critical stresses for twin initiation, estimated by in-situ neutron diffraction during compression experiments along the RD, for the alloys of the present study as function of the AI equivalent in wt.%, given by Equation 3-5. Further work has to calibrate those critical stresses for conditions during the cut itself, where strain rate and temperature deviate signifacntly form values in the present study and may alter the critical twin stress. Under current conditions the critical stress depends almost linealy on the AI equivalent in wt.%, shown in Fig. 14-1 a) for all alloys. Significant deviations occur when the critical stress is plotted as function of the AI equivalent in at.% with the same factors as in Equation 3-5. In order to promote the use of at.% instead of wt.% in praxis, in Fig. 14-1 b) plots the critical stress for twin initiation as function of the AI equivalent in at.% as given by Equation 14-1. Equation 14-1 is an adaptation of Equation 3-5 with adjusted factors according to the twin stress for substitutional elements and including *N* and *C* to appreciate their strong effect on phase stability and mechanical properties.





Fig. 14-1: True stress for twin initiation estimated by in-situ compression experiments along the RD on Engin-X as function of the AI equivalent for all alloys of this study in a) wt.% and b) at.% according to Equation 14-1.

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