

The University of Manchester

"High" Temperature Oxidation Studies of Ni-base Alloys: Understanding the Role of the "Precursor Events" during the Early Stages of Stress Corrosion Cracking

> A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy (Ph.D.) in the Faculty of Science and Engineering

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# List of Acronyms

APT	Atom Probe Tomography
AsB	Angle Selective Backscattered
ATEM	Analytical Transmission Electron Microscopy
BSE	Backscattered Electron
BRW	Boiling Water Reactor
BF	Bright-Field
CCD	Charge-Coupled Device
CERT	Constant Extension Rate Tensile
CL	Constant Load
CER	Contact Electric Resistance
CRDM	Control Rod Drive Mechanism
CEPM	Corrosion-Enhanced Plasticity Model
CGR	Crack Growth Rate
CSLB	Coincidence Site Lattice Boundary
DF	Dark-Field
DIGM	Diffusion Induced Grain Boundary Migration
EDM	Electrical Discharge Machining
EDS	Energy Dispersive Spectroscopy
EcP	Electrochemical corrosion Potential
EBSD	Electron Back Scatter Diffraction
EELS	Electron Energy Loss Spectroscopy
EsB	Energy selective Backscattered
FEG	Field Emission Gun
FIB	Focus Ion Beam
GA-XRD	Grazing Angle X-Ray Diffraction
GB	Grain Boundary
HAADF	High Angle Annular Dark Field
HELP	Hydrogen Enhanced Localized Plasticity
IG	Intergranular

IGSCC	Intergranular Stress Corrosion Cracking
INCO	International Nickel Company
LOM	Light Optical Microscope
LPSCC	Low Potential Stress Corrosion Cracking
MA	Mill Annealing
NPP	Nuclear Power Plant
NFZ	Nodule Free Zone
OPS	Oxide Polishing Suspension
PPR	Partial Pressure Ratio
PIO	Preferential Intergranular Oxide
PWR	Pressurized Water Reactor
PWSCC	Primary Water Stress Corrosion Cracking
RUB	Reverse U-Bend
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
SIMS	Second Ion Mass Spectrometry
SE	Secondary Electron
SAED	Selected Area Electron Diffraction
SIO	Selective Internal Oxidation
SDD	Silicon Drift Detector
SSRE	Solid State Reference Electrode
SA	Solution Annealed
SCC	Stress Corrosion Cracking
TT	Thermally Treated
TEM	Transmission Electron Microscopy
XRD	X-Ray Diffraction
YSZ	Yttria Stabilized Zirconia (Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> )

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## Abstract

Primary Water Stress Corrosion Cracking (PWSCC) of Ni-base alloys, such as Alloy 600 and Alloy 690, still remains one of the main issues in Nuclear Power Systems (NPPs). The Internal Oxidation model has been proposed by Scott and Le Calvar to develop a mechanistic understanding of the early stages of PWSCC and more recent advanced characterizations have consolidated this model. Preferential intergranular Oxide (PIO) have been observed to penetrate along High Angle Grain Boundaries (HAGBs) that exhibits local Diffusion-Induced Grain Boundary Migration (DIGM). However, the role of these "precursor events" (namely PIO and DIGM) in the early stages of PWSCC is still unclear and the role of GB migration on crack initiation has never been clarified.

In this study, oxidation experiments were performed in a low pressure superheated H<sub>2</sub>steam system that is capable of accelerating the oxidation kinetics of Ni-base Alloys. The capability of the H<sub>2</sub>-steam system to reproduce the correct Electrochemical Corrosion Potential (EcP) with respect to the Ni/NiO transition was assessed by *in-situ* electrochemical measurements with a Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> solid state reference electrode. The environmental conditions reproducing the Ni/NiO transition were identified between 372 °C and 480 °C and confirmed the possibility to use the superheated H<sub>2</sub>-steam as surrogate environment to perform oxidation experiments in conditions that are relevant to PWR primary water.

Solution annealed (SA) Alloy 600 samples with an OPS surface finishing were exposed to H<sub>2</sub>-steam at 480 °C at different oxidizing conditions to clarify the role of PIO/DIGM and local microchemical segregation during the early stages of PWSCC. Advanced electron microscopy techniques showed that the PIO was more susceptible to occur under reducing conditions, whereas DIGM occurred independently from the environment. These results suggest that DIGM is a not sufficient condition for the occurrence of PIO and subsequent SCC initiation. Furthermore, it was found that SCC initiation occurred in correspondence of the intergranular oxide that developed along a migrated grain boundary and displayed a local Al/Ti rich oxide. It was postulated that the local Al and Ti enrichment can create incoherent surfaces along the migrated GB and provide an accelerating factor for the inward oxygen diffusion.

Evidence of the occurrence of DIGM and minor segregation was also found in Alloy 690 TT and SA after exposure to  $H_2$ -steam at 480 °C under reducing conditions. However, the material underwent DIGM but not to PIO. It is probable that the high Cr content induced the formation of a dense and protective external Cr- rich oxide that inhibited the PIO despite providing the driving force for the occurrence of DIGM; therefore, these results show that also for the Alloy 690, the DIGM can be considered as a secondary (*e.g.* accelerating) and not sufficient phenomena for the occurrence of PIO.

Therefore, the early stages of SCC of Ni base Alloys cannot be explained only as the result of one single dominant phenomenon but due to the synergistic interactions between Al/Ti oxide and DIGM which are accelerating factors for the development of PIO which fracture upon the effect of applied stress if chemical and environmental conditions can lead to the film instability.

## Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this, or any other university, or other institute of learning.

Manchester, in the September 2019.

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## Dedication

Alla mia mamma Maria Rosaria, al mio papà Franco, a mio fratello Alessio e al piccolo Furia, per l'affetto, la fiducia ed i "pacchi-da-giù".

> A Rosaria, che ha reso tutto possibile.

> > Grazie.

## 1.Introduction

It is well known that Ni-base alloys, such as Alloy 600 and its derivate, are susceptible to Primary Water Stress Corrosion Cracking (PWSCC). SCC is driven by the synergistic interaction of mechanical, electrochemical and metallurgical factors and it is considered to be one of the most dangerous and insidious phenomena associated with the degradation of Pressurized Water Reactors (PWRs) steam generator tubes.

PWSCC represents an environmentally, economic and engineering issue for the nuclear industry that has been mitigated by the replacement of Alloy 600 component with ones manufactured out of a more resistant Alloy 690. However, recent laboratory evidence that Alloy 690 is susceptible to this form of SCC, although to date no plant failure has been reported and therefore further mechanistic studies are required to understand and to describe the initiation and propagation phases.

The PWSCC is divided in an initiation, where the proto-cracks can remain undetected for several years, followed by a propagation, in which a rapid crack growth rate is observed. Therefore, without a complete understanding of the SCC initiation stages, it is not possible to predict when the components will start to suffer cracking problems and to develop managing strategies.

Despite several mechanisms have been proposed to explain both initiation and propagation stages, the most comprehensive model capable of explain the PWSCC is the Internal Oxidation (IO) mechanisms, proposed by Scott and Le Calvar in 1993. In more recent studies, the model has been refined and advanced microstructural analyses have revealed that a Preferential Intergranular Oxide (PIO) enriched in Cr with an Al/Ti oxide core develops along a newly migrated grain boundary associated with Diffusion Induced Grain Boundary Migration (DIGM) process. However, the role of the "precursor events" PIO/DIGM is still unclear and more studies are needed to assess their role during the early stages of the PWSCC. Most importantly these results can be used to develop a model able to predict with more accuracy the life-time of the NPPs.

### 1.1. Aims and Objectives

The preferential intergranular oxidation mechanism has been found many confirmations as the most plausible model to explain the occurrence of PWSCC for Ni-base Alloys from several laboratories. However, the early stages of PWSCC and the role of the "precursor events" PIO and DIGM on the intergranular cracks are still unclear.

The aim of this study was to shed light on the intergranular oxidation mechanism and understand the possible role of the PIO/DIGM along the new oxidized grain boundaries in the "early stages" of PWSCC on Alloy 600 and Alloy 690 exposed to a low pressure superheated H<sub>2</sub>-steam environment, relevant to PWR primary water condition.

The principal objectives of this study are:

- Electrochemical *in-situ* validation of a low pressure super-heated H<sub>2</sub>-steam environment as possible surrogate of a PWR primary water environment with an in-house Ni/NiO Yttria Stabilized Zirconia Solid State Reference Electrode.
- Microstructural characterization of unstrained coupon samples of Alloy 600 SA to develop a mechanistic understanding of the "precursor events" PIO/DIGM in the grain boundaries proximity region at various oxidising potentials with respect to the Ni/NiO transition in the low pressure superheated H<sub>2</sub>-steam environment.
- 3. Microstructural characterization of strained coupon samples of Alloy 600 SA to obtain a mechanistic insight concerning the relationship between the "PIO/DIGM precursor events" and the initiation stages of the SCC relevant to PWSCC at different oxidising potentials in the low pressure superheated H<sub>2</sub>-steam environment.
- 4. Microstructural characterization of coupons of Alloy 690 SA and TT to develop a mechanistic understanding of the "precursor events" PIO/DIGM in the grain boundaries proximity region under reducing H<sub>2</sub>-steam condition.

### 1.2. Structure of the Chapters

This thesis includes an introduction, the literature review, the experimental approach and four chapters that are written in the form of journal publications (two of which have been published and two have been submitted to scientific journal for peer-review).

**Chapter 1:** This chapter introduces the topic and the knowledge gap, the possible industrial outcome and the structure of the thesis.

**Chapter 2:** The relevant literature review of the topic relevant to this study is provided in this chapter.

**Chapter 3:** It illustrates the experimental methodology and it gives descriptions of the characterization techniques.

Chapter 4: It reports the list of the references cited in the Chapters 2 and 3

**Chapter 5:** It shows the results of an *in-situ* electrochemical validation performed with a solidstate reference electrode of a low pressure superheated H<sub>2</sub>-steam environment. This environment is capable of performing accelerated oxidation experiment whilst maintaining the correct electrochemical condition of a PWR primary water environment. The data were supported by *ex-situ* microstructural characterization of Solution Annealed (SA) Alloy 600 exposed to H<sub>2</sub>-steam at different oxidising potentials. This chapter has been published in the Journal of The Electrochemical Society as L. Volpe, G. Bertali, M. Curioni, M. G. Burke, F. Scenini, Replicating PWR Primary Water Conditions in Low Pressure H<sub>2</sub>-Steam Environment to Study Alloy 600 Oxidation Processes, Journal of The Electrochemical Society 166 (2019) C1-C8 DOI: 10.1149/2.0081902jes.

#### Author contributions:

L. Volpe is the principal author. He carried out the experimental work, he processed the experimental data and he wrote the draft of the manuscript.

F. Scenini is the principal supervisor. He supervised the experimental approach, he provided conceptual guidance and extensive manuscript review.

M. G. Burke provided conceptual guidance and she contributed to the manuscript review.

M. Curioni contributed to the writing of the manuscript.

G. Bertali performed the XRD and GA-XRD examination on the Ni-200 and Ni powder.

**Chapter 6:** reports the effect of different oxygen partial pressures on the SCC "precursor events" PIO and DIGM on Alloy 600 SA coupon samples after being exposed to H<sub>2</sub>-steam environment at 480 °C. In this chapter, a comprehensive role of the precursor events PIO and DIGM associated with the early stages of SCC "precursor events", relevant to PWSCC for Alloy 600 was discussed. The chapter 7 has been published in Acta Materialia as L. Volpe, M. G. Grace, F. Scenini, Understanding the Role of Diffusion Induced Grain Boundary Migration on the Preferential Intergranular Oxidation Behaviour of Alloy 600 via Advanced Characterization, Acta Materialia 175 (2019) 238 – 249.

#### Author contributions:

L. Volpe is the principal author, he performed the experimental work, he analysed and processed the experimental data and he wrote the manuscript.

F. Scenini is the principal supervisor; he provided conceptual guidance and extensive manuscript review.

M. G. Burke provided conceptual guidance, support on the electron microscopy characterization and extensive manuscript review.

**Chapter 7:** reports the SCC behaviour of Alloy 600 SA samples under the effect of a plastic strain during exposure to H<sub>2</sub>-steam environment at 480 °C at various oxidising potentials. The aim of this chapter is to locate the proto-cracks initiation sites along oxidised GBs and to provide further mechanistic understanding on the role of the DIGM/PIO during the early stages of SCC, relevant for Alloy 600 PWSCC. The chapter 7 has been submitted to Acta Materialia as L. Volpe, M.G. Burke, F. Scenini, The Role of the Preferential Intergranular Oxidation and Diffusion Induced Grain Boundary Migration on the PWSCC Cracks Morphology.

#### Author contributions:

L. Volpe is the principal author, he performed the experimental work, he analysed and processed the experimental data and he wrote the manuscript.

F. Scenini is the principal supervisor; he provided conceptual guidance and extensive manuscript review.

M. G. Burke provided conceptual guidance and extensive manuscript review.

**Chapter 8:** in this chapter the oxidation behaviour of Alloy 690 coupon samples exposed to H<sub>2</sub>steam environment at 480 °C in thermally treated and SA condition is reported. The GB surface proximity region was analysed with advanced electron microscopy techniques to obtain a mechanistic understanding of the "precursor events" PIO/DIGM during the early stages of PWSCC for Alloy 690. This chapter has been submitted to Scripta Materialia as L. Volpe, M.G. Burke, F. Scenini, Oxidation Behaviour of Solution-Annealed and Thermally-Treated Alloy 690 in Low Pressure H<sub>2</sub>-Steam.

#### Author contributions:

L. Volpe is the principal author, he performed the experimental work, he analysed and processed the experimental data and he wrote the manuscript.

F. Scenini is the principal supervisor; he provided conceptual guidance and manuscript review.M. G. Burke provided conceptual guidance and she contributed to the manuscript review.

**Chapter 9:** This chapter shows the overall conclusions of this study, highlighting the synergic role of the "precursor events" PIO/DIGM as well as of the AI/Ti enrichment during the early stages of PWSCC for Alloy 600 and Alloy 690. Possible future works relevant to this field are also listed in this section.

**Appendices:** They include supplementary thermodynamic information regarding the low pressure superheated H<sub>2</sub>-steam environment, described in the Chapter 5 and applied to reproduce the desired environment for the oxidation experiments as shown in the Chapters from 6 to 8.

## 2. Literature Review

### 2.1. Pressurized Water Reactor

Pressurized Water Reactors represent the large majority of the word nuclear power plants and with the Boiling Water Reactors (BWRs) constitute the Light Water Reactors (LWRs) family. A PWR presents a double circuit where the radioactive coolant water is confined in the primary circuit, as schematically shown in Fig. 1 and this represent the main advantage in terms of safety if compared with a BWR. PWRs were initially designed for naval applications from Westinghouse Bettis Atomic Power Laboratory and subsequently used for commercial applications from 1960 onward. The primary coolant is pumped under high pressure to the reactor core where it is heated by the energy generated by the fission chain reaction of the uranium oxide (UO<sub>2</sub>) bars that represent the nuclear fuel. As a result of the high pressure in the primary circuit around 155 bar [1], the water reaches the temperature of 325 °C in the hot leg without boiling [2].The hot primary water is then circulated into a steam generator and the heat from the primary water is transferred to the secondary water circuit to generate pressurized steam. The pressurized steam passes through a steam turbine which transform the kinetics energy of the pressurized steam in electrical energy. Finally, the steam is cooled down, condensed and then re-circulated to back in the steam generator.



Fig. 1: Schematic diagram of a pressurized water reactor [3].

These nuclear power plants use uranium enriched in the isotope U-235 with light (or ordinary) water employed for cooling and neutron moderation [4]. The coolant present in a PWR

is substantially high purity water with less than the 2 ppb of dissolved oxygen and with boron, added as  $H_3BO_3$ , lithium as LiOH and  $H_2$  [5,6]. Boron is added to partly absorb neutrons without fissioning itself and to control the reactivity of the reactor during fuel burn-up; lithium plays the role of *pH* moderator, adjusting the *pH* at 325 °C between 6.9 and 7.4 and hydrogen (between to 2 and 4 ppm) is added to the primary water to lower the Electrochemical Corrosion Potential (EcP) close the Ni/NiO transition (-750 mV *vs.* SHE) and to suppress the oxidizing radiolysis products such as  $O_2$  and  $H_2O_2$ . However,  $H_2$  can enhance the PWSCC susceptibility [7].

### 2.2. Metallurgy of Alloy 600 and Alloy 690

#### 2.2.1. Introduction

Nickel is a corrosion-resistant metal due to its slow oxidation rate and it can find many applications in industry [8]. It can be alloyed with other metals, especially with Fe and Cr to form several engineering alloys. Generally, Ni-base alloys exhibit high mechanical strength with a yield strength between 500 and 800 MPa [9,10]. In this study, face centred cubic [11] Alloy 600 and Alloy 690 were used.

Alloy 600 (UNS N06600) with main composition of 70%Ni-15%Cr-9%Fe is a nonmagnetic high temperature alloy with moderate strength, hot and cold workability and good mechanical properties [12,13]. It is used in engineering applications that require both resistance to corrosion and high temperature [14]. It was developed in 1932 by O. B. J. Fraser [15], and it was commercially patented by the International Nickel Company (INCO). The high Ni content (72%) confers to the Alloy 600 a good resistance to corrosion in several organic and inorganic electrolytes and in reducing aqueous solutions [16,17] and suppress the susceptibility to chloride-ion stress corrosion cracking (SCC) [18] in aqueous solutions with chlorine ions. The content of Cr (14-17%) provides corrosion resistance in mildly oxidizing conditions at high temperatures [19]. Due to its versatility Alloy 600 is used in several engineering applications [11,20] such as: chemical and food processing, acid vessels, jet engines [21], steam generators [22] and it was considered a standard material for the production of several components for nuclear reactors [23,24].

Alloy 600 was used in the nuclear industry in the 1960-1980's because it presents a thermal expansion coefficient close enough to that of austenitic stainless steels [25] so they can be coupled together without suffering remarkable difference during thermal expansion.

However, Alloy 600 is susceptible to PWSCC and Alloy 690, a new Ni-base alloy was developed to be used for the construction of primary circuit components in PWRs without suffering PWSCC issues.

Alloy 690 (UNS N06690) (60Ni-30Cr-10Fe) is considered to be the successor of Alloy 600 and it was also developed by INCO Alloys International [26]. Alloy 690 shows high creep-rupture strength [27], a good metallurgical stability with favourable fabrication characteristics [28]. The main difference with the Alloy 600 is the higher content of Cr (27-31%). As the Alloy 600, also Alloy 690 has an high resistance to corrosion in many corrosive aqueous media and high temperature environments [29], and exhibits excellent resistance to SCC in high temperature water [30]. For these reasons, Alloy 600 was replaced with Alloy 690 and it is currently used for the fabrication of steam generator tubes and other components in nuclear power plant [31].

#### 2.2.2. Microstructure

Alloy 600 and 690 have a low carbon solubility and their microstructures normally contain carbides. The higher Cr content of Alloy 690 promotes the carbide precipitation but lowers the solubility, as shown in the plot of Fig. 2 and from the equations (2.1) and (2.2), where T is the temperature in Celsius and %C represents the carbon solubility [32].



Fig. 2: Revised carbon solubility-temperature diagram for Alloy 600 and Alloy 690 extracted from [33] and determined by Yamanaka and Yonezawa [32].

For Alloy 690 
$$T = 1453.1 + 66.9 \ln(\% C)$$
 (2.1)

For Alloy 600 
$$T = 1449 + 130.3 \ln(\% C)$$
 (2.2)

Both  $M_7C_3$  and  $M_{23}C_6$  intergranular carbides form in Alloy 600 [33,34], since they are both thermodynamically stable in Alloy 600 [35,36], whereas in the Alloy 690, only intergranular carbides are  $M_{23}C_6$  are stable due to the C/Cr content ratio [32–35,37]. It had been noted that the presence of "continuous" intergranular carbides and few intragranular carbides generally increased the PWSCC resistance of Alloy 600 [38].

Moreover, titanium nitrides and carbonitrides are present in both Alloy 600 and 690. Titanium nitrides and carbides are clearly visible in polished specimens using a Light Optical Microscope (LOM). They are generally randomly dispersed in the matrix and the nitrides appear to be orange-yellow and the carbides grey-lavender.

#### 2.2.3. Chemical Composition of Alloy 600 and Alloy 690

The standard chemical composition for Alloy 600 and Alloy 690 is reported in Table

2.1.

100			mposition	. (			0,000[2	<b>.</b>
Alloy	Ni	Cr	Fe	С	Mn	S	Si	Cu
600	72.0	14.0	6.00	0.15	1.00	0.015	0.50	0.50
	Min	17.0	10.00	max	max	max	max	max
690	58.0	27.0	7.00	0.05	0.50	0.015	0.50	0.50
	Min	31.0	11.00	max	max	max	max	max

Table 2.1: Chemical composition (wt.%) for Alloy 600 and Alloy 690 [26].

The proprieties of the main alloying elements are listed below.

- Cr and Fe are the principal elements of the Alloys and their chemical proprieties have been listed above.
- C is one of the most important minor alloys. The percentage of C ensures extensive intergranular carbide precipitation during subsequent thermal treatment. To ensure a desirable level of intergranular carbides, some nuclear specifications include a minimum and a maximum carbon content [26].
- Si, Al, Ti and Mn are present in the alloy for deoxidation, desulfurization. These elements positively influence the processes of deformation, recovery, recrystallization and grain growth [39].

- B has been used in small amounts to enhance the hot workability, however if present in levels of ≈50 ppm (or greater) can segregate along grain boundaries, form Cr borides, and may enhance grain boundary decohesion [40].
- S and P are tramp elements and they may segregate at grain boundaries and they can reduce the mechanical properties, for example the S content is required to be lower than the 0.02 wt % [39,41].

Nb and Mo can degrade the corrosion resistance of Alloy 690, as observed by Nagano *et al.* [42].

#### 2.2.4. Phase Diagram of Alloy 600 and Alloy 690

The Ni-Cr-Fe phase diagram with the location of the  $\gamma/\gamma+\alpha'$  boundary at 400 °C is reported in Fig. 3. Both Alloy 600 and Alloy 690 are in the  $\gamma$  field with a face-centred cubic (FCC) crystal structure.



Fig. 3: Ni-Cr-Fe ternary equilibrium phase diagram at 400 °C.

The melting point range of Alloy 600 is in between 1354 °C and 1413 °C and for Alloy 690 is between 1343 °C and 1377 °C. The  $\alpha'$  phase is a Cr-enriched bcc face. The  $\alpha'$  phase can cause embrittlement when precipitated during prolonged high temperature exposure in alloys whose compositions lie in the two-phase  $\gamma+\alpha'$  field. The  $\alpha'$  can form within the miscibility gap and by an isotropic spinodal decomposition in between relatively small temperatures (≈400 °C to 500 °C). For Alloy 600 and Alloy 690, no precipitation of  $\alpha'$  phase has been reported, since

they are both stable austenitic solid solution alloys from room temperature to melting temperature [26].

The equilibrium diagram of Ni-Cr Alloys [43], as shown in Fig. 4 indicates the existence of a Ni<sub>2</sub>Cr phase below 580 °C in the proximity of the Ni/Cr ratio equal to 70%/30% that is not far from the Ni/Cr ratio in the Alloy 690. This intermetallic phase may affect the hardness and the mechanical properties of the Alloy 690 [44], however, Smith *et al.* [44] reported that Ni<sub>2</sub>Cr phase was not found to be so marked in Alloy 690, possibly due to the presence of Fe in the matrix.



Fig. 4: Binary equilibrium phase diagram for Ni-Cr [43].

#### 2.2.5. Heat Treatments

Mill Annealing (MA) and Thermal Treatment (TT) between 700 to 720 °C are the two principal thermal treatments for Alloy 600 and Alloy 690. The aim of these two heat treatments is to control the microstructure, the amount of intergranular carbides and to relieve residual stresses of components after machining processes.

#### 2.2.5.1. Annealing

The process of annealing is performed principally for two purposes:

- Produce a fully recrystallized grain structure in the component.
- Dissolve the carbides present in the cold worked structure.

After this process, the material obtained is strain-free with carbon in a superheated solid solution. Solution Annealing (SA) is usually performed at temperature between 950 - 1050 °C

and it is followed by cooling [45,46]. The cooling rate can strongly influence the carbide precipitation. For fast cooling rates, obtained with water-quenching, there are generally "few"  $M_{23}C_6$  intergranular carbides and this means that the microstructure is highly supersaturated with C; for slower cooling rates (such as a MA process), the alloy is very susceptible to carbide precipitation and the carbide distribution depends from the temperature of the MA treatment.

Airey [47] showed how to induce significant modifications to the Alloy 600 mill annealed microstructure by using several thermal treatments. A thermal treatment between 593 °C and 650 °C for 1 h, induced the formation of discrete intergranular carbides precipitations. An extensive network of carbides was obtained by increasing the exposure time (100 h) and keeping the same temperature or equivalently by thermally treated the alloy at 750 °C for 10h. The Intergranular (IG) carbides could be coarsened by increasing the exposure temperature up to 705 °C for 24 h. Finally, discrete and large grain-boundary precipitations were found for exposure performed at 870 °C.

#### 2.2.5.2. Thermal Treatment

Thermal Treatment refers to the ageing treatment to promote carbide precipitation and it is performed after the annealing process. The material is heated to temperatures in the range 700 °C to  $\approx$ 720 °C between 5 and 15 hours and then cooled rapidly, as shown in Fig. 5.



Fig. 5: Schematic of a Time Temperature Precipitation (TTP) diagram for carbide precipitation in Alloy 600 superimposed with MA and TT cycle [41].

The path from point A to point B in the plot of Fig. 5 allows the formation of intergranular carbides, while an increased time of the treatment may cause the formation of intragranular carbides.

For stainless steel, the Cr-depleted zone contains less than 12 wt% of Cr and this can lead to SCC in oxidizing environment [48]. It was believed that the principal role of the thermal treatment is to "heal" the Cr-depleted zone at grain boundaries and to reduce the susceptibly to SCC. However, Cr depletion is still present in Alloy 600 TT [33,34,37,49]. Despite the residual depleted zone, Pessal *et al.* [50] and Economy *et al.* [51] showed that Alloy 600 TT exhibited better resistance to IGSCC in deaerated high purity water compared to that of Alloy 600 in the SA or MA condition. More recent oxidation experiments in H<sub>2</sub>-steam environment, relevant to the PWR primary water environment have shown that preferential intergranular oxidation, which is considered to be one of the main precursor events for initiation of PWSCC was negligible ( $\approx$ 10 to 50 nm) in Alloy 600 TT compared to Alloy 600 SA ( $\approx$ 500 to 1000 nm) [10].

### 2.3. Stress Corrosion Cracking

#### 2.3.1. Introduction

Stress Corrosion Cracking (SCC) is a brittle fracture of engineering alloys due to an environmentally-induced cracking process. The most dangerous aspect of SCC is the total unpredictability of the final failure, since the first embryo-crack can randomly appear after days, months or several years of exposure to the environment, making difficult the life-time prediction of the mechanical components. Generally, SCC Crack Growth Rates (CGR) measured for a variety of materials exposed in different environments can exhibit values in between 10<sup>-12</sup> ms<sup>-1</sup> and 10<sup>-5</sup> ms<sup>-1</sup>. However, in real components, cracking is often discontinuous, with common rate in between 10<sup>-11</sup> ms<sup>-1</sup> and 10<sup>-8</sup> ms<sup>-1</sup> [52].

Historically, the SCC was identified for the first time in brass by the British Army in India in the middle of the 19<sup>th</sup> century and named "season cracking" due to the occurrence during the rainy season. During the monsoon season, military activity was temporarily reduced and ammunition was stored in stables. Ammonia from horse urine combined with residual stresses in the coldworked brass caused the cracking of the several stored brass cartridges [53,54].

The occurrence of SCC and its crack propagation is due to the simultaneous influence of three key factors: 1. a susceptible material interacting with 2. a specific environment under 3. a tensile

stress (Fig. 6). The environment must react with the material, but this does not mean that the environment must be aggressive or corrosive, but specific for that material. Important variables include temperature, *pH* and chemical species. For the mechanical stress, the load can be dynamic or static, residual or applied, due to mechanical (*e.g.* cold-work, machining, corrosion phenomena) or thermal processes (*e.g.* welding, thermal cycling). If any of these factors is not present, the SCC cannot happen.



#### Fig. 6: Essential factors for Stress Corrosion Cracking [55].

Nowadays, SCC has been clearly recognized in several alloy-environment combinations and a short list is reported in Table 2.2.

Alloy	Environment		
	Hot nitrate		
Carbon Steel	Hydroxide solutions		
	Carbonate/bicarbonate solutions		
High-strength steels	Aqueous electrolytes, particularly when containing $H_2S$		
Austonitic stainloss stools	Hot, concentrated chloride solutions		
Austennic stanness steels	Chloride-contaminated steam		
Aluminium alloys	Aqueous Cl <sup>-</sup> , Br <sup>-</sup> , and I <sup>-</sup> solutions		
	Aqueous Cl <sup>-</sup> , Br <sup>-</sup> , and l <sup>-</sup> solutions		
Titanium alloys	Organic liquids		
	N <sub>2</sub> O <sub>4</sub>		
Nickel alloys	High purity water		
Magnesium alloys	Aqueous Cl <sup>-</sup> solutions		
	Aqueous Cl <sup>-</sup> solutions		
Zirconium alloys	Organic liquids		
	I <sub>2</sub> at 350 °C		

Table 2.2: Princi	pal alloy/	environment s	vstems where	SCC occurs	[54]
			,	000000000	

### 2.3.2. Stages of Stress Corrosion Cracking

The sequence of events that leads to SCC are commonly divided in three stages:

- Stage 1: Crack initiation with a very long incubation time that can last from few hours to several months or years.
- Stage 2: Steady-state crack propagation with the nucleation of the cracks.
- Stage 3: Crack coalescence and growth or final failure.

The different stages are schematically reported in the qualitative plot in Fig. 7, where the evolution of the crack propagation depth is shown as function of the time. Although the crack initiation and propagation are two different processes, it is difficult to separate them to each other, since the chemical conditions that control these two stages are very similar [54].



Fig. 7: Qualitative evolution of the depth of penetration over the time [56,57].

Local defects, such as notches or scratches, can be caused by machining processes or material processing. Also, a particular local environment may promote local oxidation or dissolution of metal contributing to the creation of localized stresses, can enhance and promote the initiation of local embryo-cracks. After nucleation, the crack can coalescence and grow; the propagation can depend not only on the stress but also from the interaction between the environment and the microstructure that can influence local chemical reactions including adsorption, dissolution and diffusion of ions.

SCC is frequently studied as a function of the stress intensity factor, K, and the crack propagation velocity, da/dt, is measured using pre-cracked compact tension specimens [54]. The crack propagation rate, da/dt, is plotted versus K, that represents the magnitude of the stress distribution at the crack tip. Usually, three regions of crack propagation rate as function of K are

found during crack propagation experiments, identified as stage 1, 2, or 3, as it is shown in Fig.



Fig. 8: Simplified representation of the CGR vs. stress intensity factor K [22].

Below the threshold stress intensity level,  $K_{ISCC}$ , no crack propagation is observed. This threshold stress level is determined by the combination of the environment, the metallurgical condition of the alloy and the applied stress, and it represents the minimum stress level for synergistic interaction between the environment and the material.

For stress intensity levels included in the stage 1, the crack propagation rate strongly depends from the stress intensity factor and rapidly increases with increasing *K*. For stress intensity levels included in the stage 2, the crack propagation rate becomes constant and in independent of *K*, the plateau depends from rate-limiting environmental chemical phenomena on the metal, such as mass transport of environmental species up the crack to the crack tip velocity. In stage 3, the rate of crack propagation exceeds the plateau velocity as the stress intensity level approaches the critical stress intensity level for mechanical fracture,  $K_{lc}$  [54].

#### 2.3.3. Primary Water Stress Corrosion Cracking

SCC of Alloy 600 has been referred to primary water stress corrosion cracking because of its occurrence in the primary loop of a PWR. This phenomenon is sometimes referred to as Low Potential Stress Corrosion Cracking (LPSCC) due to the low electrochemical corrosion potential region in which it occurs [22] or as Intergranular Stress Corrosion Cracking (IGSCC) due to the SCC fracture morphology of Alloy 600 in the primary side environment. The first evidence of SCC in Nuclear Power Plant was identified in CEA laboratories by Coriou *et al.* [58] in 1959 on several Inconel alloys (Ni-(19.0-13.6)Cr-(7-0.35)Fe) exposed to highpurity water at 350 °C. Several unsuccessful attempts were performed by several laboratories [22,59] to reproduce the results of Coriou *et al.*. The debate about the SCC susceptibility of Alloy 600 ended with the study of Van Rooyen *et al.* [60] in the late 1960's, who demonstrated the occurrence of stress corrosion cracking in laboratory. Further confirmations arrived in 1971, where SCC was identified on the primary side of the Obrigheim plant [61]. The major events in the detection of Alloy 600 stress corrosion cracking are reported in Fig. 9.



Fig. 9: Service and laboratory experience for Alloy 600 PWSCC [22].

In old nuclear power plants, PWSCC of Alloy 600 and its weld alloys (Alloy 82/182) represents a major concern for the nuclear power industry, because PWSCC has been responsible for significant downtime and replacement costs. A considerably less susceptible material to PWSCC is Alloy 690 and it has been used as replacement for PWRs components from the mid-1980's onward.

#### 2.3.3.1. Parameters Influencing Alloy 600 PWSCC

The mechanism(s) for PWSCC initiation and propagation are not yet fully understood. The prediction of crack initiation is difficult due to the uncertainty of numerous variables. The principal parameters that can affect the PWSCC are: temperature [55,56], electrochemical potential as influenced by the hydrogen partial pressure [55,62–65], alloy Cr content [66,67], C content, carbide precipitation [45,68–70], residual or applied stress [71,72], cold work [73–75], surface preparation [76] and surface finishing (*i.e.* machining operations and associated localized deformation) [41,77].

#### Temperature

Temperature is a major factor affecting the PWSCC of Alloy 600, strongly influencing both initiation and propagation of cracks [51,78–80]. This indicates a thermally-activated process, according to the equation (2.3) [54].

$$k = A \cdot exp\left(-\frac{Q}{RT}\right) \tag{2.3}$$

Where k is the reaction kinetics, A is a constant, R is the gas constant and Q is an "activation energy" that can be associated with the minimum energy required to initiate the crack growth. The "activation energy" can be calculated through a linear fit of the experimental data and by measuring the slop of the interpolating line divided by the gas constant R. The plot a of Fig. 10 shows the experimental data and the interpolation for the initiation time for Alloy 600, whereas the plot b shows CGR data and fitting lines for several batch of Alloy 600.



Fig. 10: Arrhenius plots for (a) IGSCC initiation time and (b) IGSCC crack growth rate [51].

The values for crack initiation cover the range from 90 kJ/mol to 355 kJ/mol [22,51,81,82] and for crack propagation from 80 kJ/mol to 225 kJ/mol [83–85] and reasonable values for crack initiation and crack propagation are considered to be in the range of 167 to 230 kJ/mol [22] and 126 to 147 kJ/mol [83,84] respectively. The values of *Q* for initiation and propagation are different, suggesting two mechanistic processes involved.

Rebak *et al.* [79] proposed a mechanistic interpretation of SCC in Alloy 600. They compared the IGSCC activation energy for unstressed Alloy 600 (252 kJ/mol) with the activation energies for Ni self-diffusion (278 kJ/mol) and for Ni dissolution in HCl (88 kJ/mol), and proposed

a solid-state diffusion mechanism rather than a chemical dissolution process. Further experiments of Economy *et al.* [51] supported the solid-state diffusion mechanism. A monotonic dependence of the IGSCC activation energy was observed as function of the temperature from SCC initiation experiments using Alloy 600 Reverse U-Bend (RUB) samples tested in liquid water at 310 °C and super-saturated steam at 400 °C. This suggests that a single mechanism is responsible for the occurrence of Alloy 600 IGSS for both water and steam. Moreover, since metal dissolution is not expected to occur rapidly in steam, IGSCC of Alloy 600 is not primarily controlled by a dissolution-controlled process.

The monotonic dependence between high pressure water and steam suggested that the mechanistic processes for the occurrence of PWSCC were the same, and experiments in hydrogenated steam ( $T \ge 400$  °C) could be compared with experiments performed in hydrogenated water (T = 320 °C). A similar monotonic trend in subcritical and supercritical water was found by Moss and Was [86] for Alloy 600 MA and Alloy 690 MA with the values of activation energies equal to 121 ± 13 kJ/mol and 92 ± 12 kJ/mol respectively.

In a more recent studies performed by Bertali *et al.* [68], Alloy 600 SA coupons were exposed to simulated primary water at 320 °C and super-heated steam at 400 °C and were shown to be susceptible to preferential intergranular oxidation and diffusion-induced grain boundary migration, as already discovered for the same material exposed to low pressure H<sub>2</sub>-steam environment at 480 °C [10,46], strongly suggested that the oxidation mechanism is the same for all the temperature examined.

#### Electrochemical Corrosion Potential and Hydrogen Partial Pressure

PWSCC is strongly affected by the electrochemical corrosion potential, controlled by chancing the dissolved hydrogen in the primary circuit.

Staehle and Gorman [22] showed for the first time the sensibility of LPSCC to little changes in potential, using galvanic couples of Alloy 600 connected to active or noble alloys in de-aerated high temperature water. Soustelle *et al.* [87] clearly identified the susceptibility evolution of Alloy 600 to IGSCC as function of the EcP, with a maximum CGR at a hydrogen concentration of 2.73 ppm, close to the expected Ni/NiO transition, as shown in the plot in Fig. 11.



Fig. 11: CGR trend as function of the H<sub>2</sub> partial pressure for Alloy 600 at 360 °C [87].

Economy *et al.* [62] exposed RUB samples at 400 °C in both steam and in a variety of H<sub>2</sub> partial pressures; his data showed a clear trend of the high susceptibility to IGSCC of Alloy 600 in the proximity of the Ni/NiO transition. The plot in Fig. 12 shows the results of Economy *et al.* [62] re-published by Scott *et al.* [88], where the H<sub>2</sub> partial pressure was converted into an equivalent potentials normalized to the Ni/NiO transition. The maximum susceptibility for cracking at the Ni/NiO transition proposes that the NiO formation might influence the IGSCC susceptibility of Alloy 600.



Fig. 12: Time to 30% IGSCC in relation of the total fracture surface vs. H<sub>2</sub> partial pressure and electrochemical potential plot [62].

Later Smialowska *et al.* [89] conducted constant extension rate tests (CERT) on Alloy 600 at different partial pressures of hydrogen at the temperature of 350 °C, applying an external potential via a potentiostat. The IGSCC susceptibility drastically changed in the proximity of the Ni/NiO transition, but IGSCC was found to occur only for lower potential than the Ni/NiO transition (Fig. 13). These results were in contrast to the data of Economy *et al.* [62].


Fig. 13: Percentage of Alloy 600 IGSCC in relation to the total fracture surface are (IGSCC %) as a function of electrochemical potential (Potential,  $mV_H$ ) at 350 °C [89].

Lee *et al.* [63] and Totsuka *et al.* [90], confirmed the work of Economy *et al.* [62] by using CERT tests, as shown in Fig. 14 and Fig. 15. The CGR data exhibited a characteristic bell-shape curve as function of hydrogen partial pressure, where the maximum susceptibility occurred close to the Ni/NiO transition.



Fig. 14: CGR curve as function of the EcP with respect to the Ni/NiO transition for Alloy 600 at 338 °C [64].



Fig. 15: CGR as function of H<sub>2</sub> partial pressure for Alloy 600 at 330 °C [63].

Constant Load (CL) experiment showed a similar parabolic trend by measuring the maximum crack growth length on cold-rolled Alloy 600 dog-bone samples exposed at 400 °C in low pressure H<sub>2</sub>-steam at different oxidizing condition by changing the H<sub>2</sub> partial pressure [65]. The plot in Fig. 16 showed the maximum crack length as a function of the parameter that is defined as the ratio of the oxygen partial pressure at Ni/NiO transition over the oxygen partial pressure in the system. These data indicate that the maximum crack length exhibits the characteristic bell-shaped curve. The results obtained by Lindsay *et al.* [65] from the H<sub>2</sub>-steam constant load experiments corroborated the bell SCC shape curve for Alloy 600 in the proximity of the Ni/NiO transition and the dependence of PWSCC as function of H<sub>2</sub>; moreover, these data strongly support the hypothesis that there is one single mechanism for the occurrence of Alloy 600 IGSCC in both pressurized water and superheated H<sub>2</sub>-steam environments.



Fig. 16: Updated plot [65] with the data from [77,91] showing the maximum crack length for Alloy 600 exposed to 400 °C H<sub>2</sub>-steam under CL as a function of the oxygen partial pressures ratio (expressed as *R*) in the proximity of Ni/NiO transition.

### Locating the Ni/NiO Transition in H<sub>2</sub>-Steam Environment

The maximum PWSCC susceptibility of Alloy 600 occurs in the proximity of the Ni/NiO transition [62,88,92] which is close to the electrochemical operating conditions for NPPs, as shown in the Pourbaix diagram in Fig. 17 [22]. Therefore, it is critical to identify the exact environmental condition reproducing the Ni/NiO transition in both pressurized water and low pressure H<sub>2</sub>-steam, a surrogate environment used to perform accelerated oxidation and SCC experiments on Ni-base alloys relevant to PWR primary water.

Attanasio *et al.* [93] assessed the Ni/NiO transition using the Contact Electric Resistance (CER) technique coupled with direct observation of the surface appearance of coupon samples

tested in de-aerated water with dissolved hydrogen less than 20 cc/kg between 288 °C and 360 °C.



Fig. 17: Pourbaix diagram for Alloy 600 at 290 °C and 360 °C [22].

They empirically measured the values of enthalpy  $\Delta H_{298}$  and entropy  $\Delta S_{298}$  from which they evaluated the mathematical formula of the hydrogen partial pressure  $(p_{H_2})$  as reported in equation (2.4). The experimental results (black line in Fig. 18) did not follow the theoretical trend (dotted line in Fig. 18) of the Ni/NiO transition [94]. Attanasio *et al.* [93] were not, however, able to explain this deviation. Possible sources of error in calculation of the Ni/NiO transition in the work of Attanasio *et al.* [93] were attributed to the standard free energy of formation of NiO [64] and in the difficulty to evaluate the Henry's law coefficient at high temperature.

$$p_{H_2} = \exp\left(-\frac{20100 - 11T}{RT}\right)$$
 (2.4)



Fig. 18: Ni and NiO regimes as function of the cc/kg H<sub>2</sub> chart [93].

In a later study, Attanasio *et al.* [95] performed CER experiments on Alloy 600 and Alloy X-750 to better evaluate the location of the Ni/NiO transition between 288 °C and 360 °C. Coupon samples exhibited a surface oxide layer for values of hydrogen less than 4 cc/kg for 288 °C and less than 25 cc/kg for 360 °C. The summary of the experimental data is reported in the plot of Fig. 19, where a much better agreement between the experimental and the theoretical Ni/NiO transition was found [94] and the mathematical relationship between the hydrogen concentration and the temperature was finally obtained, as reported in equation (2.5).

$$[H_2]_{Ni/NiO} = \frac{\exp\left(-\frac{4619.2}{T} + 5.2302\right)}{k_H}$$
(2.5)

Where  $[H_2]_{Ni/NiO}$  is the hydrogen concentration (in cc/kg) at the Ni/NiO transition,  $k_H$  is the Henry's law coefficient in atm/(cc/kg H<sub>2</sub>) and *T* is the temperature in Kelvin. An improved [H<sub>2</sub>]-T relationship [94] was obtained by using specific Henry's law coefficients for the different temperatures, as evaluated by Moshier and Witt [95,96] and by more precise measurements of the H<sub>2</sub> fugacity at high temperature. Based on the data of Attanasio *et al.* [95], a more user-friendly [H<sub>2</sub>]-T relationship was obtained and reported in the EPRI document 1015288 [7] (equation (2.6)).

$$[H_2]_{Ni/NiO} = 10^{(0.0111T(^{\circ}C) - 2.59)}$$
(2.6)



Fig. 19: Ni and NiO regimes as function of the cc/kg H<sub>2</sub> [95].

Scenini *et al.* [41] performed oxidation studies on Alloy 600 and Alloy 690 SA and TT at the temperature of 400 °C and at the total pressure of 20.7 MPa. The hydrogen partial pressure was monitored with a Pd-23%Ag sensors. After the exposure, the samples have been analysed with optical and grazing-angle XRD examinations and they found that the H<sub>2</sub> partial pressure corresponding to the Ni/NiO is between 24.8 and 31.7 kPa, which is close to the literature value of 42.8 kPa of  $pH_2$  [41].

More recently, Moss and Was [97] identified the environmental conditions to reproduce the Ni/NiO transition using Ni coupons exposed from 320 °C to 450 °C in subcritical and supercritical water at 25 MPa with different dissolved hydrogen concentrations, as shown in the plot of Fig. 20. For clarity, a fluid is considered supercritical when above a critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ), only a single gaseous phase is present [98]: for the water, the critical conditions (critical point in the plot of Fig. 21) are reached for a  $T_c$  equal to 373.99 and a  $P_c$  of 217.75 atm.





The thermodynamic model (red curve in the plot of Fig. 20) fits with excellent agreement the experimental data and previous study in subcritical water, where the standard enthalpy of formation  $(\Delta H_{f,NiO}^{\Theta})$  and standard entropy of formation  $(\Delta S_{f,NiO}^{\Theta})$  for NiO were respectively equal to 48119 J/mol and to 65.6 J/mol·K. These values were close to those reported by Attanasio *et al.* [95]. However, their thermodynamic model was not able to accurately predict the Gibbs free energy values associated to the Ni/NiO transition in supercritical water conditions [95].



Fig. 21: Phase diagram for water showing the supercritical point [99].

In a later study, Capell and Was [100] investigated the mechanism of Selective Internal Oxidation (SIO) in low pressure H<sub>2</sub>-steam environment for five Ni alloys exposed to different oxidizing conditions. Each condition was defined with the parameter Partial Pressure Ratios (*PPR*), defined as the ratio between the hydrogen partial pressure over the steam partial pressure ( $p_{H_2}/p_{H_2O}$ ). The formation of an external and uniform Ni(OH)<sub>2</sub> layer was found to occur between *PPRs* equal to 0.001 and 0.09 as shown in the plots (a) and (b) of Fig. 22.



Fig. 22: O/Ni peak for corrosion coupons after exposure at 400 °C as function of the PPRs [100].

A detailed classification of the surface oxides identified in this study is reported in Fig. 23, where a high percentage of NiO and Ni(OH)<sub>2</sub> at *PPR* = 0.09 was found with XPS analysis of the surface, while at *PPR* = 50 the composition was similar to that representative of the bulk material.



Fig. 23: Composition of the surface region of the alloys exposed at 400 °C after XPS analysis [100].

However, the *PPR* value considered by Capell was  $\approx$ 70 times lower than the value evaluated by Scenini based on the thermodynamic calculations of Kubaschewski *et al.* [101], and, if converted in electrochemical corrosion potential, corresponded to  $\approx$ 100 mV, placing the Ni/NiO transition in completely different potential region. A second discrepancy can be attributed to their use of the standard free energy of formation calculated by Attanasio *et al.* [93,95]. Capell and Was [100] used these values for the evaluation of the Ni(OH)<sub>2</sub> formation, although they [93,95] calculated these values for the formation of NiO. In a more recent work, the environmental condition identifying the Ni/NiO transition was indirectly identified by Bertali *et al.* [10] in low pressure H<sub>2</sub>-steam environment. Their X-Ray diffraction analyses of Ni powder exposed for 200 h at 400 °C under more reducing and more oxidizing conditions with respect to the Ni/NiO transition confirmed the presence of Ni and NiO, in agreement with Kubaschewski *et al.* [101].

# Alloy Composition

### Role of Cr and Ni

The chemical composition (*e.g.* Ni and Cr content) can play an important role to the SCC susceptibility [92,102]. The effect of nickel on the SCC susceptibility evaluated for the first time the effect of Nickel content on SCC was evaluated for the first time by Coriou *et al.* [103], who exposed several Alloy with different Ni concentration in pure water or chlorinated water. The plot in Fig. 24 shows the trend of the SCC as function of the Ni concentration, where alloys with

low % of Ni are more susceptible to chloride-ion induced SCC, while Ni-base alloys are more susceptible to PWSCC.



Fig. 24: Effect of nickel content for different alloys in pure and chlorinated water [103].

Nagano *et al.* [66] studied the effect of the Cr content on RUB specimens with chemical composition equal to Ni-10Fe-xCr, where the Cr composition was varied between 0 and 30%. The specimens were exposed to simulated PWR primary water and the summary of their results is presented in Fig. 25, where the time-to-failure was plotted against the different Cr %. They noticed three different behaviours dependent upon their Cr composition: a maximum SCC susceptibility was observed between 5% and 10% Cr; the cracking susceptibility was observed to decrease between 10% and 17%, and no cracking were observed for Cr values between 17% and 30%.



Fig. 25:Time-to-Failure for RUB specimens tested in primary water plotted as a function of Cr content for Ni-10Fe-xCr alloy [66].

A later study performed by Yonezawa *et al.* [67] confirmed the studies of Nagano *et al.* [66]. The SCC susceptibility drastically decreased for alloy Cr content between 3 and 17%, with no cracks observed in higher Cr content alloys.



Fig. 26: Initiation time as a function of Cr content on Ni-10Fe-xCr alloy [67].

Results from numerous laboratories showed a significantly improved resistance to PWSCC for Alloy 690 (Cr  $\approx$ 30 wt.%) compared to Alloy 600 [35,92,104,105]. These results confirmed that an increase of Cr can be beneficial to mitigate the occurrence of PWSCC in PWR primary water environment. A possible explanation to justify the better and improved resistance to PWSCC for higher Cr content can be the capability of Cr as a solid solution-strengthener for Ni, which can affect creep and deformation, as it also reduces the stacking fault energy. An increase in creep strength and a decrease of intergranular cracking [106] was observed for Cr content between 15 and 30%. Moreover Cr can easily form a protective external chromium oxide layer (Cr<sub>2</sub>O<sub>3</sub>) [107] that can inhibit the inward oxygen diffusion. This layer can be continuous with a constant thickness only for Cr concentrations greater than the 15% [108]. Vaillant *et al.* [109] discovered that an increased chromium (and carbon) also promote the formation of intergranular carbides that may mechanically prevent grain boundary sliding as well as increase the strength of the alloy.

### Role of Carbon and Intergranular Carbides

The PWSCC behavior for Alloy 600 is highly susceptible to the microstructure and in particular from the intergranular precipitations [33,35,110–117]. Airey [47] showed that

different thermal treatment can induce a different microstructure in the Alloy 600 by changing the dimension and the density of the intergranular carbides. Burke and Symons [112] identified that the Alloy 600 microstructure could significantly influence the SCC behavior. They observed the occurrence of a pseudo-linear SCC fracture for the Alloy 600 with a well-defined dislocation subgrain structure (as received condition). This dislocation subgrain structure provided an obstacle within the material as opposed to the classic smooth intergranular fracture (and more likely to occur), that was found in the same alloy after heat treatment for 1 week at 982 °C) [118].

Several studies have shown the important role of intergranular carbides in reducing the PWSCC susceptibility of Alloy 600 [69,70]. Sung and Was confirmed that Grain Boundaries (GBs) carbides improved the resistance to PWSCC using CERT tests in pure water at 360 °C [119,120] and it was concluded that the resistance of Alloy 600 to PWSCC can be increased with an "extensive network" of intergranular carbides as shown in the plot of Fig. 27. Similar results were found in different independent studies [35,110–113].

Alloy 600 with GBs highly decorated with intergranular carbides are less susceptible to PWSCC [114,115] and the density of the intergranular carbides can be increased with a thermaltreated process. However, the presence of numerous undissolved intragranular carbides is associated to a higher PWSCC susceptibility. Intragranular carbides as hard, non-deformable particles, may homogenize the deformations through the grain [34].



Fig. 27: Influence of carbide distribution on SCC initiation [121] and propagation [22].

The reason for the apparent positive effect of a "continuous network" of intergranular carbides in reducing the PWSCC susceptibility is still under debate. Several studies [70,109,110,122] showed the beneficial effect of the intergranular carbides on the grain boundary sliding, reducing the SCC initiation and propagation. J.M. Boursier *et al.* [123] and J.L.

Hertzberg and G.S. Was [124] reported that intergranular carbides can lower the creep rate of Alloy 600. Moreover, Bruemmer *et al.* [125] proposed that intergranular carbides will enhance the generation of dislocations, which can reduce macroscopic stress under low strains, thus reducing the PWSCC CGR.

Conversely, the intergranular carbides showed a detrimental effect on Alloy 690 with cold work, exposed to simulated primary water environment in long SCC experiments. It is believed that the PWSCC response was attributed to the increased yield strength resulting from the deformation associated to the cold work. Under PWSCC condition the intergranular carbides could act as preferential site for crack nucleation [116,126–130].

Studies [45,131–133] performed in high temperature H<sub>2</sub>-steam environment at 480 °C, in conditions of interest with regards to PWR primary water [51], have shown the positive effect of the intergranular carbides on oxidation processes (internal oxidation and preferential intergranular oxidation). The authors showed that a semi-continuous network of intergranular carbides (present in Alloy 600 TT) can limit the inward diffusion of oxygen along the grain boundaries. The M<sub>7</sub>C<sub>3</sub> intergranular carbides were observed to be as an active source of Cr during the oxidation. The partial "dissolution" of the carbides released free Cr that promoted the formation of a protective Cr-rich surface oxide [131]. In fact, there was negligible PIO along GBs in Alloy 600 TT compared with extent of PIO observed in Alloy 600 SA, thus providing support for the beneficial role of the intergranular carbides. The reduction in PIO was confirmed in [132] and it was observed that the intergranular carbides also pinned the grain boundaries so that additional boundary migration (*e.g.* DIGM) did not occur. Note that both PIO and DIGM were identified as important SCC "precursor" phenomena.

### **Grain Boundaries**

Intergranular corrosion and SCC susceptibility was primarily mitigated with the control of the environment or the material chemistry. However, the microstructure, and hence the grain boundaries, can also play a fundamental role in the SCC susceptibility [134]. The grain boundaries are described by the Coincidence Site Lattice (CSL) and the associated sigma ( $\Sigma$ ) that represents the reciprocal density of coincidences sites. A boundary with an high  $\Sigma$  exhibits an higher energy than one with low  $\Sigma$ ; such as grain boundaries with a low misorientation (less than 15°) are called *low angle grain boundaries*, and grain boundaries with a high misorientation (higher than 15°) are called *high angle grain boundaries*. Specifically, low- $\Sigma$  boundaries may present special properties, such as coherent twin boundaries ( $\Sigma$ 3) and high-mobility boundaries

in FCC materials ( $\Sigma$ 7). Palumbo and Aust [135] observed that boundaries close to low CSL relationships were observed to be most resistant to the initiation of localized corrosion on pure Ni rod with different S concentrations (0.3, 3, 10, 50 wt ppm) exposed to a deaerated 2 N H<sub>2</sub>SO<sub>4</sub> solution at 303 K. A similar study was conducted by Lin *et al.* [136] on Alloy 600 where a much better corrosion resistance was found to occur in Alloy 600 with an higher number of GBs with  $\Sigma$ ≤29. Palumbo *et al.* [137] showed the importance of grain boundary design and control to obtain IGSCC resistance. It was shown that IGSCC resistance can be obtained when a small fraction of the GBs are not susceptible to IGSCC but only if there is a finite number of non-susceptible grain boundaries in the distribution.

A further study regarding the study of the IGSCC susceptibility as function of the CSL was performed by Alexandreanu *et al.* [138] for Alloy 600. The results showed that the high angle boundaries are more susceptible to crack than the CSLBs regardless of the microstructure and the experimental conditions. A more recent study by Gertsman and Bruemmer [139] highlighted that only  $\Sigma$ 3 boundaries do no undergo SCC and that the grain boundary orientation with respect to the applied load played an important role to the SCC susceptibility.



Fig. 28: IGSCC resistance limit vs. grain boundary misorientation and energy [139].

The most likely explanation of the higher resistance to SCC from several studies is that CSLBs might limit the velocity of dislocation absorption into the grain boundary with an increasing of the lattice hardening [140,141].

### Stress and Strain

An applied or residual stress is an important parameter that affects the PWSCC susceptibility of Alloy 600 and its welds. In particular, the susceptibility increases when the total stress is close to or higher than the yield strength. For constant load experiments, the dependence of PWSCC time-to-failure on stress can be modeled according to the equation (2.7).

time to failure = 
$$A \cdot \sigma^{-n}$$
 (2.7)

where  $\sigma$  is the applied stress, A is a constant and n is the stress exponent. The stress exponent for Alloy 600 MA present some uncertainty, since it was evaluated to be equal to 4 [142] and 5.7 [143], as reported in the two plots of Fig. 29.



Fig. 29: (a) Fraction of yield stress vs. time-to-failure for Alloy 600 MA [142]; (b) applied stress vs. SCC initiation for Alloy 600 [142,143].

The effect of stress on IGSCC is also usually performed with crack growth experiments in which the applied load is constantly controlled in order to have a constant stress intensity factor  $K_i$  during the test. Rebak *et al.* [71] studied the effect of the applied stress intensity factor  $K_i$  Alloy 600 at 330 °C and 400 °C.

The CGR as function of  $K_l$  for Alloy 600 MA is reported in the Fig. 30, where two main trends were identified. For values of  $K_l$  less than 10 MPaVm, the CGR trend was very small and it was considered to be a lower threshold for crack growth in Alloy 600. However, Andresen *et al.* [72] supported the idea that the  $K_l$  minimum threshold does not exist and cracking always occurs but at very low rate. A rapid increase of the CGR was associated with a rapid increase of  $K_l$  increases up to 60 MPaVm, confirming the strong dependence of crack growth on applied stress, as shown in the plot of Fig. 30 [71].



Fig. 30: CGR vs. K<sub>1</sub> for various Alloy 600 MA tubing tested in different laboratories in primary water conditions [71].

From the two SCC experiments, it was possible to assess that the crack growth strongly depended on the load and higher load leading to shorter time-to-failure and the prevention for cracking cannot be guaranteed either at really small loads and the  $K_{ISCC}$  threshold is still under debate.

Morton *et al.* [144] suggested the plastic strain could be a much better parameter than stress to characterize the SCC susceptibility. Boursier *et al.* [123] showed that the crack growth rates during the slow- and rapid- propagation stages only depends on the strain rate, as show in the plot of Fig. 31, with a difference between the slow-propagation and rapid-propagation rate of 10. From this result, the applied stress (above the yield strength of the material) has been proposed to be necessary to generate creep strain.



Fig. 31: Dependence of the CGR from the strain-rate [123].

## Cold Work

Cold Work (CW) strongly increased the PWSCC CGR [150], but its effect on IGSCC is still unclear and under debate. Rebak et al. [79] reported the trend of the CGR as function of the CW

level on specimens previously bent and tested under CERT conditions. As shown in the plot in Fig. 32, higher crack growth rate values [79] were observed to occur for higher CW level.



Fig. 32: Crack growth rate vs. cold work trend for Alloy 600 MA at 330 °C and 350 °C [79].

The increased SCC susceptibility of Alloy 600 in PWR primary water with increasing amount of cold work was confirmed by several others laboratories [79,89,145]. On the other hand, Le Hong *et al.* [75] found that crack initiation times decreased when the specimens were cold-worked for CW value between 0% to 20%, suggesting that CW could be beneficial in mitigating the SCC initiation (Fig. 33). Arioka *et al.* [126] observed a temperature dependence of the cold work on Alloy 690 TT and Alloy 600 MA. The effect of CW was more important in the range between 0 and 30 cc/kg H<sub>2</sub> for specimens tested in 320 °C primary water compared to those tested in 360 °C PWR primary water.



Fig. 33: Influence of cold work on SCC initiation time [75].

## Surface Preparation and Machining Effects

The surface condition, such mechanical preparation or the machining processes, can strongly influence the SCC susceptibility of Ni-based Alloy [146]. Many laboratories have shown the influence of machining on residual stresses [147,148], microstructure [76,147,149] and oxide growth [76] and these different surface conditions can direct influence the SCC behaviour.

Scenini *et al.* [76] performed experiments on Alloy 600 MA tubing with two different surface preparation. They prepared RUB sample with half longitudinal side mechanical polished and the other one electropolished. Contrary to common belief, the electropolished samples were more susceptible to SCC than the mechanically polished. The presence of a CW might generate a surface-deformed layer with a high number of dislocations that can enhance the outward diffusion of Cr with the formation of a protective Cr-rich external oxide layer.

In a more recent study of Turnbull *et al.* [146], SS 304 with four different surface preparation (transverse grinding; longitudinal grinding; transverse dressing; and transverse milling) has been tested under a constant four-point bend loading in a methanolic solution of MgCl<sub>2</sub> designed to leave a residue of 5-10  $\mu$ g/cm<sup>2</sup> of salt on the specimen. The different machining processes strongly influence the mechanical proprieties and the SCC susceptibility of the material. Higher SCC susceptibility was reported for samples prepared using longitudinal grinding whereas transverse grinding promoted lower SCC susceptibility.

More recently, Chang *et al.* [151] performed Slow Strain Rate Tensile (SSRT) tests at 300 °C in simulated PWR primary water environment on warm-forged Type 304L stainless steel samples, with highly polished surfaces and machined surfaces obtained by three difference machining processes. Although, the SCC was observed to initiate both on the machined surfaces and on the highly polished surface, the machined surfaces were more resistant to SCC initiation than a stress-free surface. This behaviour was related with the formation of an ultrafine-grained layer just beneath the surface, which promoted faster but uniform oxidation in contrast to the oxidation behaviour of the polished surface.

### 2.3.3.2. Proposed Mechanisms to Account for PWSCC

Several mechanisms have been proposed to explain the occurrence of PWSCC in Ni-base alloys, but although some model can produce a valid explanation of the occurrence of PWSCC, no single model can completely describe both initiation and propagation of PWSCC taking in account the numerous parameters affecting this phenomenon. The most relevant models that can help in understanding the mechanistic processes of PWSCC will be briefly described in this section. These include: 1. Hydrogen Embrittlement: Lattice Decohesion (also known as Hydrogen-Enhanced Decohesion, HEDE), 2. Hydrogen-Enhanced Localized Plasticity (HELP), 3. Corrosion-Enhanced Plasticity Model, 4. Slip dissolution/film rupture mechanism, 5. Internal Oxidation.

## Brief Summary of Hydrogen-Assisted Mechanisms

In this section, a very brief synopsis of relevant hydrogen embrittlement mechanisms is presented. However, the reader is referred to the following references [152–155] for a detailed review.

### Hydrogen Embrittlement: Lattice Decohesion

In this mechanism, H<sub>2</sub> may be absorbed into the metal and concentrate in regions of high triaxial stress, such as crack tip or surface defects and it was proposed for the first time by Troiano *et al.* [156], as schematically reported in Fig. 34. The high presence of hydrogen can weak the metal bonding and facilitate the nucleation of embryo-cracks causing the fracture of the material [156,157].



Fig. 34: Schematic illustration of the decohesion model for hydrogen embrittlement proposed by Troiano [156] and refined by Oriani *et al.* [157].

### Hydrogen Enhanced Localized Plasticity

The Hydrogen Enhanced Localized Plasticity (HELP) model is based on the interaction between hydrogen, which diffuses into the metal, and the mobile dislocations present during deformation. At PWR temperatures (300 - 400 °C) cross slips occur and mobile dislocations are

able to pile-up behind an obstacle and the short-range stress field produced by the dislocations can influence the separation distance between the other dislocations. The presence of hydrogen can affect and reduce this short-range stress field [158–160] and the dislocations can pass an obstacle and move closer to each other increasing the creep deformation. Paraventi *et al.* [161,162] reported that hydrogen can reduce the stress field of dislocations and enhance the creep with an effect on dislocation-controlled deformation behaviour of Alloy 600 in PWR primary water conditions.

The addition of hydrogen can reduce the stress and dislocations can move closer to each other, as shown in Fig. 35. In the image on the right, the addition of 106.66 mbar of hydrogen drastically reduced the distance between the dislocations, labelled from *A* to E in Fig. 35.



Fig. 35: High voltage electron microscopy showing (a) the original position dislocation pileup in Ni-16Cr-9Fe alloy before hydrogen was introduced (0 torr), where each dislocation was labelled with a letter. In (b), the spacing between the dislocations reached the minimum by adding 80 torr of H<sub>2</sub>. The position was checked with respect the immobile dislocation labelled in both micrographs as "Ref. point" [161].

Moreover, it was noticed a change of the creep behaviour of Ni-16Cr-9Fe at 360 °C by changing the environment from Ar to  $H_2$ . The Fig. 36 shows a jump in transient creep, associated with a reduction in shielding stress with the consequent contraction of dislocation pile-up.



Fig. 36: Effect of hydrogen on creep for the Ni-16Cr-9Fe [162].

# Corrosion-Enhanced Plasticity Model

Magnin *et al.* [163] proposed the Corrosion-Enhanced Plasticity Model (CEPM) to explain the brittle transgranular SCC occurrence of SS 316 exposed to  $Mg_2Cl$  at 153 °C. The model has been revised several times [164–168] to explain the intergranular behavior of SCC. In its latest form [169], the main steps responsible of the crack propagation are listened below and schematically shown in Fig. 37.

- The rupture of the {111} slip planes, leads to depassivation and injection of hydrogen into a localized region at the crack tip (1 and 2 in Fig. 37).
- 2. The interaction of hydrogen with the dislocations on the slip planes leads to a easy dislocation motion and to a softened region ahead the crack tip.
- 3. The dislocations can move easily in the softened zone of the material and pile up at an obstacle, if present (3); the addition of other dislocations in the proximity of the obstacle can generate a small cavity or a crack-embryo (4).
- 4. Once the crack embryo is formed, the main crack (on surface) can go into the material and reach the crack embryo (5). The grain boundary or the {111} plane are used by the crack to move forward (5).
- The process can repeat and go on with the injection of new hydrogen at the new crack tip.



Fig. 37: CEPM schematic [165].

This model was able to describe the hydrogen embrittlement susceptibility related to higher CW and the role of intergranular carbides as hydrogen traps, but it did not clarify the initiation stages of the process [84]. In fact, this mechanism was strongly criticized by Young *et al.* [84] since Alloy 600 presents a typical intergranular fracture and not a the "zig-zag" micro-cracking and the transgranular fracture mode proposed in this mechanism.

However, Burke and Symons [112] found evidence of this model after fracture analysis on an Alloy 600 sample that presented a dislocation subgrain structure. After exposure to simulated PWR environment, the material exhibited a pseudo-intergranular fracture similar to that proposed in [169].

# Slip Dissolution/Film Rupture Mechanism

Logan *et al.* [170] proposed the slip-dissolution model for the first time in 1952 in order to explain the high potential SCC of several alloys systems, such as Al alloys, brass, Mg alloys, carbon and stainless steels. The model was later refined and re-named "Film-rupture mechanism" by Smith and Staehle [171]. The slip-dissolution mechanism consists of the repetition of three stages: 1. the protective oxide film that cover the underneath metal cracks due to plastic strain thereby exposing the unprotected metal. 2) An anodic and localized dissolution reaction of the exposed metal can occur followed by 3) a re-passivation of the metal. The process can repeat with the fracture of the new protective oxide layer at the crack tip due to dynamic plastic strain with the occurrence of more metal dissolution. The steps of the Slip dissolution are shown in Fig. 38.



Fig. 38: Scheme of the slip dissolution mechanism [172].

This model presents two limitations: 1. A defect on the surface is needed, otherwise it is not possible to break the passive film on the surface and 2. grain boundaries are considered one of such point due to strain and stress localization during deformation.

The film-rupture mechanism model was also adopted by Andresen [173] and Ford and Andresen [174] to describe SCC occurrence for lower potential in PWR primary water conditions. The model well described the crack growth rate of Alloy 600 in both pressurized water at 330 – 360 °C and steam at 400 °C as reported by Rebak *et al.* [71]. However, Staehle *et al.* [22] and Scott *et al.* [175] noticed that there is no continuum of the crack growth rate as function of the potential, as it is shown in Fig. 39.

The film rupture kinetics decreased when the H<sub>2</sub> partial pressure was reduced, but it is in contrast with the well-known bell-shaped relationship with the higher susceptibility to SCC of Alloy 600 in the proximity of the Ni/NiO transition [175]. Also Hall [176] criticized the Ford-Andresen model [174], since he noticed several inconsistency in the model, such as: 1. the expression of the crack density lacked on the necessary dependence on the crack tip strain rate and 2. the mathematical approach considered independent the film rupture and re-passivation.



Fig. 39: CGR vs. H<sub>2</sub> partial pressure plot for A600 at 360 °C [175].

A more recent model was developed by Hall [177]. This model predicted that creep was necessary for sustaining the crack growth, where the creep rate limited the crack velocity for a constant *K* and dK/da loading. Moreover, it was extrapolated from the mathematical model that the crack tip strain induced by the crack advance is the effect and not the cause of the crack growth.

# Internal Oxidation Mechanism

Internal oxidation (IO) is a process in which oxygen can dissolve in the alloy, diffuses into the alloy matrix and forms oxide particles of the less noble alloying elements [54,178]. Internal oxidation occurs when the alloy is composed by a solvent metal A and at least one solute metal B (with a lower free energy for the oxide phase than the solvent metal A) and when the oxygen partial pressure is not sufficient to oxidise the main alloying element A.

The percentage of the solute metal B can influence the oxide morphology. If the solute concentration is low, the BO oxide particles will remain discrete within the alloy matrix; on the contrary, if the solute concentration is high enough, there will be the creation of BO oxide particles that can form a protective and uniform surface oxide layer [179]. A description of the internal oxidation process is described in section "2.4.1. – Overview on the Elevated Temperature Internal Oxidation, Introduction" The rate of the internal oxidation strongly depends on the inward oxygen diffusion and on the solute atoms diffusion; usually oxygen diffusion is generally much faster than the diffusion of metal atoms. However, this mechanism is only valid at high temperature, where oxygen diffusion is enhanced. For example, the internal oxidation process can be a serious problem for Ni-base alloys and superalloys used in jet engines,

due to the high working temperature (T > 800 °C) [48,180,181]. Grain boundaries can represent a preferential way for oxygen diffusion, where the oxygen diffusion is faster than the oxygen diffusion in within the alloy matrix [180,182]. Diffusion of oxygen along grain boundary becomes more and more important when the temperature decreases, leading to a faster diffusion compared with the bulk diffusion.

Scott & Le Calvar [183] proposed in 1993 the "Internal Oxidation" model as possible mechanism to describe the Alloy 600 PWSCC. For Alloy 600 and in general for Ni-base alloys, Ni is the solvent and Cr and Fe represent the solute element. As schematically reported in Fig. 40, the mechanism is the cyclic repetition of three steps: 1. formation of the brittle oxide ( $Cr_2O_3$ ) layer at the GBs with 2. The formation of nano-cracks under an applied or residual tensile stress. 3. the cracks can propagate with cyclic oxidation/embrittlement of the GBs. The crack propagation can be modelled as a succession of periodic GB brittle ruptures followed by formation of intergranular brittle oxide ahead the crack tip, with the formation of the characteristic brittle failure of Alloy 600. This mechanism can be applied to both crack initiation and propagation and it composed by the following stages.

Since its development, the IO model [183] received some critiques and several development that proved the hypothesis proposed in 1993. More details and controversy regarding this model will be discussed in details in the section "2.4.3.5, Consideration about the Internal Oxidation Model".



Fig. 40: The "Internal Oxidation" model of Scott and Le Calvar [183].

# 2.4. Overview on the Elevated Temperature Internal Oxidation

# 2.4.1. Introduction

Oxidation is considered to be the most relevant corrosion reaction and one of the main "precursor events" associated with SCC in PWR primary water reactor. In this chapter, the oxide evolution, the formation mechanism and the parameters affecting the oxidation will be introduced. For a metal *M*, the high temperature reaction with the oxidizing species, such as oxygen, *O* is reported in equation (2.7) [180,184–187].

$$aM + \frac{b}{2}O_2 = M_a O_b \tag{2.7}$$

The Wagner [180] theory for the oxidation of metals gives a fundamental understanding of the high temperature growth at high scale. The model assumes that the oxide is dense, continuous, in a single phase and covers the whole surface of the sample. The oxide growth involves both ionic and electronic charges fluxes, as shown in Fig. 41 [180].



Fig. 41: Transport processes and interfacial reactions in the growth of the oxide MO according Wagner's theory [180].

However, the Wagner model is an ideal standard that deviates from the reality, in fact pores and voids can be found in real oxides [188,189]. This model can be considered only to help in the understanding of the high oxidation steps. The reaction path and oxidation events involve many individual phenomena and they may depend from several factors [180], however, a simplified process associated with the high temperature oxidation steps can be described as:

- 1. The oxygen is absorbed on the metal surface.
- 2. Oxygen can dissolve into the metal, leading at the formation of an oxide on the surface.
- 3. The oxide layer can be continuous with a cut off the O source, protecting the underneath metal from further oxidation with the creation of a passive layer (passivation process).

This kinetics associated with the oxide formation can follow different rates during its formation stages. The oxide growth is generally fast during the initial stages to change to a parabolic rate [180,184]. During this second stage, the rate-controlling step is the diffusion of the reactants through the oxide layer, where the diffusion is a thermally-activated process and it generally follows an Arrhenius relationship [180]. In some circumstances, the oxidation of metal follows a linear rate law and it can happen when the oxide is volatile, porous and non-protective [180]. Controversy, for relatively low temperature between 300 °C and 400 °C, the oxidation rates are usually logarithmic [180].

At thermodynamic equilibrium, the oxygen partial pressure  $(p_{O_2})$  required to form an oxide species is called dissociation pressure  $(p_{O_2 M_a O_b})$  and it can be easily calculated from the standard Gibbs free energy of formation associated with that oxide species [180]. If the  $p_{O_2}$  in the system is higher than the  $p_{O_2 M_a O_b}$ , the formation of the oxide is promoted and lower is the standard Gibbs free energy [98,101,180], more stable is the oxide.

In a PWR primary water environment, at the temperature of 360 °C, the equation (2.8) shows the stability of any oxides that is possible observe in Alloy 600, where the  $Cr_2O_3$  is the most stable:

$$Fe_2O_3 > NiO > Fe_3O_4 > Cr_2O_3$$
 (2.8)

However, when the PWR primary water operates in the more reducing side than the Ni/NiO transition, only  $Fe_3O_4$  and  $Cr_2O_3$  are thermodynamically stable.

For a generic alloy, the diffusing oxygen can react with the less noble solute element in the alloy to form internal oxidation [190]. In the simplest case of a binary alloy A-B, with the B the less noble metal, oxygen can diffuse in forming BO<sub>x</sub> discrete particle oxides within the matrix, according to the equation (2.9).

$$B + xO \to BO_x \tag{2.9}$$

The higher stability of the oxides, the lower is the associated standard Gibbs free energy of formation, and it is for this reason than in Alloy 600 exposed to PWR primary water

environment,  $Al_2O_3$ ,  $SiO_2$ ,  $TiO_2$  and  $Cr_2O_3$  [191,192] are found to be stable internal oxides. The kinetic controlling the internal oxidation is diffusion controlled and the extent of the internal oxidation zone  $\xi$  is expressed by the equation (2.10) [193,194].

$$\xi = \left(\frac{2N_O^S D_O t}{\nu N_B^O}\right)^{1/2} \tag{2.10}$$

Where  $N_O^S$  is the solubility of the oxidant in the alloy,  $D_O$  is the diffusivity of the oxidant in the alloy,  $N_B^O$  is the initial solute concentration in the A-B alloy, t is the time and v is the stoichiometric coefficient of oxygen to form the specific oxide.

The transition from internal to external oxidation is strongly affected by the concentration of the less noble alloying elements in a generic alloy. In a simple case of a dilute binary alloy A-B, if the oxygen partial pressure is high enough to oxidize the less noble element B, a BO<sub>x</sub> oxide nucleates in the A rich matrix to form a discrete internal oxide [180]. If the element B presents a fast diffusion rate and the concentration is high enough, it can reach the surface and maintain an active source to form a complete external layer of BO<sub>x</sub> oxide. Therefore, the internal to external oxide transition is defined by the oxygen partial pressure and by the fluxes balance between the oxygen and B components. The minimum volume fraction, *f*\*, was proposed by Wagner [194] and later his theoretical calculation were experimental confirmed by Rapp *et al.* [195] in their studies on Ag-In alloys.

# 2.4.1.1. Surface Preparation Effect

The surface preparation can play an important role in the transition from internal to external oxidation. Mechanical polishing can create a superficial deformed layer with an increased number of fast diffusion paths, such as dislocations or slip bands that can be used by the less noble metals in the alloys to outward diffuse at higher diffusion rate than the inward diffusion of oxygen.

The surface preparation effect was studied by Rapp *et al.* [195] on the Ag-In alloy and by Ostwald and Grabke [196] on steels with a different Cr concentration. They noticed that a superficial cold worked layer promoted external oxidation by increasing the bulk diffusivity of the less noble metal.

Scenini *et al.* [73,76] exposed electropolished and mechanically polished and electropolished Alloy 600 samples in  $H_2$ -steam at 480 °C. They found internal oxidation in the

electropolished samples, whereas the mechanically-polished samples presented an external oxide layer. They suggested that the deformed layer might increase the resistance to intergranular oxidation and so to SCC. The findings of Scenini *et al.* [73,76] were strongly criticized because the electropolishing was believed to the remove the cold-worked surface layer and increase the Alloy 600 PWSCC resistance. The findings of Scenini *et al.* [73,76] were later confirmed by Morris *et al.* [197], that observed a less susceptibility to intergranular oxidation on as-machined Alloy 600 if compared to electrochemically-polished or solution annealed Alloy 600. A further evidence of the less susceptibility to intergranular oxidation and SCC was found by Lindsay *et al.* [65] on OPS and P600 grit Alloy 600 samples exposed to  $H_2$ -steam at 400 °C.

# 2.4.2. PWR Oxidation

The Alloy 600 oxide structure that form in PWR simulated environments was studied by several laboratories [87,108,198–201]. The oxide, as shown in Fig. 42, is a dual layer oxide. The inner and thin layer (1-10 nm) is a  $Cr_2O_3$  layer [198]. This oxide is probably the main protective layer and it grows by a solid-state diffusion mechanism [87]. The outer layer presents a mixture of large and small octahedral crystals which create a non-protective iron-rich oxide [200]. The oxide crystallites forming the outer layers are Cr-free and contain Fe and Ni, where the composition strongly depends on the surface finishing and on the concentration of Fe<sup>2+/3+</sup> and Ni<sup>2+</sup> cations in the aqueous environment. On Ni-base alloys this layer is mainly composed by (Ni<sub>x</sub>Fe<sub>1-x</sub>)Fe<sub>2</sub>O<sub>4</sub> ferrite [198]. Panter *et al.* [199] observed a Cr- and Fe-depleted layer and the diffusion of oxygen at the grain boundary.



Fig. 42: Schematic representation of the oxide species formed on Alloy 600 in simulated PWR primary water condition [108].

Delabrouille *et al.* [108] have suggested that there is a "affected zone" below the oxide similar to that observed in Alloy 690 oxidation [202], where an a fine grained microstructure region similar in appearance to a deformed layer was observed. Machet *et al.* [203,204] proposed that the passivation of the Alloy 600 exposed to high temperature water of a ultrathin (1 nm thick)  $Cr_2O_3$  layer.

### 2.4.2.1. Effect of Cr

The Cr content can strongly increase the passivity and the re-passivation rate [44] and it can influence the oxide layer formation, where a minimum threshold of 15 wt.% was observed to obtain the formation of a protective surface oxide layer on Ni-base alloys [43]. A higher Cr content in Ni-base alloys (*e.g.* Alloy 690), should increase the oxidation resistance and promote the formation of a protective surface oxide layer, in fact it was observed that the inner oxide layer formed on Alloy 690 is similar to that formed on Alloy 600 but it is thicker, more protective and probably with a higher percentage of  $Cr_2O_3$  [107]. Legras *et al.* [106] studied the oxidation behavior of Ni-base alloys containing Cr between 5 wt.% and 30 wt.% exposed to simulated PWR primary water at 360 °C. They noticed that the higher was the Cr concentration in the baseline material, the higher was the presence of Cr in the external oxide and thinner was the depleted zone underneath the surface. Moreover, a minimum Cr concentration of 15 wt.% was necessary for the formation of an inner and protective oxide layer.

## Effect of Dissolved H<sub>2</sub>

The dissolved H<sub>2</sub> is another important parameter that can influence the oxide formation on Alloy 600 exposed to high-temperature water. Terachi *et al.* [201] performed oxidation experiments on Alloy 600 in simulated primary water at 320 °C with different H<sub>2</sub> concentration (0, 1, 2.75, 4 ppm of hydrogen) and they observed a multi-layered oxide structure according to the dissolved H<sub>2</sub> concentration, where the results are summarized in Fig. 43. A continuous and stable NiO layer was found for low dissolved H<sub>2</sub>; for the intermediate values of dissolved H<sub>2</sub> (around 1 ppm) the NiO was less stable and the Alloy 600 surface was decorated with a needlelike oxide. For dissolved H<sub>2</sub> contents between 1 ppm and 2.75 ppm, a Ni-Fe spinel oxide was the dominant phase, with a thin Cr-rich oxide layer beneath it. The spinel oxide thickness increased as the dissolved H<sub>2</sub> was increased above 2.75 ppm. Further studies on the effect of dissolved  $H_2$  on the Alloy 600 oxide film formation were performed by Combrade *et al.* [200] and Soustelle *et al.* [87]. For potential close to the Ni/NiO transition, at which the Alloy 600 exhibits the highest susceptibility to PWSCC, the Cr-rich spinel oxide layer was thicker and the outer oxide layer was more pronounced but less protective. Alloy 600 was covered mainly with  $Cr_2O_3$  [199] when Alloy 600 was exposed to low redox potentials (*i.e.* under reducing conditions with respect to the Ni/NiO transition).



Fig. 43: Evolution of the oxide composition and structure on Alloy 600 exposed to high temperature water at 320  $^{\circ}$ C for different dissolved H<sub>2</sub> concentrations [201].

### 2.4.2.2. Oxides in PWR Primary Water Environment

As discussed in the previous section, Ni-Cr-Fe Alloys exposed to high temperature PWR primary water environment can exhibit a huge variety of oxides. According to the electrochemical potential, NiO with FCC form, hexagonal  $Cr_2O_3$  can be observed on Alloy 600 and Fe-Ni-Cr spinel oxides with FCC form can be observed. Spinel oxides having general formula  $AB_2O_4$  represent the majority of the oxides that form on Fe-Ni-Cr alloy surface when exposed to high temperature water. They can be chromite-type (FCC), enriched in Cr with normal spinel structure and general formula  $(Ni_xFe_{1-x})(Cr_{1-y}Fe_y)_2O_4$  or Ni Ferrite-type (FCC) with a Fe-rich oxide with inverse spinel structure and general formula  $(Ni_xFe_{1-x})(Cr_{1-y}Fe_y)_2O_4$  or Ni Ferrite-type (FCC) with a Fe-rich oxide with inverse spinel structure and general formula  $(Ni_xFe_{1-x})(Fe_{1-2}Cr_z)_2O_4$ . When the variables x and z are equal to 0, the oxide corresponds to magnetite (Fe<sub>3</sub>O<sub>4</sub>) and when x is equal to 1 and z is equal to 0, the oxide corresponds to nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>).

# 2.4.3. Internal Oxidation

The grain boundary oxidation can become an important issue at relatively low temperature. In fact, the higher oxygen diffusivity at grain boundary than the matrix can generate the oxidation and internal oxidation along grain boundaries can occur.

In the following sections, the results of internal and intergranular oxidation behavior of Ni-Alloys exposed to 1200 °C in gas atmosphere, ≈400 °C in steam, and ≈300 °C in PWR simulated primary water have been described in detail.

### 2.4.3.1. Internal Oxidation of Alloy 600 in PWR

The main results related to the PWSCC initiation and intergranular oxidation in PWR simulated environment are reported in this section. Several laboratories detected the occurrence of intergranular oxidation at grain boundaries below the oxidized surface of Alloy 600 in PWRs operational temperatures.

A 10  $\mu$ m oxygen penetration at grain boundary triple points was detected by Delabrouille *et al.* [108] by performing Second Ion Mass Spectrometry (SIMS) experiments and similarly, Panter *et al.* [199] detected Cr and O enrichment at triple GB junctions with EDS analysis on Alloy 600 tested at 360 °C in high temperature water.

Thomas and Bruemmer [205] tested Alloy 600 Reverse U-Bend specimens at 330 °C for 5435 h in simulated primary water. STEM-EDXS microanalysis revealed a complex oxide morphology along the intergranular crack tip. The oxide along the crack wall was composed principally by NiO with some Fe- and Cr-enriched regions and the crack path exhibited 400 nm intergranular oxides penetration mainly composed by Cr<sub>2</sub>O<sub>3</sub> and with a thickness between 5 nm and 20 nm. The oxide presented several discontinuous and extremely small pores. At the crack tip, the oxide was principally Cr<sub>2</sub>O<sub>3</sub>, as schematically reported in Fig. 44.



Fig. 44: Representation of a PWSCC crack tip morphology observed in Alloy 600 exposed to PWR primary water [205].

Sennour *et al.* [206] and Guerre *et al.* [207] obtained a first hint of Internal Oxidation occurring along a GB and ahead the crack tip for Alloy 600 exposed to simulated primary water at 330 °C. The High Angle Annular Dark Field (HAADF) STEM image and corresponding elemental maps acquired from the STEM-EDX dataset showed a Cr-enriched oxide at the crack tip, as shown in the Cr elemental map in Fig. 45.



Fig. 45: HAADF STEM image and EDX elemental maps of an oxidized grain boundary tip.

The authors argued that PWSCC of Alloy 600 was dependent on the  $Cr_2O_3$  and  $Ni(Fe,Cr)_2O_4$  growth along grain boundaries due to an inward oxygen diffusion and an outward Cr diffusion ahead the oxide tip, where a schematic is reported in Fig. 46.



Fig. 46: Schematic representation of the SCC model as subsequent of cracking, where the yellow triangles are Ni(Fe,Cr)<sub>2</sub>O<sub>4</sub>, green areas are NiO and the orange triangle is Cr<sub>2</sub>O<sub>3</sub> [206].

Schreiber *et al.* [208] analysed unstressed Alloy 600 coupons exposed to PWR primary water at 325 °C for 500 h in order to obtain GB compositional information as result of the oxidation. The intergranular oxide was composed with a nanocrystalline (≈100 nm) Cr-rich MO-structure and spinel oxides followed by discontinuous and discrete Cr-rich sulphide particles, as shown in the HAADF image and corresponding elemental maps extracted from the STEM-EDX spectrum imaging dataset reported in Fig. 47, however these results have never been reproduced and confirmed from other laboratories.



Fig. 47: STEM-EDX elemental maps of the intergranular attack, showing Cr-rich oxide and localized depletion of Ni and Fe, followed by Cr-rich sulphides with Fe and Ni depletion [208].

Other confirmation of the IO model were found by Dugdale and Lozano-Perez [209]. They tested Alloy 600 using triangular micro-cantilevers and analysed the oxidized GBs under an external stress. Thanks to the not completely failure of the cantilever, it was possible obtain a direct correlation between the cracks and the intergranular oxide. They observed that the fracture stopped where the oxide terminated and the cracks propagate along the metal-oxide interface and not through the oxide or the matrix (Fig. 48).



Fig. 48: Fracture of oxidized GB with an intergranular carbide [209].

Similar findings were found by Dohr *et al.* [210] who studied micro-beam mechanical tests on Alloy 600 containing oxidized GBs in a similar experimental apparatus. They confirmed that the crack front arrested at the point where the intergranular oxide terminated and the metal/oxide interface was the preferred crack path.

More recently confirmation about the role of the "selective" intergranular oxidation as precursor of PWSCC were found by Shen *et al.* [211]. They investigated the SCC behavior of Alloy

600 MA exposed to PWR primary water at 320 °C to understand the precursors and the early stages associated with the SCC crack propagation. They analyzed three active SCC crack tips on different energy grain boundaries by using Electron Energy Loss Spectroscopy (EELS). Similar oxide morphologies were detected for three different grain boundaries ( $\Sigma$ 1,  $\Sigma$ 25b,  $\Sigma$ >29), although a deeper oxide penetration was observed for the high energy GBs. The oxide was found to be just ahead the Cr and Fe depleted zone and it was highly enriched in Cr with sporadically Ni and Cr spinels. As already observed in previous studies, the crack preferred to propagate along the intergranular oxide zone-matrix interface. From their observations, they supported the hypothesis that the dominant mechanism leading to SCC is intergranular internal oxidation, with the main precursors are the Cr depletion zone and the formation of a porous oxide.

### 2.4.3.2. Internal Oxidation above 500 °C

Ni-Cr alloys and superalloys are susceptible to internal oxidation for temperatures higher than 1000 °C exposed to air or to low oxygen partial pressure environments [212–215]. For these temperatures, the grain boundary diffusivity is comparable with the matrix diffusivity.

The first study that reported the effect of temperature on the internal oxidation was performed by Stott *et al.* [216]. They observed the formation of different internal oxides such as internal oxidation, intergranular oxidation and voids in Ni-15Cr-1Al and Ni-28.8Cr-1Al after exposure to 1 atm of oxygen between 1000 °C and 1200 °C. For the samples exposed at 1200 °C, they noticed a similar oxide penetration along the grain boundaries and within the matrix, whereas for the samples exposed at 1000 °C, a deeper penetration along the grain boundaries was noticed.

Similar results were obtained by Shida *et al.* [217] for Ni-40%Cr alloy. They argued that these different oxidation morphologies might be attributed to the void formation along the grain boundaries with the creation of a fast diffusion path for oxygen. However, also the temperature itself has an effect on the diffusion coefficient of oxygen.

Maybe, the most significant evidence of the effect of the temperature on the internal to intergranular oxidation is reported in the studies of Wood *et al.* [218]. They studied the internal oxidation behaviour of binary Ni alloys with 1-5% of Cr between 800 °C to 1000 °C in Ni/NiO Rhines packs. At 1000 °C the oxide grew as discrete particles within the alloy matrix whereas at 800 °C it grew preferentially at the grain boundaries. These results strongly demonstrated the dependence of the diffusion coefficients of oxygen from the temperature

where an intergranular oxide formation is favoured at lower temperatures since the diffusivity ratio between grain boundary and matrix is higher at lower temperature. A schematic representation is shown in Fig. 49.

Despite the high temperature, the work performed by Wood *et al.* [218] can be used to describe the oxidation behavior in PWR conditions. In fact, differently from the 1 atm of oxygen, the Rhines pack method suppressed the formation of a superficial and protective NiO layer, with the formation of an extensive intergranular oxide penetration, as it is possible to observe in a PWR primary water environment. The slightly reducing conditions with respect to the Ni/NiO transition at which a PWR operates does not allow the formation of an external NiO layer.



Fig. 49: Types of intergranular oxidation observed at high temperature in Ni-Cr alloys in Ni/NiO powder Rhines packs [218].

# 2.4.3.3. Internal Oxidation below 500 °C

The main results about the internal oxidation below 500 °C are reported in this section. Although the oxidation kinetic is relatively slow for temperature below and the extent of internal intergranular oxidation is much lower and difficult to detect, several laboratories demonstrated the internal oxidation and preferential intergranular oxidation for Ni-base alloys.

The first occurrence of oxygen penetration along grain boundaries was detected by Gendron *et al.* [219]. They exposed Alloy 600 at to H<sub>2</sub>-steam at 400 °C for 8 h and they detect a 1  $\mu$ m deep Cr<sub>2</sub>O<sub>3</sub> intergranular oxide using SIMS analysis. Sui *et al.* [92] performed steam experiments at 380 °C on RUB specimens of both Alloy 600 and Alloy 690 and both alloys presented intergranular cracks. Further evidence of intergranular oxidation was observed on electropolished Alloy 600 sample exposed to H<sub>2</sub>-steam at 400 °C by Newman *et al.* [220].

Also Persaud *et al.* [221] confirmed the susceptibility to internal and intergranular oxidation of Alloy 600. They performed H<sub>2</sub>-steam environment experiments by setting the oxygen partial pressure 30 times below the Ni/NiO dissociation pressure. A Cr and O enrichment associated with a Fe and Ni depletion in the near surface region and at the grain boundaries was observed by using high resolution STEM-EDX microanalysis. The most evident characteristic was the difference in depth between the internal oxidation within the matrix and the intergranular oxidation along the grain boundaries, being at least four times deeper than the internal oxidation within the matrix. The authors argued that grain boundaries can provide a short-circuit diffusion paths for oxygen, particularly evident at relatively low temperature.

Similar results about the oxidation of Alloy 600 were obtained by Bertali *et al.* [46] by using advanced ATEM techniques. The intergranular oxides were enriched in Cr with a Ti and Al enriched core. Away from the grain boundaries, internal oxidation was observed. Some internal oxidation examples indicated dislocations as preferential diffusion paths. These studies confirmed that Alloy 600 was susceptible to preferential intergranular oxidation in H<sub>2</sub>-steam environment, as shown in the SE image obtained from the FIB-produced cross-section of an oxidized grain boundary in Fig. 50.



Fig. 50: SE image of a FIB cross section obtained on a grain boundary after exposure to H<sub>2</sub>-steam environment at 480 °C for 35 h [46].

In order to prove the oxidation mechanisms of Alloy 600 were similar in both H<sub>2</sub>-steam environment and in simulated PWR primary water, Economy *et al.* [30] conducted oxidation and SCC experiments on Alloy 600 in the two different environments from 320 °C to 400 °C. They observed very similar morphologies of the fracture surfaces, suggesting that the mechanism is similar for both environments. However, a faster occurrence of cracks was noticed in the samples exposed to H<sub>2</sub>-steam at 400 °C. The effect of temperature was also studied on the intergranular oxidation behaviour on Alloy 600 SA by Bertali *et al.* [68]. They exposed coupon samples to high pressure H<sub>2</sub>-steam at 400 °C and to simulated PWR primary water at 320 °C. An intergranular oxide enriched in Cr with a local enrichment of Al and Ti was observed in both samples exposed at 400 °C and 320 °C (Fig. 51a and Fig. 51b respectively), as already observed in Alloy 600 samples exposed to H<sub>2</sub>-steam at 480 °C [46]. These results strongly support that the oxidation mechanism of Alloy 600 is the same for both superheated steam and PWR primary water environment and that the H<sub>2</sub>-steam environment can be used to perform experiments relevant to a PWR primary water environment.



Fig. 51: BSE images showing FIB cross-section of a. a GB exposed to high-pressure steam at 400 °C for 500 h and in b. a GB exposed to high-pressure steam at 320 °C. Both grain boundaries showed an intergranular oxide penetration associated with DIGM [68].

# 2.4.3.4. Parameters Affecting the Internal Oxidation

## H<sub>2</sub> Content

As already discussed in the previous section, PWSCC of Alloy 600 is strongly influenced by the amount of dissolved hydrogen that directly control the EcP, where the maximum susceptibility to PWSCC for both initiation [222] and propagation [64] is located in the proximity of the Ni/NiO transition. Fournier *et al.* [223] performed oxidation experiment on Alloy 600 in simulated PWR primary water at different dissolved hydrogen concentration. They noticed that the maximum internal penetration was observed at 30 kPa of  $p_{H_2}$ , corresponding at Ni/NiO transition. The penetration decreased or became negligible for more reducing (650 kPa of  $p_{H_2}$ ) or more oxidizing (1 kPa of  $p_{H_2}$ ) environments. The deeper intergranular oxidation found at the Ni/NiO can be easily related to the formation of a surface meta-stable and not protective oxide layer. The lower intergranular penetration rate in more reducing is probably associated to the exhaustion of available oxygen in the simulated PWR primary water environment, whereas in more oxidizing environment to the formation of a more tick and protective oxide.
#### Cr content

The effect of Cr content on the intergranular oxidation of Ni-base alloys has a similar beneficial effect as already observed for the PWSCC susceptibility. For a higher Cr content, a more protective and dense oxide layer enriched in Cr can be formed with a limit on the SIO penetration, in fact several studies [208,223,224] have reported an intergranular penetration of  $\approx 1 \,\mu$ m on polished Alloy 600 after 500 hours of exposure to PWR primary water at 325 °C and of  $\approx 10 \,\mu$ m after 4000 hours of exposure to PWR primary water at 338 °C. In contrast, no intergranular oxide penetration was observed in Alloy 690 after 1000 hours exposure at 360 °C in a PWR primary water environment [225]. Similar results were obtained by Persaud *et al.* [226] on polished Alloy 690 exposed to superheated H<sub>2</sub>-steam environment at 480 °C for 120 h, where the material did not present intergranular oxidation but the GB was covered with an external oxide layer.

#### Role of the Intergranular Carbides

It is well known that an extensive network of intergranular carbides can decrease the PWSCC susceptibility [50,51] of Ni-base alloys. A similar behaviour has been observed for the PIO susceptibility. The intergranular carbides can be oxidized or consumed during the exposure of Ni-base alloys in a PWR primary water environment [196,203,208]. The role of the carbides in Alloy 600 TT has been shown in a more recent study of Bertali *et al.* [131], who exposed Alloy 600 TT coupon samples to H<sub>2</sub>-steam environment at 480 °C.

Advanced microscopy characterizations have revealed a negligible PIO penetration of about 10 to 50 nm in contrast with what observed in Alloy 600 SA, where the PIO was about 100 to 500 nm deep. The carbides were observed to be partially dissolved and acted as reservoirs of Cr (Fig. 52), where the Cr "was used" to create a protective oxide layer, inhibiting further oxygen diffusion along the GB. The enhanced oxidation/dissolution of carbides oxidation in PWR primary water environment is also supported by thermodynamic calculations from Laghoutaris *et al.* [131], which showed that Cr-rich carbides are more easily oxidized. Moreover, the inward diffusion of oxygen can be limited by intergranular carbides that create a more tortuous grain boundary.

Langelier *et al.* [132] showed similar results by comparing SIO between Alloy 600 SA and TT after exposure in a similar environment used by Bertali *et al.* [131]. The Cr carbides in 600 TT are proposed to reduce not only the oxygen penetration but also the diffusion induced grain

boundary migration, believed to be one of the "precursors event" of PWSCC. Inhibiting DIGM, intergranular carbides affect intergranular oxide growth since they reduce the fast supply of solutes to grain boundary due to the less pronounced DIGM. A more detailed analysis about the DIGM will be described in the dedicated section "2.4.3.6, Diffusion Induced Grain Boundary Migration".



Fig. 52: HAADF STEM image and corresponding STEM-EDX elemental maps showing the decomposition of the intergranular carbide after 120 h of exposure to H<sub>2</sub>-steam at 480 °C [131].

The intergranular carbides can also play an important role in oxidation processes. The oxygen can be trapped by the intergranular carbides. In this scenario, the intergranular carbides can limit the oxygen diffusion along the grain boundary, decreasing the grain boundary oxidation [46,199]. Dungale *et al.* [209] proposed that the intergranular carbides can form a different oxide at the grain boundary, which might be more dense and protective, thus reducing the intergranular oxidation rate.

#### **Role of Minor Elements**

As already discussed above, internal oxidation of minor solute elements in an alloy can occur if the oxygen partial pressure is not high enough to fully oxidize the alloy. For this reason, Al, Ti and Cr-enriched oxides can be easily found after high temperature oxidation [180], if present in the alloy composition.

Bertali *et al.* [68,227] observed significant local segregation along oxidized GBs of Al and Ti in Alloy 600 SA after exposure in H<sub>2</sub>-steam environment. The authors suggest that the Ti- and Al-enrichment may play an important role in the early stages of PIO, since it preceded the  $Cr_2O_3$ formation, due to the favourable activation energy and these minor elements might form an amorphous oxide layer that may enhance the oxygen diffusivity along the GB. A representative oxidized grain boundary showing the Al and Ti local enrichment is showed in the HAADF-STEM image and corresponding elemental maps in Fig. 53.

Persaud *et al.* [228] confirmed the previous findings of Bertali *et al.* [68,227] and they suggest that the high concentration of minor elements can be related to an enhanced diffusivity, thanks the dislocation pipe diffusion mechanism and due to the formation of an incoherent oxide metal interface. A third parameter that can enhance the diffusivity of minor reactive alloying elements can be the DIGM. In order to prove the real effect of the DIGM on the diffusion of the minor elements, they theoretically calculated the number of ions expected to be, finding good agreement with the experimental data. The initial Ti and Al can provide additional short-circuit diffusion path for oxygen or Ni on the oxide/metal interface by forming discrete oxide particles along the GB. Although it is clear that the minor elements play an important role in the early stage of SCC, their mechanism remains still unclear.



Fig. 53: HAADF STEM image and corresponding elemental maps showing the local Al- and Tienrichments along the oxidized grain boundary [227].

#### 2.4.3.5. Consideration about the Internal Oxidation Model

One of the most discussed criticism to the Internal Oxidation model [183] is that the predicted oxygen diffusion is too low to account for the experimentally observed crack growth rates. Extrapolation of oxygen diffusion from PWR temperature data, conducted by Staehle *et al.* [229] revealed a discrepancy of 4 order of magnitude between the oxygen diffusivity along GB and the observed crack growth rate for PWR service failures. This discrepancy can be easily observed in the plot of Fig. 54 that shows the experimental data available for oxygen diffusivity and the predicted value of Scott and Le Calvar [175,183].



Fig. 54: Temperature dependence of oxygen diffusion coefficient in Ni [230].

The oxygen diffusion proposed by Staehle *et al.* [229] was extrapolated from previous works of Iacocca, Bricknell and Woodford [231,232] who evaluated the oxygen diffusivity in Ni at temperatures between 800 °C and 1300 °C by measuring the formation of internal  $CO_2$  cavities in the metal. However, this method presented the limitation that it did not consider the amount of oxygen diffusing in the metal without being enough to form visible cavities, leading to an underestimation of the oxygen diffusion coefficient.

Park *et al.* [233] evaluated the diffusion of oxygen in Ni between 850 – 1400 °C by using a solid-state electrochemical method. The diffusion coefficient extrapolated at 320 °C was equal to  $1.4 \times 10^{-20}$  m<sup>2</sup>s<sup>-1</sup>, that is two orders of magnitude higher than the one predicted by Staehle [135]. The value extrapolated by Park *et al.* was still 2 orders of magnitude higher than the value observed for the crack growth rates ( $1.4 \times 10^{-20}$  m<sup>2</sup>s<sup>-1</sup>), but not sufficient to account the observed crack growth rate ( $10^{-18}$  m<sup>2</sup>s<sup>-1</sup>) [234,235]. Later studies from Laghoutaris *et al.* [234] strongly supported the internal oxidation model and the Scott's assumption [175,183] for the oxygen diffusivity. The results of Laghoutaris *et al.* [234] are over imposed on the plot of Fig. 54 and shown in Fig. 55.



Fig. 55: Oxygen diffusion coefficients in nickel measured by SIMS [235], ( $D_{GB}$  is the GB diffusion coefficient,  $D_{App}$  is the apparent diffusion coefficient,  $D_{Bulk}$  is the bulk diffusion coefficient).

This difference of magnitude might be related to any phenomena that may increase the oxygen diffusion in Ni-based alloys. The presence of an incoherent oxide/metal interface at the grain boundaries can enhance the oxygen diffusion. High temperature studies on Ni-Al alloys [236] showed that the apparent O diffusion coefficient increased at 800 °C due to the presence of an incoherent and continuous oxide/matrix interface [236]. An analogous mechanism can enhance the oxygen diffusivity during oxidation experiments of Alloy 600, where a continuous oxide region has been observed along the grain boundaries [205–208,223]. However, this mechanism has not yet been experimentally demonstrated. A second parameter that it may accelerate the transport of elements and the oxygen diffusion of Ni-based alloys exposed to high temperature environments is the presence of a Cr-depleted and Ni-enriched region beneath the intergranular oxide tip [107,206–208,221,223,224,237]. A possible mechanism that might explain the enhanced diffusivity of oxygen along grain boundaries is the DIGM.

### 2.4.3.6. Diffusion Induced Grain Boundary Migration (DIGM)

The diffusion induced grain boundary migration is another important parameter that could enhance the diffusivity during high temperature oxidation processes. A  $10^4$  times higher chemical diffusion coefficient of Zn in  $\alpha$ -Fe was found on a moving boundary than for stationary ones [238] and similar results were found for Al diffusivity in a deformed supersaturated Ni- Cr-

Al solid solution [239]. The DIGM was first identified by Rhines *et al.* [240] and then reported by others laboratories in a variety of different alloying systems [238,241]. DIGM can be described as the lateral motion of a grain boundary occurring in association with the diffusion of a solute along it; If solute atoms diffuse along a grain boundary where the lattice diffusion length is short, the boundary is observed to migrate with the formation of an alloyed zone in its wake. On contrary, if solute atoms diffuse along a boundary to a sink, the boundary is observed to move laterally but leaving behind it a solute-depleted region (Fig. 56A). The motion of the GB is usually not uniform and different part can move even in the opposite directions forming bulges (Fig. 56B). The principal effect of DIGM is to relief the stresses due to the diffusion of the solute elements [242].



Fig. 56: A. Schematic diagram of diffusion-induced grain boundary migration (DIGM) and B. schematic diagram of the top view of a grain boundary bulging which occurs during early stages of DIGM [243].

DIGM was also observed to occur in both Alloy 600 and Alloy 690 after exposure to both high pressure water and H<sub>2</sub>-steam environments. Many laboratories have observed grain boundaries to deviate from their original position with an associated depleted zone in Cr and Fe [206,208,211,223,225,244]. However, the first unequivocal evidence of DIGM related to PWR experiments was reported by Bertali *et al.* [10,46] and subsequently confirmed by Persaud *et al.* [132,228] and Langelier *et al.* [132]. Using TEM they were able to document the original grain boundary position as it had been decorated with fine, discrete carbides and identify pronounced grain boundary migration in Alloy 600 SA after exposure to low-pressure H<sub>2</sub>-steam environment at 480 °C. In a more recent study, Bertali *et al.* [68] demonstrated the occurrence of DIGM also in high-pressure steam at 400 °C and in simulated primary water at 320 °C. The authors believe that the DIGM mechanism could play an important role in the PWSCC initiation process due to its role in enhanced solute diffusion. In fact, the measured Cr and O diffusion coefficients in Nibase alloys exposed to PWR environmental condition were in good agreement with the extrapolated Cr and O diffusivity coefficients [46,231,245,246]. When a grain boundary migrates, the atoms in the matrix can diffuse along the boundary itself and leave a sink after having been collected by the migrating boundary [241]. This phenomenon can explain the enhanced diffusivity in Alloy 600 tested exposed to high temperature of Cr and O and the higher availability of Cr and Fe along a migrating boundary than a stationary GB.

#### 2.4.3.7. Stress Development and Its Relief in Oxide Films

Residual or imposed stresses can be another factor that can influence the diffusion coefficient of oxygen. In fact, the oxygen diffusion along a grain boundary is faster if the grain boundary is subjected to an external stress. Ghonem *et al.* [247] observed a 2-4 orders of magnitude higher oxygen diffusivity at grain boundary when the stress intensity factor was increased in Alloy 718 during fatigue tests at 650 °C. Fujii *et al.* [246] observed an increased oxygen diffusivity for stressed grain boundaries in Ni-base alloys and confirmed that an external stress can enhance oxygen diffusivity. Residual stress has also been reported to affect oxygen diffusivity. Using FIB micro-hole drilling, Bertali *et al.* [227,237] measured residual stresses across grain boundaries and proposed that residual stress due to internal and intergranular oxidation can play an important role in changing the oxygen diffusivity in Alloy 600.

The oxidation process can locally induce compressive stresses at the oxide/alloy matrix interface, due to the larger volume of the new oxide. Wood *et al.* [218] calculated the volume associated with the formation of an oxide in a Ni-Cr alloy. A stress gradient between the relaxed surface and the compressed areas around the oxidized area is always presents along the grain boundaries of an alloys susceptible to intergranular/internal oxidation. The mechanism involved in the relief of these stresses may play an important role in the internal oxidation processes.

### **Ni-Al Alloys**

Internal stress can be released by grain boundary sliding in Ni-Al alloys in high temperatures environment, as summarized in Fig. 57 [248]. The free oxide regions in the proximity of the grain boundaries appeared extruded out from the surface and the morphology of the internal oxide particles changed as function of the penetration; in particular, for low temperature the oxidation of grain boundary was more considerable. Moreover, the oxygen partial pressure can influence the effect of stress generation. When the oxygen partial pressures is lower than the dissociation pressure at NiO, the stress is more significant because the oxidation process would lead to an injection of vacancies when forming the NiO scale and thus accommodate the volume change [248].



Fig. 57: Schematic diagram of the proposed mechanism for stress relief of internally oxidized Ni-Al Alloys tested at high temperatures [248].

Ni-Cr Alloy and Alloy 600

In his studies on Ag-In alloys, Guruswamy *et al.* [249] reported the formation of silver nodules on the surface during internal oxidation, where the total volume of the nodules was equivalent to the internal oxide particles volume. The formation of the nodules was associated with the release of the high compressive stresses generated with the formation of the internal oxide particles. A pipe-diffusion controlled creep mechanism was proposed to explain the silver diffusion to the surface.

Bradley et al. [250] observed on Ni-Cr similar features to those discovered in recent studies performed by Guruswamy et al. [249] and these observations strongly supported the pipe-diffusion mechanism. However, the experimental conditions were different from an environment relevant to a PWR primary water conditions and therefore cannot be considered relevant for PWSCC studies. More relevant tests for the occurrence of PWSCC were performed by McIntyre et al. [251]. They reported similar features on Ni-18%Cr alloy tested at 500 °C in vacuum chambers at low pressure. The internal oxidation was associated with the formation of surface nodules similar to those detected on Ag-In and Pd-Ag alloys. The nodules were preferentially observed on scratches and on grain boundaries. A rapid outward movement of Ni was proposed as process responsible for the formation of the nodules. However, it was also observed that the nodules were not completely composed by pure metallic Ni, but for short exposure times Cr<sub>2</sub>O<sub>3</sub>, metallic Ni and NiO were detected in the nodules; for longer oxidation times, multi-phase nodules were reported: an external region of oxidized Cr and Ni and an internal core of spinel  $NiCr_2O_4$ . Maybe the more oxidizing environment than the Ni/NiO transition at which experiments were performed might have caused the presence of oxides in the nodules.

Scenini *et al.* [73] proposed a stress-relief mechanism invoking creep on Alloy 600 exposed to H<sub>2</sub>-steam environment reproducing PWR primary water conditions. Alloy 600 was exposed at 480 °C with an oxygen partial pressure set 24 times lower than the dissociation pressure of Ni/NiO at that temperature. They observed the formation of intragranular shiny nodules and split ridge GBs morphology on the surface (Fig. 58), similar to those on the Ag-In alloys surface [249].



Fig. 58: SE image of Alloy 600 surface after exposure in H<sub>2</sub>-steam environment [73].

They proposed the same mechanism reported by Guruswamy *et al.* [249] to be responsible for the formation of the intragranular nodules, and the same stress-relief mechanism. However, the model proposed for the homogeneous and constant internal compressive stress at the internal oxide front by Guruswamy *et al.* was not completely able to explain the presence of the nodule-free zone (3-4  $\mu$ m width) in the proximity of the grain boundaries, and the coarser nodule size compared to the GBs ridges. A variable compressive stress model was proposed to explain the formation of the pure Ni nodules on the alloy surface. The stress decreased when a grain boundary is approached and turns to a tensile stress at the grain boundary.

Bertali *et al.* [227] confirmed the stress profile proposed by Scenini *et al.* [73] by using the micro-hole drilling, a novel technique to evaluate the local stress at microscopic scale. They noticed that the residual compressive stresses in the material were not constant but they changed in the proximity of the GB, especially for GBs that exhibited a nodule-free zone and a split-ridge morphology: the stresses decreased in the vicinity of the GB whereas they increased in the vicinity of GB with a crest morphology. The prolife stresses were consistent with the low susceptibility of the GB with nodule-free zone. The higher compressive stresses discovered in the GB without nodule-free zone could induce tensile stresses that might promote intergranular oxidation. In addition, STEM-EDX microanalysis supported the dislocation pipe diffusion as mechanism responsible for the Ni extrusion on the surface. A narrow Ni-enriched "filament" detected beneath the Ni-nodule appeared to "link" the nodule with the grain [227]. In a more recent study, Langelier *et al.* [252] used Atom Probe Tomography (ATP) to investigate the intragranular internal oxidation of Alloy 600 when exposed to H<sub>2</sub>-steam environment with an oxygen partial pressure below the dissociation pressure of NiO. Those ATP analyses revealed that the Ni-nodules were connected with the grain by a continuous network of Ni-rich filaments, such that crystallographic orientation between that nodule and grain was maintained. Short-circuit diffusion created by a continuous interface between the oxides and the Ni-rich matrix metal was necessary to obtain the epitaxial surface nodules.

# **3. Experimental Approach**

# 3.1. Low Pressure Superheated H<sub>2</sub>-Steam System

A low pressure superheated H<sub>2</sub>-steam system was used to perform accelerated oxidation and SCC experiments relevant to a PWR primary water environment [51]. This low-pressure H<sub>2</sub>-steam system was originally developed by Scenini *et al.* [41,73,76], and it has been used in other laboratories [132,226,228,253]. This system was subsequently improved and refined in further studies [46,131,254], and it will be mentioned trough the text as "Manchester system". The environmental conditions of the H<sub>2</sub>-steam environment can be fully described with a ratio *R* (equation (4.1)) between the oxygen partial pressure at the Ni/NiO transition  $(p_{O_2 Ni/NiO})$  and the oxygen partial pressure in the system  $(p_{O_2})$ , *i.e.* for values lower than 1, NiO phase is stable (oxidizing environment), for values higher than 1, Ni phase is stable (reducing environment), whereas for *R* equal to 1, the system is at the Ni/NiO transition.

$$R = \frac{p_{O_2 Ni/NiO}}{p_{O_2}}$$
(4.1)

The  $p_{O_2}$  was varied by controlling and changing the H<sub>2</sub> and the H<sub>2</sub>O flow rates to simulate different oxidizing and reducing environments with respect to the Ni/NiO transition. A more comprehensive description of the thermodynamic calculation is reported in "appendix A.I".

### 3.1.1. Experimental Systems

The low pressure system, schematically represented in Fig. 59, consists of a stainlesssteel reaction tube, where the gaseous  $H_2/H_2O$  mixture interacts with the exposed samples [46,76]. The stainless-steel reaction tube was placed inside a tubular furnace to reach the desired temperature. Deionized water was pumped from a feed-tank at 1.50 mL/min by using a High-Performance Liquid Chromatography Shimadzu pump LC-20AT, preheated to 200 °C and mixed with the  $H_2$  and Ar mixture gas in an evaporator before being injected into the reaction tube. The outlet steam was stored in a tank and the gas mixture was vented in a fume cupboard. The  $H_2$  and Ar gas flow rates were controlled with two independent Bronkhorst flowmeters F-201CV. Inert Ar gas was varied accordingly to maintain the total gases flow rate ( $H_2$  and Ar) equal to 40 cc/min for all the experiments performed.



Fig. 59: Schematic diagram of the low pressure superheated H<sub>2</sub>-steam rig ("Manchester system") used for the measurement of the redox potential in H<sub>2</sub>-steam environment and for oxidation experiments on Alloy 600 coupons. The position of the SSRE is also shown.

For some of the oxidation experiments, the oxidation system described above was modified to reproduce the system used by Capell and Was ("Michigan system") [100]. This system was able to reproduce a H<sub>2</sub>/steam environment at high PPRs, and hence produced very reducing environments with respect to the Ni/NiO transition. The Fig. 60 shows a simplified schematic of the Capell system [100]. The H<sub>2</sub>/Ar mixture gases were injected into the bottom of sealed jar filled with deionized water. The jar was immersed in a large tank of water kept at the temperature of 74 °C, in order to keep deionized water in the sealed jar at the constant temperature of 70 °C. The Ar and H<sub>2</sub> flowed through the water, picked up water vapor and flowed out of the exit line of the jar. The water vapor in the exit gas was considered to be in equilibrium with the liquid water in the jar; from this assumption, it was possible calculate the oxygen partial pressure in the system. To prevent any condensation from the jar to the stainless steel reaction tube in the furnace, the pipes were heated at 74 °C using a heated tape. The gaseous mixture passed throw the stainless steel reaction tube were the samples were exposed.



Fig. 60: Low pressure superheated H<sub>2</sub>-steam rig modified according to the schematic of the "Michigan system" [255].

For both systems, the procedures of switch on/off are similar and it is possible summarize them as follow:

- The samples were situated on a quartz boat and inserted in the stainless steel reaction tube in the proximity of a thermocouple, and the tube was placed in the circular furnace.
- 2. All the Swagelok joints were tightened and to verify the presence of any leaks, the pressure was increased to 4 bar and kept stable for 10 minutes.
- 3. If the pressure value was stable, the pressure was released, and the system purged with pure Ar to refresh the refresh the environment for a minimum of 60 times.
- The temperature was set at the desired value and the high-performance liquid chromatography (HPLC) Shimadzu pump was purged.
- 5. At the desired temperature, the H<sub>2</sub> gas was set to the desired value by controlling the dedicated flow meter and the Ar gas flow was set accordingly to the H<sub>2</sub> flow rate.
- 6. The pump was switched on and the experiment started.
- At the end of the experiments, the pump was switched off, the H<sub>2</sub> flow rate was set to zero and the Ar was increased to accelerate the cooling down procedure.

8. At the temperature of  $\approx$ 60 °C, the H<sub>2</sub> and Ar cylinders were closed and the samples removed from the SS reaction tube.

The schematics of the rigs reported in Fig. 59 and Fig. 60 are simplified and only the pipes used during the experiments were reported and not the many by-pass pipes and valves used during the start-up and switched off procedures.

# 3.2. Material

The Alloy 600 (Heat no. 93510) used in this study was manufactured by B&W Tubular Products Division and provided by Westinghouse. The Alloy 690 (Heat no. 670743) was provided by Sumitomo and both Ni-base alloys used in this study are mainly used for the production of Control Rod Drive Mechanism (CRDM). Their chemical composition and the mechanical proprieties of Alloy 600 are reported in Table 3.1 and Table 3.2.

Matarial ->	A600	A690		
	Heat No. 93510	Heat no. 670743		
С	0.047	0.020		
Mn	0.23	0.27		
Р	0.005	0.007		
Si	0.30	0.24		
Cr	15.42	29.6		
Ni	74.43	59.9		
Со	0.57	0.057		
Fe	8.94	9.9		
Cu	0.01			
S	0.002			
Ті	0.34	0.3		
AI	0.19	0.4		
Ν	-	0.04		
Мо	-	0.3		

Table 3.1: Chemical composition (wt.%) for Alloy 600 and Alloy 690 used in this study.

Material	Ultimate Strength, MPa	Yield 2%
A600, heat No. 93510	680	270
A690	703	350

Table 3.2: Mechanical proprieties for Alloy 600 and Alloy 690.

### 3.2.1. Sample Preparation

All Alloy 600 and Alloy 690 coupon samples were metallographically prepared. Any additional stage or specific variation will be reported in the specific sample preparation. The surface preparation of the samples is of particular importance for the experiments because the condition of the surface can strongly influence the morphology and the composition of the oxide after the exposure to H<sub>2</sub>-steam environment. The surface preparation, such as the presence of deformed layer due to grinding or minor change in chemical composition, can highly affect the surface morphology [76,77].

Alloy 600 was provided in a low temperature mill-annealed condition whereas Alloy 690 was provided in the thermally-treated condition. Alloy 600 and a part of the Alloy 690 material were solution-annealed (SA) at 1100 °C in air for 30 min and subsequently water-quenched at room temperature within 10 seconds in order to minimize intergranular carbide precipitation and to create a coarse-grained, fully recrystallized microstructure for the subsequent experiments concerning the oxidation behaviour and SCC precursor studies. Alloy 600 SA and Alloy 690 TT and SA samples were extracted with a cutting disk and cut in coupons of  $1.5 \times 20 \times 20 \text{ mm}^3$ . To avoid any kind of contamination from the SA process, all the surfaces were previously ground with a P400 grit paper. The samples were mounted in Bakelite to have a better grip and to facilitate the grinding and polishing procedures. Supplementary coupon samples of Alloy 600 SA samples of  $1.3 \times 5.0 \times 25.5 \text{ mm}^3$  were prepared using Electrical Discharge Machining (EDM) for SCC initiation stages studies. The same grinding and polishing steps were used for these coupon samples.

The samples were polished using a silica Oxide Polishing Suspension (OPS), that allows to produce a stress-free surface with no deformed layer and hence a surface that is more representative of the bulk material. The grinding steps used to prepare the sample surfaces were P320, P400, P600, P800, P1200, P2400 and P4000. Each stage of grinding was applied for a minimum of 2 minutes per stage; then rotated by 90 degrees between the grinding papers to confirm that all previous grinding damage had been removed. Between grinding steps, the samples were rinsed with de-ionized water before moving to the next stage to avoid any contamination from residual particles on the sample.

After the P4000 grinding step, the samples were metallographically polishing with a 3  $\mu$ m and a 1  $\mu$ m polycrystalline diamond polishing suspension. The samples were polished for a minimum of 5 minutes per step. In between the polishing steps, the samples were thoroughly washed with soapy water and rinsed with ethanol before drying under a flow of hot air to remove any contamination from the polishing process. For the final polishing step, a 24-40 nm silica OPS was used to remove any residual stress produced by the previous polishing steps (Beilby layer) and to produce a mirror finish with a stress-free surface. The samples were polished for a minimum of 40 minutes with the OPS solution. The samples were rinsed with soapy water, then ultrasonically washed in de-ionized water for 15 minute, rinsed with ethanol and then dried in a stream of hot air to remove any silica contamination from the surface.

# 3.3. Experiments Performed

### 3.3.1. Electrochemical Corrosion Potential

The Electrochemical Corrosion Potential or redox potential associated with the H<sub>2</sub>/Steam mixture (equation (4.2)) in the low pressure H<sub>2</sub>-steam environment was monitored *in-situ* with a high temperature Yttria Stabilized Zirconia (YSZ) Solid State Reference Electrode (SSRE).

$$H_2 O_{(g)} \rightleftharpoons H_{2(g)} + \frac{1}{2} O_{2(g)}$$
 (4.2)

The relationship between the H<sub>2</sub>/steam mixture and the EcP can be described by using the Nernst equation in equation (4.3) and the mathematical description can be found in the Appendix A.II.

$$E_{eq. vs. Ni/NiO} = \frac{RT}{4F} \cdot \ln\left(\frac{p_{O_2}}{p_{O_2 Ni/NiO}}\right)$$
(4.3)

The studies of O'Neill [256] were considered in this study to validate the experimental parameters reproducing an electrochemical environment relevant to a PWR primary water circuit and the Ni/NiO transition in H<sub>2</sub>-steam. The electrochemical cell is formed by two electrodes, separated by an electrolyte, acting as oxygen-conductor [257–259]. The sensor measures the difference between the two cells in terms of oxygen partial pressure; if one is

known, the other can be automatically determined. The known cell is usually determined by using a stable metal/oxide phase, such as  $Cu/Cu_2O$  or  $Fe/Fe_3O_4$  [260–262].

In our system, the redox potential was monitored with an Ivium potentiostat COMPACTSTAT.h. A mixture powders of pure Ni and NiO was used as reference and connected with the potentiostat with a pure Ni wire, the yttria stabilized zirconia acted as electrolyte, a Pt wire coiled around the sensing tip of the SSRE acted as working electrode (see inset of Fig. 61). Pt was chosen because acted as inert metal in this environment and therefore its contribution to the measurement of the redox potential associated with equation (4.3) was negligible. The SSRE reported in Fig. 61 was based on a replica of a Cu/Cu<sub>2</sub>O SSRE used in [260]. More details regarding the fabrication of the SSRE are reported in the section "A.III – Manufacturing the Ni/NiO Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> SSRE" [263].

The sensor was then inserted in the H<sub>2</sub>-steam system as already illustrated in Fig. 59. The redox potential was monitored at the temperature of 372 °C, 400 °C, 430 °C and 480 °C. For each temperature, the H<sub>2</sub>/steam ratio was kept constant for 700 s for a desired *PPR*<sup>-1</sup>, then the H<sub>2</sub> flow rate was decreased to reproduce a different electrochemical condition (different *PPR*<sup>-1</sup>), and the redox potential was recorded with every second ranging from an more reducing to more oxidising conditions with respect to the Ni/NiO transition.



Fig. 61: Schematic diagram of the Ni/NiO Yttria Stabilized Zirconia SSRE used for the evaluation of the Ni/NiO transition in the H<sub>2</sub>-steam environment at 400 °C.

## 3.3.2. Oxidation Experiments

Several oxidation experiments were performed in the low pressure H<sub>2</sub>-steam system to examine the early "precursor" stages associated with the PWSCC in both Alloy 600 and Alloy 690.

Alloy 600 SA coupon samples were exposed to H<sub>2</sub>-steam environment at 480 °C for 210 h to evaluate the influence of the  $p_{O_2}$  on the Preferential Intergranular Oxidation mechanism. The list of the 9 oxidation experiments is reported in Table 3.3. The experiments from 1 to 6 were exposed to H<sub>2</sub>-steam by using the system described in the section "2.1.1 – Experimental systems", whereas the experiment from 7 to 9 were exposed in a replica of the system used by Capell and Was [100,255]. Coupon samples of Alloy 690 TT and SA were exposed to  $H_2$ -steam environment at 480 °C for 120 h in Manchester system [41]. The summary of the Alloy 600 Alloy 690 oxidation experiments is reported in Table 3.3.

System	Test			R	PPR	EcP	Time
	no.	Material	Environment	$\frac{p_{O_{2 Ni/NiO}}}{p_{O_2}}$	$rac{p_{H_2O}}{p_{H_2}}$	mV <i>vs.</i> Ni/NiO	h
Manchester	1	A600 SA	NiO stability	1/24	1304	52	210
	2	A600 SA	NiO stability	1/6	633	28	210
	3	A600 SA	Ni/NiO transition	1	268	0	210
	4	A600 SA	Ni stability	1.5	219	-7	210
	5	A600 SA	Ni stability	6	113	-28	210
	6	A600 SA	Ni stability	24	55	-52	210
Michigan (Capell Was)	7	A600 SA	Ni stability	200	19	-90	210
	8	A600 SA	Ni stability	900	9	-111	210
	9	A600 SA	Ni stability	4000	4	-135	210
Manchester	10	A690 TT	Ni stability	24	55	-52	120
	11	A690 SA	Ni stability	24	55	-52	120

Table 3.3: Summary of the experiments carried out in the superheated H<sub>2</sub>-steam at 480 °C.

### 3.3.3. Oxidation Experiments to Examine the Effect of Strain

Further experiments were designed to identify a direct link with between the precursor events PIO and DIGM and the SCC initiation for Alloy 600 SA. Samples of  $25.5 \times 5 \times 1.3 \text{ mm}^3$  was inserted in a specifically designed 4-point bending tool. The tool with the sample inserted in the low pressure H<sub>2</sub>-steam environment is schematically shown in Fig. 62 and the detail of the tool is shown in the inset of Fig. 62.



Fig. 62: Schematic diagram of the low pressure super-heated H<sub>2</sub>-steam environment ("Manchester system") containing the 4-point bending tool for the oxidation experiments under stress. In the inset, a detailed schematic of the 4-point bending tool with an OPS Alloy 600 SA coupon sample in blue is shown.

Oxidation experiments under the effect of strain were performed at 480 °C under different oxidising conditions for 120 h to analyse the evolution of the precursor events (PIO/DIGM) and cracks associated with Alloy 600 SA SCC. The summary of the experiments is listed in Table 3.4. More details about this set of experiments can be found in the relevant section in the chapter 7.

System	Test	Material	Environment	R	EcP	
	no.			$\frac{p_{o_{2 Ni/Ni0}}}{p_{o_2}}$	mV <i>vs.</i> Ni/NiO	
Manchester	12	A600 SA	NiO stability	1/24	52	
	13	A600 SA	NiO stability	1/6	28	
	14	A600 SA	Ni stability	2	-7	
	15	A600 SA	Ni stability	24	-52	

Table 3.4: Summary of the oxidation experiments under the effect of strain performed on Alloy 600 SA exposed to superheated  $H_2$ -steam at 480 °C for 120 h.

# 3.4. Characterization Techniques

The samples were characterized with a variety and complementary techniques to evaluate the effect of the H<sub>2</sub>-steam environment on the microstructure of the material. The principal techniques used for the characterization of the samples prior and after exposure in the super-heated H<sub>2</sub>-steam environment are listed in this chapter.

# 3.4.1. Light Optical Microscopy (LOM)

A Carl Zeiss light optical microscope equipped with an AxioCam ERc5s digital camera was used to analyse the surface of the sample before exposure to H<sub>2</sub>-steam environment to ensure the correct grinding and polishing procedures. The images were acquired and post-processed with the Zeiss Axio software version no.6.5.

## 3.4.2. X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a non-destructive measuring technique that provides information about atomic structures of different inorganic of organic compounds and physical

properties such as stresses of the material. A parallel beam of monochromatic X-rays is directed onto a sample and the intensity of the diffracted X-rays is measured as a function of the diffracting angle  $\theta$ . XRD examinations were conducted with a Philips X'Pert MPD system equipped with a Cu K $\alpha$  source with a 2 $\theta$  between 5° and 85° with a 0.05° step size.

Grazing angle XRD uses low incident angles ( $\alpha \le 3^{\circ}$ ), so the technique can be used to analyse the surface of the sample. The grazing-angle XRD examinations were conducted with a Philips X'Pert MPD system equipped with Cu K $\alpha$  source for a comprehensive analysis of the phases formed in the external oxide layer. The incident angle ( $\alpha$ ) used was 3° while the detector scanned from 20 in between 10° to 95° with a 0.05° step size.

The XRD and GA-XRD data were analysed and processed with the software OriginPro 2017 [264].

# 3.4.3. Scanning Electron Microscopy (SEM)

Several scanning electron microscopes were used to characterize the sample surfaces before and after the exposure to H<sub>2</sub>-steam environment. The main electron imaging modes used in this project were the Secondary Electron (SE) and Backscattered Electron (BSE) modes. The SE imaging mode allows to obtain surface topographic information with a high signal to noise ratio. The BSE imaging modes provides qualitative chemical information, since it is dependent from the atomic number (Z number) of the elements present in the material. In this work, the Energy-selected Backscatter (EsB) detector and the Angle-selected Backscatter (AsB) detectors were used. Energy Dispersive X-ray Spectroscopy was also used to obtain compositional data from the oxidized surface and grain boundaries.

The specific SEMs used in this project are listed below:

1. FEI Quanta 650 Field Emission Gun (FEG)-SEM equipped with an Oxford Instruments X-Max 150 Silicon Drift Detector (SDD) and an Electron Backscatter Diffraction (EBSD) analysis system was used to EBSD analysis to calculate the grain size of the baseline material for the Alloy 690 TT and SA (Chapter 8). Specifically, the EBSD were performed at 20 kV with a pixel size or 1.1  $\mu$ m on a 700 x 700  $\mu$ m<sup>2</sup>. The data were acquired with Oxford Instrument NanoAnalysis AZtec software v3.3 and the data processed with Oxford Instrument Channel5.

- Zeiss Ultra 55 FEG-SEM equipped with an Oxford Instruments Si(Li) EDX detector and an INCA analysis system was used to preliminary studies on the baseline and the oxidized samples.
- Zeiss Sigma FEG-SEM equipped with an Oxford Instruments X-Max 150 SDD EDX, an EBSD detector system was used to perform high-resolution analysis of the oxidized surface in SE and BSE mode using the Zeiss AsB detector.
- 4 Zeiss Merlin FEG-SEM equipped with an Oxford Instruments X-Max 150 SDD, an Oxford Instruments Extreme 100 windowless SDD and Aztec analysis system was used to perform high-resolution analysis of the oxidized surface in BSE imaging mode and to perform qualitative EDX analysis at low voltage (2 to 5 kV) to analyse the chemical redistribution of the elements along the GBs before and after exposure to H<sub>2</sub>-steam environment. Specifically, the SEM Spectrum Imaging (SI) showed in the Chapter 6 were acquired with an Oxford Instruments Extreme 100 windowless SDD detector operated at 3.5 kV, with a pixel size of 5.47 nm with a process time equal to 5 and for 865 seconds of live-time. The SI data were weight% type and background subtracted, processed with the Oxford Instrument NanoAnalysis AZtec software v3.3.

### 3.4.4. Focus Ion Beam (FIB) Microscopy

The Focused Ion Beam (FIB) was mainly used to prepare cross sections, to obtain 3D information using the serial sectioning technique and to prepare electron transparent specimens for subsequent analytical TEM analysis with the *in situ* lift-out technique. Statistical data were obtained for the data presented in the Chapter 6 to 7. Specifically, the length for the PIO was measured for 20 GBs per environmental conditions and the area, length and width associated with DIGM were measured for over 50 grain boundaries as shown in the Chapter 6. Moreover, the length of the PIO and cracks and the area of the DIGM as shown in the Chapter 7 were measured for 20 GBs for each environmental condition. These data were measured on SE-FIB cross-sections by using the software ImageJ Fiji2 [265,266] and the statistical analyses were performed with the software OriginPro 2017 [264]. The Focused Ion Beam (FIB) microscopes used in this project were:

- 1. FEI Quanta 3D An FEI Quanta 3D Dual Beam FIB/SEM was used for the preparation of cross-section specimens for subsequent analysis.
- 2. A FEI Helios 660 FEI Helios 660 Dual Beam FIB with an Oxford Instruments X-max 150 SDD

and an Oxford EBSD detector was used to prepare site specific cross-sections and electron transparent specimen for further analytical transmission electron microscopy (ATEM) analysis.

### 3.4.5. Analytical Transmission Electron (ATEM) Microscopy

Transmission Electron Microscopy (TEM) was used to characterize the base material and to obtain detailed analysis of the oxidized grain boundaries after oxidation in the H<sub>2</sub>steam environment. Bright-Field (BF) imaging, Dark-Field (DF) TEM imaging, Selected Area Electron Diffraction (SAD) analysis, Scanning Transmission Electron Microscopy (STEM) analysis and STEM-EDX microanalysis and spectrum imaging were used to perform the ATEM characterizations. The specific TEMs used in this project are listed below:

- Philips CM20 LaB<sub>6</sub> TEM operated at 200 kV equipped with a Gatan Charge-Coupled Device (CCD) camera. The system was used to perform preliminary evaluation of the FIB lift-out specimens to assess their quality for further and more detailed analysis and for conventional TEM imaging and electron diffraction.
- 2. FEI Tecnai G2 T20 LaB<sub>6</sub> Analytical TEM operated at 200 kV equipped with an Oxford Instruments windowless XMax 80 TLE SDD and AZtec analysis system, BF/DF STEM detectors, and a Gatan CCD camera. This system was used for conventional TEM imaging and electron diffraction. Discrete STEM-EDX "spot" analyses were performed to analyse the local compositional variation in the proximity of the oxidised grain boundaries oriented parallel to the incident electron beam for the samples analysed in the Chapter 6 and 8. These EDX spectra were acquired with a live-time of with a 60 seconds and quantified with the Oxford Instruments NanoAnalysis Aztec software (version 4.0) with theoretical "k-factors".
- 3. FEI Talos F200X S/TEM with an X-FEG operated at 200 kV and ChemSTEM<sup>™</sup> technology (four SDDs for improved X-ray collection and EDS spectrum imaging analysis) and BF/DF and a High Angle Annular Dark Field (HAADF) STEM detectors. The system was used to semi-quantitative analysis of the redistributed elements in the proximity of the oxidized grain boundaries and near-surface region. The STEM-EDX spectrum image data presented in the Chapter 6 were performed with a dwell time of 200 µs for a total live time of 30 min and with a pixel size equal to 1.328 nm. STEM-EDX Spectrum Image (SI) datasets were analysed using Thermo Fisher Scientific Velox software (version 2.4).

Similar data acquisition settings were used to acquire the data shown in the Chapter 8, but they were analysed with Thermo Fisher Scientific Velox software version 2.6. The STEM-EDX spectrum image data for data shown in the Chapter 8 were performed with a dwell time of 200 µs for a total live time of 30 min and with a pixel size equal to 1.875 nm. STEM-EDX Spectrum Image (SI) datasets were analysed using Thermo Fisher Scientific Velox software (version 2.6). All the STEM-EDX SI (Chapters 6 to 8) were presented as weight% and background subtracted.

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## Introduction to Chapter 5.

Chapter 5, entitled "Replicating PWR Primary Water Conditions in Low Pressure H<sub>2</sub>-Steam Environment to Study Alloy 600 Oxidation Processes", has been published as a research paper in the Journal of the Electrochemical Society.

One of the main challenges in obtaining data on Ni-base alloys oxidation and stress corrosion cracking behaviour is the experimental complexity and the long time needed to replicate reliably pressurized water reactor conditions. In this work, the possibility of using H<sub>2</sub>-steam as a reliable surrogate for pressurized water reactor conditions with respect to nickel oxidation is explored and validated by thermodynamic calculations, *in-situ* potential measurements, performed by an Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> solid state reference electrode operated under variable temperature and hydrogen partial pressures, and microstructural analyses on Alloy 600 coupons.

#### Author contribution:

L. Volpe is the principal author. He carried out the experimental work, he processed the experimental data and he wrote the draft of the manuscript.

F. Scenini is the principal supervisor. He supervised the experimental approach, he provided conceptual guidance and extensive manuscript review.

M. G. Burke provided conceptual guidance and she contributed to the manuscript review.

M. Curioni contributed to the writing of the manuscript.

G. Bertali performed the XRD and GA-XRD examination on the Ni-200 and Ni powder.

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## 5.Replicating PWR Primary Water Conditions in Low Pressure H<sub>2</sub>-Steam Environment to Study Alloy 600 Oxidation Processes

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#### Abstract

The effects of thermodynamic parameters associated with low pressure H<sub>2</sub>-steam on the oxidation behaviour of Nickel have been investigated to simulate PWR primary water conditions. An Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> solid state reference electrode operated between 372 and 480 °C, and exposed to variable hydrogen partial pressures, was used to obtain *in-situ* potential measurements to identify the Ni/NiO transition. Microstructural analyses on Alloy 600 coupons exposed to H<sub>2</sub>-steam under different oxidizing conditions showed a marked dependence of the intergranular oxidation processes, as expected for a PWR environment. Overall, the H<sub>2</sub>-steam simulated an environment that can be considered to be representative of PWR primary water.

Keywords:

Ni/NiO transition; Redox Potential; H2-steam; Solid State Reference Electrode

## 5.1. Introduction

It is well known that the operating electrochemical corrosion potential of structural alloys in the primary circuit of a Pressurized Water Reactor (PWR) is located in the proximity of Ni/NiO transition [1] where Alloy 600 (Ni-15Cr-10Fe) [2] and its related welding alloys display the highest susceptibility to Primary Water Stress Corrosion Cracking (PWSCC) initiation and propagation [1,3–5]. The main parameter controlling the potential is the dissolved H<sub>2</sub> (DH),

which is generally added to the primary water to suppress the formation of radiolytic products and decrease the electrochemical corrosion potential of Ni-base alloys [6,7]. Consequently, identifying the exact environmental condition associated to the Ni/NiO transition is a requirement to perform laboratory experiments that are relevant to nuclear power plant operation.

The environmental condition to reproduce the Ni/NiO transition has been identified in high temperature water and in supercritical water, since these environments have been already employed to replicate nuclear power plant operating conditions [5,8]. Specifically, Attanasio *et al.* [5] employed Constant Electric Resistance (CER) techniques on Alloy 600 samples to identify the amount of DH associated to the Ni/NiO transition at temperatures between 260 °C and 360 °C. However, whilst the thermodynamic transition was identified, it was shown that the values of enthalpy and entropy were not in complete agreement with those reported in the older literature [9,10]. More recently, Moss and Was [8] identified the environmental condition to reproduce the Ni/NiO transition using Ni coupons exposed from 320 °C to 450 °C at 25 MPa in both subcritical and supercritical water at different DH concentrations. The experimental values of the standard enthalpy of formation ( $\Delta H_{f,NiO}^{\phi}$ ) and standard entropy of formation ( $\Delta S_{f,NiO}^{\phi}$ ) for NiO were close to the values reported by Attanasio *et al.* in subcritical water [5].

In more recent years, a low pressure super-heated H<sub>2</sub>-steam system has been employed to perform oxidation and SCC experiments relevant to the PWR primary water environment requiring shorter times compared with conventional experiments performed in high pressure autoclaves. In fact, Economy et al. [11] showed that the activation energy associated with PWSCC initiation for Alloy 600 did not change significantly between 320 °C in high pressure water and 400 °C in high pressure steam. These findings suggested that the initiation mechanism was the same at different temperatures [12–19]. However, although the H<sub>2</sub>-steam environment has been widely used by different laboratories [17,20,21], a comprehensive experimental assessment to clarify the significant discrepancy in locating the Ni/NiO phase transition reported in literature has yet to be performed. Capell and Was [20] used X-ray Photoelectron Spectroscopy (XPS) for identifying *ex situ* the transition on several Ni-base alloys exposed under several oxidising conditions. However, in their studies they employed the thermodynamic calculations for the formation of NiO despite their identification of Ni(OH)<sub>2</sub> as the oxidized phase of Ni. Moreover, the experimental energy of formation of Ni(OH)<sub>2</sub> was surprisingly reported to be similar to that found by Attanasio et al. [5] who obtained these values in high pressure water. However, Capell and Was [20] identified the Ni/NiO transition to be in conditions significantly more reducing than what was predicted by Scenini et al. [17] and later Bertali et al. [12,14,15].

Therefore, the aims of this study are: i) to validate super-heated low pressure H<sub>2</sub>-steam environment as possible surrogate system to perform oxidation and SCC experiments relevant to a PWR primary water environment, and ii) to clarify the discrepancy with the literature data via electrochemical characterization of the environmental conditions reproducing the Ni/NiO transition using a solid state (oxygen concentration cells) reference electrode. Past studies have already identified the Ni/NiO transition using a similar reference electrode [22,23], but a complete assessment of the Ni/NiO transition in a low pressure H<sub>2</sub>-steam environment has never been performed by date.

The thermodynamic characterization in gaseous hydrogen/water mixture was achieved via *in situ* electrochemical analysis using an Yttria Stabilized Zirconia (YSZ) Solid State Reference Electrode (SSRE) filled with Ni and NiO powder coupled with a Pt wire [24]. YSZ sensors have applications in monitoring the corrosion of metal components exposed to high temperature aqueous environments in Nuclear Power Plants (NPPs) [25–29] and they can be used to monitor the redox potential of PWR primary water environment or supercritical aqueous solutions where the electrochemistry is mainly determined by hydrogen concentration.

In this paper *ex situ* characterization techniques were also employed to consolidate the electrochemical results; specifically, Grazing Angle X-Ray Diffraction (GA-XRD) and XRD analyses were performed on commercially pure Ni-200 coupons and highly sensitive Ni powder exposed to low pressure H<sub>2</sub>-steam. Moreover, two examples of the highly sensitive dependence of Alloy on the oxidation in the proximity of the Ni/NiO transition are reported with the focus on the intergranular oxide penetration, which is believed to be the main responsible factor for the occurrence of the PWSCC [30]. It is worth noting that the work reported in the literature mainly focused on the behaviour of Alloy 600 in the Ni stable region and not across the Ni/NiO transition [12,15,16,20,21,31–35] that is presented in this work.

## 5.2. Experimental

#### 5.2.1. H<sub>2</sub>-Steam Environment

A low pressure super-heated H<sub>2</sub>-steam system was used to create an environment that is relevant to the PWR primary water environment. The approach was originally developed by Scenini *et al.* [17], used by other laboratories [21,33,34], and subsequently improved in further studies [12,15,16]. The experimental apparatus, schematically represented in Fig.1, consists of

a stainless-steel reaction tube that contains the solid-state reference electrode and is where the gaseous H<sub>2</sub>/steam mixture interacts with the exposed samples [12,31]. The reaction tube was placed inside a tubular furnace in order to reach the desired temperature. To generate the steam, a constant flow of 1.50 mL/min of deionized water was pumped using a Shimadzu high performance liquid chromatography pump LC-20AT, preheated to 200 °C and mixed with the H<sub>2</sub> and Ar mixture gas in an evaporator before being injected into the reaction tube. The outlet gas mixture was then vented in a fume hood. The H<sub>2</sub> and Ar gas flow rates were controlled with two independent Bronkhorst flowmeters F-201CV in order to change the partial pressure ratio between hydrogen and steam, and consequently the oxidizing potential; inert Ar gas, was varied accordingly to maintain the total gases flow rate (H<sub>2</sub> and Ar) equal to 40 cc/min. The total flow of 40 cc/min was chosen to be consistent during the multiple measurements.



Fig. 1: Schematic of the experimental rig used for the oxidation and electrochemical characterization of the low pressure super-heated H<sub>2</sub>-steam environment.

#### 5.2.2. Thermodynamic Calculations

The desired oxygen partial pressure  $p_{O_2}$  was controlled by changing the ratio between steam and H<sub>2</sub> according eq. (1), under the assumption that the ratio between the partial pressures was equal to the volume ratio at atmospheric pressure between steam and H<sub>2</sub>. The  $p_{O_2}$  (eq. (2)) can be calculated using the standard Gibbs free energy of decomposition of H<sub>2</sub>O<sub>(g)</sub>, defined as $\Delta G_{f,H_2O}^{\Phi}$ .

$$H_2 \mathcal{O}_{(g)} \rightleftharpoons H_2 + \frac{1}{2} \mathcal{O}_2 \tag{1}$$

$$p_{O_2} = p^{\Theta} \cdot \left(\frac{1}{PPR}\right)^2 exp\left[-\frac{2\Delta G_{f,H_2O}^{\Theta}}{RT}\right]$$
(2)

Where  $p^{\bullet}$  is the standard pressure, equal to 1 atm,  $\Delta G_{f,H_2O}^{\bullet}$  is the standard Gibbs free energy of formation for H<sub>2</sub>O<sub>(g)</sub> as defined above, *R* is the universal gas constant, *T* is the absolute temperature in Kelvin and *PPR* is equal to  $p_{H_2}/p_{H_2O}$ . For a given temperature, the  $p_{O_2}$  is dependent by the square of the ratio between the partial pressure of hydrogen over the partial pressure of steam (*PPR*) and by the standard Gibbs free energy of formation of water  $\Delta G_{f,H_2O}^{\bullet}$ , as reported in eq. (2). It is worth noting that *PPR* was originally defined by Capell and Was [20] and it is usually less than 1. Since the decomposition of steam in H<sub>2</sub> and H<sub>2</sub>O was considered in this paper, the reciprocal of this parameter (*i.e. PPR*<sup>-1</sup>) is more convenient to be considered.

The expression of the dissociation pressure at Ni/NiO transition  $(p_{O_2 Ni/NiO})$  is reported in eq. (4) and it was calculated similarly to eq. (2) from the Gibbs free energy of formation of NiO<sub>(s)</sub>  $(\Delta G_{f,NiO})$  associated with the reaction (3).

$$Ni_{(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NiO_{(s)}$$
(3)

$$p_{O_{2 Ni/NiO}} = p^{\Theta} \cdot exp\left[-\frac{2\Delta G_{f,NiO}^{\Theta}}{RT}\right]$$
(4)

#### 5.2.3. Characterization of the H<sub>2</sub>-Steam Environment

#### 5.2.3.1. In situ Electrochemical Characterization

The equilibrium potential associated with the decomposition of the water (eq. 1), normalized with respect to the Ni/NiO formation can be expressed according the Nernst equation (eq. (5)), where the electrochemical potential is reported as function only of the  $PPR^{-1}$  corresponding to the Ni/NiO transition ( $PPR_{Ni/NiO}$ ) over the *PPR*.

$$E_{eq\,vs.\ Ni/NiO} = \frac{RT}{4F} \ln\left[\frac{\left(\frac{p_{H_2O}}{p_{H_2}}\right)^2}{\left(\frac{p_{H_2O}}{p_{H_2}}\right)^2_{Ni/NiO}}\right] = \frac{RT}{2F} \ln\left[\frac{PPR_{Ni/NiO}}{PPR}\right]$$
(5)

The redox potential expressed in eq. (5) was experimentally measured using an Ivium potentiostat COMPACTSTAT.h connected to a Pt wire and an yttria stabilized zirconia SSRE, which were exposed to the hydrogenated steam and schematically represented in Fig. 1.

The experimental approach in identifying the electrochemical potential and the Ni/NiO transition was similar to that used by O'Neill [23], who, however, did not characterize the Ni/NiO transition in H<sub>2</sub>-steam environment. The cell consists of two electrodes, separated by a Y<sub>2</sub>O<sub>3</sub>- $ZrO_2$  membrane, acting as oxygen-conducting electrolyte [36–38]. The method measures the difference between the two cells in terms of oxygen partial pressure; if one is known, the other can be calculated, as shown in eq. (5) for the *PPR*. Usually, the one known cell consists of a metal/oxide stable phase mixture, such as Cu/Cu<sub>2</sub>O or Fe/Fe<sub>3</sub>O<sub>4</sub> [24,26,39].

The Ni/NiO yttria stabilized zirconia SSRE used in this study was a replica of a Cu/Cu<sub>2</sub>O SSRE used in [26] with a mixture of Ni and NiO powder used as reference placed in the Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> tube, a schematic representation of which is shown in Fig. 2. A Ni wire was used to create the electrical contact between the mixture powder and the potentiostat. A working Pt electrode wire was coiled at the sensing tip of the reference electrode to minimise the electrical resistance (see inset in Fig. 2). Pt, a noble metal, was chosen, as it is inert in this environment and, therefore, the measured redox potential corresponds to potential associated with eq. (1). The redox potential was monitored at 372 °C, 400 °C, 430 °C and 480 °C. For each temperature, the *PPR* was kept stable for 700 s, then the H<sub>2</sub> flow rate (and hence *PPR*) was varied and the redox potential was recorded every second.



Fig. 2: Schematic representation of the Ni/NiO Yttria Stabilized Zirconia SSRE. The inset shows the virtual cross section of the tip filled with Ni/NiO powder mixture with a Pt wire coiled around the tip which acted as working electrode.

Since the oxygen sensor used different metals in contact with the corresponding electrodes, the thermoelectric voltage due to this couple of metals was considered and used to correct the sensor voltage. The thermoelectric voltage of the Pt-Ni couple was measured by spot welding a

Ni wire to the Pt coil in a similar setup used for the SSRE; this value was 4.5 mV at 372 °C, 4.9 mV at 400 °C, 5.7 mV at 430 °C and 7.5 mV at 480 °C.

#### 5.2.3.2. Ex situ Electrochemical Characterization

Complementary ex situ GA-XRD, XRD, and microstructural analyses were performed to consolidate the electrochemical measurements. Commercially pure 99.6% Ni-200 coupons were exposed to the environment and subsequently analysed with a grazing angle XRD [40] using an incident angle equal to 3°. The characterization was conducted before and after exposure to H<sub>2</sub>steam environment at PPR<sup>-1</sup> equal to 59.4 for 200 h at 480 °C. The grazing angle XRD analyses were performed at  $2\theta$  between 30° and 85° with a 0.05° step size with a Philips X'Pert MPD system equipped with a Cu K $\alpha$  source with a scanned angle. These experiments were also repeated on pure (99.999%) Ni powder with a particle diameter between 3-5  $\mu$ m with the advantage of having a very large effective surface and hence the ability to detect very small amount of a thin surface oxides using a conventional XRD. 5 grams of Ni powder were placed in a quartz boat and inserted in the stainless-steel reaction tube (Fig. 1) for exposure to  $H_2$ -steam environment at PPR<sup>-1</sup> equal to 54.9 and then to 632.5 for 200 h at 480 °C. The XRD analyses were performed before and after exposure of the powder in  $H_2$ -steam environment. These analyses were performed using a Philips X'Pert MPD system equipped with a Cu K $\alpha$  source with a 2 $\theta$ between 5° and 85° with a 0.05° step size. The experimental peaks of both conventional and grazing angle XRD were compared with the Ni reference data (PDF card no. 00-004-0850) [41] and the NiO reference data (PDF card no. 00-044-1159) [41–43] for Cu Kα source.

Further microstructural characterizations were performed on coupon samples of Alloy 600 after exposure to the H<sub>2</sub>-steam mixture. The alloy was provided by B&W Tubular Products Division and supplied by Westinghouse with the chemical composition reported in Table 1. The material was solution annealed at 1100 °C for 30 minutes and water-quenched within 10 seconds to suppress the formation of intergranular carbides [12]. Further details can be found in [12]. Squared samples of 20 x 20 x 2 mm<sup>3</sup> were cut, ground and metallographically polished with a 3 µm and a 1 µm diamond polishing suspension. A 24-40 nm Silica Oxide Polishing Suspension (OPS) was used to remove any surface deformation due to the previous grinding polishing that can affect the oxidation behaviour of the material and to have a surface more representative of the bulk material. The samples were exposed to H<sub>2</sub>-steam at 480 °C for 210 hours in the Ni stability (*PPR*<sup>-1</sup> = 54.9) and NiO stability (*PPR*<sup>-1</sup> = 1305) of the Ni/NiO transition. After the exposure, the samples were characterized using a Field Emission Gun (FEG) – Scanning Electron Microscope (SEM) Zeiss Sigma FEG-SEM equipped with an Oxford Instruments X-max 150 silicon drift detector (SDD) and an Aztec analysis system for Energy dispersive X-ray spectroscopy imaging and analysis was used to characterize the surface of the coupon samples after the exposure to H<sub>2</sub>-steam environment. Secondary electron (SE) and annular selective backscattered (BSE) detectors were used at 5 kV accelerating voltage to analyse the morphology of the surface in the vicinity of grain boundaries. For each sample, twenty FIB cross-sections were prepared for specific sites containing at least one oxidized grain boundary using an FEI Helios 660 Dual Beam SEM/FIB. The SE and BSE detectors were used at 5 kV to image the cross-section microstructures.

Table 1: chemical composition (wt%) of Alloy 600 used in this study

Heat no.	С	Mn	S	Р	Si	Cr	Ni	Cu	Al	Ti	Fe
93510	0.047	0.23	0.002	0.005	0.30	15.42	74.43	0.01	0.19	0.34	8.94

## 5.3. Results

# 5.3.1. Measurement of the Redox Potential of the H<sub>2</sub>/Steam Mixture

The redox potential associated with the  $H_2$ /steam gaseous mixture for each value of *PPR* was monitored as function of time, and a representative set of measurements performed at 400 °C of the redox potential associated with the  $H_2$ /steam mixture are shown in Fig. 3.



Fig. 3: Evolution of the redox potential of steam in H<sub>2</sub> and O<sub>2</sub> at 400 °C as function of the time. Each transient region was obtained keeping constant a desired *PPR* for 700 seconds.

During each test the temperature was kept constant and the hydrogen content was progressively decreased (*i.e.*  $PPR^{-1}$  increased) nine times whilst the tenth acquisition was at conditions identical to the first one. Although for very reducing conditions the potential required a few hundred seconds to stabilize, the potential of steam was very sensitive to the changes in environmental conditions. The value of redox potential associated with the decomposition of steam in hydrogen and oxygen changed from -67 mV (at  $PPR^{-1} = 40.3$ ) to +30 mV (at  $PPR^{-1} = 1641$ ), thus spanning the region from Ni stability to NiO stability. A 10<sup>th</sup> measurement was performed using the same  $PPR^{-1}$  used for the acquisition of the first transient region at the end of the acquisition in order to verify a possible excess of O<sub>2</sub> in the yttria stabilized zirconia tube. The SSRE demonstrated a minimal hysteresis since the redox potential of steam acquired during the final measurement was slightly higher (by  $\approx 10$  mV) than the potential acquired in the first transient; thus, it is reasonable to assume that oxygen saturation in the reference electrode did not occur during the experiments (Fig. 3).

This experiment at 400 °C was repeated three times in order to evaluate the reproducibility of the results and the reference electrode was regenerated prior each set of measurements. The average of the stabilized potential once the transient was completed is reported as a function of the *PPR*<sup>-1</sup> in Fig. 4; the values predicted by the Nernst equation (eq. (10)) using the thermodynamic data from Kubaschewski *et al.* [9] is also reported (black solid line).



Fig. 4: Experimental redox potential associated with the H<sub>2</sub>O equilibrium with H<sub>2</sub> and O<sub>2</sub> at 400 °C behaviour as function of *PPR*<sup>-1</sup>. The experimental data were compared with the theoretical redox potential at 400 °C calculated from the free energy of dissolution for water (black solid line) [9].

Further experiments were conducted at 372 °C, 430 °C and 480 °C in order to evaluate the response of the reference electrode as function of the temperature. A summary of the evolution of the redox potential for the temperature examined in this work is reported in Fig. 5.

The experimental curves at 372 °C and 400 °C agreed well with the theoretical data, confirming the Nernstian behaviour of the potential as function of the  $PPR^{-1}$  in H<sub>2</sub>-steam environment. However, at 480 °C (blue downward triangle in plot d), a considerable deviation of the experimental potential from the theoretical data was observed in the more oxidising conditions with respect to the Ni/NiO transition.



Fig. 5: Experimental redox potential of steam trend as function of the *PPR*<sup>-1</sup> at (a) 372 °C, (b) 400 °C, (c) 430 °C and (d) 480 °C. The experimental data were also compared with the theoretical redox potential of steam (solid black line) for the temperatures examined calculated from reference [9].

#### 5.3.2. XRD

Grazing angle XRD analyses were performed on commercially pure Ni-200 coupons before and after exposure in the H<sub>2</sub>-steam environment. A representative grazing angle diffractogram for Ni coupon before the exposure (a) is shown in Fig. 6, which confirmed the absence of any external oxide on the surface, since the only peaks present in the plot are characteristic of Ni. The coupon was then exposed in the H<sub>2</sub>-steam environment at 480 °C for 200 h at the *PPR*<sup>-1</sup> equal to 54.9, which is a reducing condition with respect to the Ni/NiO value (*i.e.* the measured redox potential of Pt was -59 mV vs. the SSRE). The diffractogram (b) of Fig. 6 showed the main peaks of pure Ni [41], confirming that the coupon was exposed in a reducing environment, however secondary peaks approximately at 38°, 65° and 78° were identified after the exposure. These peaks did not correspond to the NiO peaks, but they are consistent with the formation of

iron silicate (Fe<sub>2</sub>SiO<sub>4</sub> at  $2\theta = 38^{\circ}$  and  $78^{\circ}$ )) and manganese oxide (MnO<sub>2</sub> at  $2\theta = 65^{\circ}$ ), as expected from the minor impurities present in the commercially pure Ni-200.



Fig. 6: Grazing-angle XRD spectra of Ni coupons before (a) and after exposure in H<sub>2</sub>-steam environment for 200 h at 480 °C at *PPR*<sup>-1</sup> = 54.9 (b). The diffractograms are shifted in the Y-axis for clarity.

Further experiments were also conducted using Ni powder to corroborate the previous results and exclude the possibility that a very thin oxide what might have been undetected by the grazing angle XRD. Two tests were conducted: one in a reducing condition (b) and the other in an oxidizing condition (c) with respect to the Ni/NiO. The XRD results are shown in Fig. 7 alongside the base line powder characterization. The diffractogram of the Ni powder exposed at  $PPR^{-1}$  equal to 54.9 exhibited only the peaks associated with metallic Ni and no evidence of NiO. This result confirmed that the environment was more reducing than the Ni/NiO transition, in fact, from Fig. 5 a steam redox potential of -59 mV was predicted. The second test was conducted at  $PPR^{-1}$  equal to 632.5 ( $E_{eq} = 20.8 vs. Ni/NiO$ ), and the characteristic XRD peaks of NiO can be clearly identified in the diffractogram in Fig. 7 (c).



Fig. 7: XRD spectra of high purity Ni powder before (a), after exposure in H<sub>2</sub>-steam environment at 480 °C for 200 h at  $PPR^{-1}$  = 54.9 (b) and at  $PPR^{-1}$  = 632.5 (c). The diffractograms are shifted in the Y-axis for clarity.

Specifically, the main NiO reflections were located at 20 values of 37.3°, 43.3° and 63° [42,43] as well as those for the baseline Ni matrix; no Ni(OH)<sub>2</sub> was identified by XRD for the powder exposed to the more oxidising conditions (Fig. 7 (c)). It was thus experimentally observed that the Ni/NiO transition at 480 °C occurred at *PPR*<sup>-1</sup> between 54.9 and 632.5. Whist this range of *PPR*<sup>-1</sup> is relatively wide, it is worth noting that Ni was predicted to be in the oxidized state even at *PPR*<sup>-1</sup> equal to 11, significantly lower than the *PPR*<sup>-1</sup> = 54.9 according to Capell and Was [20].

### 5.3.3. Microstructural Characterization of Alloy 600

The work reported in the literature by those laboratories who used low pressure H<sub>2</sub>-steam to simulate electrochemical conditions of a PWR primary water environment is limited to very reducing conditions with respect to the Ni/NiO transition [12,15,19–21,31–34,44] whilst the effect of oxidizing potential has not been investigated. In the present work, Alloy 600 SA coupon samples were exposed in H<sub>2</sub>-steam environment at 480 °C for 210 h, either in reducing or oxidizing conditions with respect to the Ni/NiO transition. Recalling that PWSCC susceptibility is highest in the proximity of the Ni/NiO transition [1], a similar trend would also be expected for the evolution of preferential intergranular oxide (PIO) penetration. Consequently, if such a correlation was found, this would provide confidence on the validity of using low pressure hydrogenated steam system as a surrogate for PWR primary water.

Representative SE and BSE micrographs of the surface of the sample exposed to reducing conditions ( $PPR^{-1} = 54.9$  and  $E_{eq} = -52$  mV vs. Ni/NiO) are shown in Fig. 8. The surface appeared to be uniformly covered with randomly dispersed brightly-imaging (in BSE images) particles that are consistent with metallic Ni nodules that are known to form as a consequence of the internal compressive stresses generated by the formation of internal oxides [12,21,31]. Also, the grain boundaries regions appeared to be protruded and to form "split-ridges", highly decorated with brightly-imaging particles; furthermore, on both side of the grain boundaries, an approximately 2-3 µm nodule-free zone was observed as in previous studies [12].



Fig. 8: (a) SE and (b) BSE images of the surface in the proximity of grain boundary regions for the sample exposed in the more reducing environment (*PPR*<sup>-1</sup> = 54.9 and  $E_{eq}$  = -52 mV vs. Ni/NiO).

Conversely, the surface of the sample exposed to the more oxidising environment (*PPR*<sup>-1</sup> = 1305 and  $E_{eq}$  = +52 mV vs. Ni/NiO) showed a completely different surface morphology. The SE-SEM images showed a rough appearance of the surface, indicating a possible external oxide layer that uniformly covers the surface of the sample (Fig. 9-a). The BSE-SEM image (Fig. 9-b) showed a bright region of  $\approx$ 2 µm along the grain boundary (GB), traversed by a continuous and undulated dark feature; this feature, being darker, is consistent with a lower atomic number and it may indicate the presence of a thin surface oxide.



Fig. 9: (a) SE and (b) BSE images of the surface in the proximity of the grain boundary regions for the sample exposed in the more oxidizing environment ( $PPR^{-1} = 1305$  and  $E_{eq} = +52$  mV vs. Ni/NiO).

Marked differences between the two samples can be also observed from the SE images of the FIB cross-sections shown in Fig. 10-a and Fig. 10-b that contained at least one oxidized grain boundary. The grain boundaries were decorated with fine intergranular  $M_{23}C_6$  carbides, identified in previous studies of this alloy via electron diffraction [12], and are clearly visible as fine darkly-imaging features on the grain boundaries. For the sample exposed in the more reducing environment (Fig. 10-a), a coarse, continuous and highly interconnected darkly-imaging feature was observed along the grain boundary indicating the occurrence of PIO, and consistent with previous detailed microstructural studies [12–14,16,21,45]. However, it is also possible that local variations in oxidation tendency depending on grain boundary angle and grain orientations are present, but this has not been investigated in detail in this work and it is the subject of ongoing investigations. In contrast, no intergranular oxidation was observed along the grain boundary (Fig. 10-b) of the sample exposed in the more oxidising environment.



Fig. 10: SE images of the FIB-prepared cross-section of a grain boundary region for the Alloy 600 sample exposed in (a) more reducing environment than the Ni/NiO transition (*PPR*<sup>-1</sup> = 54.9 and  $E_{eq}$  = -52 mV vs. Ni/NiO) showing interconnected and deep PIO; and (b) in more oxidizing environment than the Ni/NiO transition (*PPR*<sup>-1</sup> = 1305 and  $E_{eq}$  =+52 mV vs. Ni/NiO) where no relevant PIO was detected.

## 5.4. Discussion

The experimental redox potential associated with the H<sub>2</sub>/steam gaseous mixture shown in Fig. 4 can be considered, with good approximation, to be the potential associated with the redox equilibrium of the reaction (1). In fact, the decomposition of the steam on the Ni metal surface is much greater than the dissolution of the Pt working electrode [28,46], which did not interact with the environment and alter the measured redox potential. The oxygen partial pressure inside the yttria stabilized zirconia tube sensor was kept constant by the presence of two stable phases (Ni and NiO) and the redox potential measured was only associated with the decomposition of steam and hence influenced only by the  $p_{O_2}$  in the system. The redox potential of H<sub>2</sub>/steam mixture shown in the previous plot of Fig. 4 was compared with the *PPR*<sup>-1</sup> values imposed during the acquisition and reported in the plot of Fig. 11.



Fig. 11: Evolution of the experimental redox potential of steam (solid black line) acquired during the experiment and overlapped with the expected redox potential of steam for the desired *PPR*<sup>-1</sup> ratio (dashed red line).

As expected,  $PPR^{-1}$  and the redox potential were proportional to each other. A good correspondence between the experimental redox potential and the thermodynamic predictions was noted. However, for the highest temperature and for more oxidizing environments, the experimental data deviated slightly and the potential of steam was underestimated by up to  $\approx 10$  mV. The buffer capacity of H<sub>2</sub>/H<sub>2</sub>O mixtures became very poor for high *PPR*<sup>-1</sup>, as shown in the plot d (blue downward triangle in plot d) of Fig. 5.

The values of *PPRs*<sup>-1</sup> associated with the Ni/NiO transition extrapolated from the data in Fig. 4 and Fig. 5 were calculated, reported in the Arrhenius plot in Fig. 12, and compared with the data from other laboratories [8,9,20]. From the results of the present work presented in Fig. 12 it was determined that  $\Delta H_{f,mix}^{e}$  was equal to 12430 J/mol and the  $\Delta S_{f,mix}^{e}$  was equal to 30.51 J/mol·K, where  $\Delta H_{f,mix}^{e} = \Delta H_{f,H_2O}^{e} - \Delta H_{f,NiO}^{e}$  and  $\Delta S_{f,mix}^{e} = \Delta S_{f,H_2O}^{e} - \Delta S_{f,NiO}^{e}$ . These experimentallyderived values are in good agreement with previous values calculated by Kubaschewski *et al.*  $(\Delta H_{f,mix}^{e} = 12091.9 J/mol$  and  $\Delta S_{f,mix}^{e} = 30.51 J/mol \cdot K)$  [9], shown as the black line in the plot of Fig. 12. Moreover, the *PPRs*<sup>-1</sup> corresponding to the Ni/NiO transition (*i.e.* green points shown in Fig. 12) were used to calculate the theoretical redox potential using eq. (5); importantly, the results shown in Fig. 13 indicate that the discrepancy between experiments and theory is negligible.



Fig. 12: Arrhenius plot showing the  $PPR_{Ni/Ni0}^{-1} vs. 1000/T$  for the experiments carried out in this work, the data of Attanasio *et al.* [5] Moss *et al.* [8], Capell *et al.* [20] and the theoretical standard Gibbs free energy of the mixture H<sub>2</sub>O-NiO, calculated from Kubaschewski *et al.* [9].

In contrast, Capell and Was [20] predicted the Ni/NiO phase transition to be at a much lower value of *PPR*<sup>-1</sup> for 400 °C (11 vs. 337 measured in this work) with a predictable discrepancy of  $E_{eq}$  = -100 mV calculated using eq. 5. The discrepancy by Capell and Was might be due to the fact that their experimental results were based on the formation of Ni(OH)<sub>2</sub>, which was detected via XPS and not NiO. Furthermore, although they claimed that their Gibbs activation energy was in good agreement with the high pressure water results of Attanasio *et al.*, the thermodynamic conditions associated with the Ni/NiO transition depend on the state of the media, which was different. In fact, the different physical condition of water influences the  $\Delta S_{f,mix}^{\phi}$  and, for this reason, thermodynamic data obtained at high pressure and low-pressure systems cannot be compared. It is also not surprising that the data extracted from Moss *et al.* [8] (also reported in Fig. 12,  $\Delta H_{f,mix}^{\phi} = 19281 J/mol$  and  $\Delta S_{f,mix}^{\phi} = 37.32 J/mol \cdot K = 37.32$ ), are different from the values identified in the present study.



Fig. 13: Comparison between the theoretical redox potential (red, dashed line) and experimental redox potential (black circles) associated with the dissolution of steam at the Ni/NiO transition.

One of the objectives of this work was to validate the super-heated low pressure H<sub>2</sub>-steam environment as a possible surrogate system to perform oxidation and SCC experiments relevant to the PWR primary water environment. For this reason, two Alloy 600 oxidation tests were conducted to understand the oxide morphology evolution (Fig. 8 to Fig. 10). Specifically, tests conducted at PPR<sup>-1</sup> equal to 54.9 ( $E_{eq}$  = -52 mV vs. Ni/NiO), showed that the surface appeared to be covered with randomly dispersed discrete, brightly-imaging particles, identified in previous studies as Ni-nodules [12,21,31]. Metallic Ni nodules are formed to counteract the internal compresses stresses generated by the formation of discrete internal oxides of Cr (i.e., Cr<sub>2</sub>O<sub>3</sub>) [12,14,15]. Internal oxidation can occur in an alloy when the PPRs<sup>-1</sup> are sufficient to oxidize one of the less noble alloying elements [47]. A similar oxidation process can be attributed to the protruded grain boundary, and previous studies have already shown significant PIO along grain boundaries with "split-ridge" oxide morphologies in such environments [12,14,15,21,31,34]. In contrast, Alloy 600 samples tested at PPR<sup>-1</sup> equal to 1305 ( $E_{eq}$  = +52 mV vs. Ni/NiO) were characterized by a surface covered with an external oxide layer, probably enriched in NiO, Ferich oxides and spinels, such as NiCr<sub>2</sub>O<sub>4</sub> [48]. The morphology of the grain boundaries was different from that observed in the sample exposed to the more reducing environment. The undulated black linear features associated with the grain boundaries observed in the BSE image of Fig. 9 appear to be related to presence of the surface oxide. The SE images of the FIB crosssection (Fig. 10) showed a negligible PIO as well as a less internal oxidation in contrast to the sample exposed to the more reducing environment. The thin surface oxide layer above the GBs (Fig. 9) can act as a barrier layer inhibiting further inward oxygen diffusion. In contrast, the grain boundary exposed to the more reducing environment (Fig. 10-a) showed an interconnected and deep PIO penetration of ≈500 nm.

Therefore, the oxide characterization conducted in this study highlighted a very high sensitivity of PIO to the electrochemical potential with respect to the Ni/NiO equilibrium electrode potential, whereby significant, deep PIO was identified in the Ni stability region.

Recalling that PIO is considered to be the main precursor event of PWSCC of Alloy 600 [30,35], a good correlation was identified between the behaviour of Alloy 600 in low pressure hydrogenated steam environment and in high pressure simulated PWR primary water. PWSCC initiation has been shown to predominantly occur in reducing simulated PWR primary water environments [4], and to exhibit a maximum of crack growth for conditions close to the Ni/NiO transition, but in the Ni stability region [1]. A probable diffusion induced grain boundary migration [49,50] associated with the formation of the PIO and external oxide layer was identified in the SE images in Fig. 10-a and Fig. 10-b. This phenomenon was already observed for Alloy 600 exposed to high temperature H<sub>2</sub>-steam environment [12,14–16,21,33,34] and it was reported to occur also at lower temperatures on Alloy 600 exposed to simulated PWR primary water [19,35,51]. This suggests that the mechanism is similar in both environments. This work has also shown low pressure hydrogenated steam is valid as an accelerating environment that can be considered to be representative of PWR primary water.

## 5.5. Concluding Remarks

The aim of this study was to validate the super-heated low pressure H<sub>2</sub>-steam environment as surrogate to a PWR primary water environment. The following conclusions can be drawn from this investigation:

- The environmental conditions reproducing the Ni/NiO transition in a low pressure super-heated H<sub>2</sub>-steam were identified at temperatures between 372 °C and 480 °C using an Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> solid-state reference and *ex situ* XRD characterization of Ni-200 coupons and pure Ni powder.
- The Gibbs free energy associated with the formation of NiO and decomposition of H<sub>2</sub>O was dependent on the media considered, *i.e.* high-pressure water or steam *vs.* superheated low-pressure steam. The results of this work showed that the

Kubaschewski *et al.*'s data [9] can be used to predict the oxidizing potential in H<sub>2</sub>-steam. However, our findings are in disagreement with the activation energy calculated by Capell and Was, who conducted the experiments in a low-pressure superheated system [20].

 The oxidation of Alloy 600 coupons was used to highlight the high dependence of this alloy to preferential intergranular oxidation as a function of the oxidizing potential in the H<sub>2</sub>-steam environment. These results also provide confidence that superheated H<sub>2</sub>steam can be used to reproduce the similar oxidizing conditions to those of PWR primary water, thereby providing accelerated test conditions for PWSCC-related research.

## 5.6. Acknowledgments

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## Introduction to Chapter 6.

Chapter 6, entitled "Understanding the Role of Diffusion Induced Grain Boundary Migration on the Preferential Intergranular Oxidation Behaviour of Alloy 600 via Advanced Microstructural Characterization", has been submitted as a research paper in Acta Materialia.

Stress Corrosion Cracking (SCC) is an important topic that affects the nuclear materials and, despite significant research effort has been invested, there is still not the consensus over the mechanism of SCC initiation and the role of the oxidation precursors events.

In this work, a systematic oxidation programme of Alloy 600 (nickel base alloy) that is widely used in pressurized water reactor conditions, was conducted to elucidate the role of the preferential intergranular oxidation and grain boundary migration associated with the early stages of SCC of Alloy 600. The samples, after exposure to H<sub>2</sub>-steam, were characterized using advanced analytical techniques and the results were compared with SCC data available in literature. It has been demonstrated that grain boundary migration can be considered to be an accelerating factor for the development of intergranular oxidation; but it is not a sufficient condition for the occurrence of PIO.

#### Author contribution:

L. Volpe is the principal author, he performed the experimental work, he analysed and processed the experimental data and he wrote the manuscript.

F. Scenini is the principal supervisor; he provided conceptual guidance and extensive manuscript review.

M. G. Burke provided conceptual guidance, support on the electron microscopy characterization and extensive manuscript review.

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# 6.Understanding the Role of Diffusion Induced Grain Boundary Migration on the Preferential Intergranular Oxidation Behaviour of Alloy 600 via Advanced Characterization

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## Abstract

This present work introduces a new understanding of the precursors events to Stress Corrosion Cracking (SCC) initiation in nuclear power plant components, exploring the role of grain boundary migration and Preferential Intergranular Oxidation (PIO). In this work, a systematic evaluation of Alloy 600 exposed in low pressure H<sub>2</sub>-steam over a range of oxidizing potentials in the vicinity of the Ni/NiO transition has revealed a notable decrease in PIO for conditions more oxidizing than the Ni/NiO transition, whilst local diffusion-induced grain boundary migration occurs irrespective of the oxidizing potential. Thus, grain boundary migration in itself is not a unique signature for PIO and SCC incubation, but it represents a critical acceleration factor for more reducing conditions (such as those in pressurised water reactors) where oxide film instability allows for the initiation of PIO. It is also shown that Al/Ti enrichments that develop along the migrated GBs correlate with the occurrence of PIO when the alloy develops a non-protective external oxide.

Keywords:

Alloy 600; PWSCC; Preferential Intergranular Oxidation; Internal Oxidation; Diffusion-Induced Grain Boundary Migration.

## 6.1. Introduction

Alloy 600 was widely used for structural components in Pressurized Water Reactors (PWRs), but it was discovered to be susceptible to Primary Water Stress Corrosion Cracking (PWSCC) [1]. The primary water chemistry contains H<sub>2</sub> addition to minimize the radiolytic products and maintain reducing conditions [2]; indeed, at low Electrochemical Corrosion Potential (EcP) the SCC susceptibility of core components is mitigated [3–6]. However, several studies have shown that the Crack Growth Rate (CGR) for Alloy 600 presented its maximum susceptibility located in the proximity of the Ni/NiO transition, which represents the electrochemical conditions for typical operation of nuclear power plants [7,8], and that the CGR exhibits a characteristic bell shape curve as function of H<sub>2</sub> concentration [4,9]. SCC initiation studies of Alloy 600 in hydrogenated water at 330 °C performed by Molander et al. [10,11] showed that the Time-To-Initiation (TTI) exhibited some similarities to the trend observed for the CGR in the sense that the highest susceptibility for crack initiation was located in the proximity of the Ni/NiO transition but shifted to slightly more reducing conditions [4]. In contrast to the CGR trend, the TTI was much less dependent on dissolved H<sub>2</sub> for conditions more reducing than the Ni/NiO transition, and only increased for very reducing conditions. Conversely, in the NiO stability region, a relatively small decrease of dissolved H<sub>2</sub> resulted in a rapid increase in TTI, as reported by Molander et al. [10]. However, the asymmetry with respect the Ni/NiO transition in the TTI curve remains still unclear.

Several mechanisms have been proposed to account for the occurrence of both initiation and propagation of PWSCC in Ni-base Alloys, although the one believed to be most suitable explanation is Selective Internal Oxidation proposed by Scott and Le Calvar in 1993 [12] and refined based on advanced analytical microstructural characterisation data [13–21]. Internal oxidation can occur in a binary or ternary alloy than contains a noble metal as solvent and one or more less noble metals as solutes [22]. Specifically, when the oxygen partial pressure  $(p_{o_2})$  is lower than the dissociation pressure of the most noble metal, the oxygen can diffuse into the matrix and oxidize the less noble metals with the formation of discrete particles oxide. This mechanism has been showed to occur in Alloy 600 oxidized in conditions relevant to PWR in low pressure H<sub>2</sub>-steam environment [23] and later confirmed by other laboratories [13–15,24,25], with resulting discrete Cr<sub>2</sub>O<sub>3</sub> oxides formed beneath the surface of exposed Alloy 600 specimens.

Several oxidation studies were performed on Alloy 600 to investigate the influence of dissolved  $H_2$  on the morphology of the external oxide layer. Terachi *et al.* [26] performed oxidation experiment on Alloy 600 coupon samples in high temperature water at 320 °C and

identified a stable and continuous NiO layer for low levels of the dissolved hydrogen (DH), whereas when the H<sub>2</sub> content was increased (DH = 1.0 ppm), the NiO became less stable and exhibited a needle-like oxide structure. For a much higher dissolved H<sub>2</sub> content (DH > 2.75 ppm), NiO was no longer detected whilst a NiFe<sub>2</sub>O<sub>4</sub> spinel oxide with a thin Cr-rich oxide layer adjacent to the Alloy 600 surface was observed. Combrade *et al.* [27] and Soustelle *et al.* [28] also demonstrated that the electrochemical potential strongly influenced oxide film formation on Alloy 600. For EcP values close to the Ni/NiO transition, the Cr-rich spinel oxide layer was thicker with a high Cr content, and the external oxide was thicker and less protective; for even lower EcP, the oxide was mainly composed of Cr<sub>2</sub>O<sub>3</sub> [29] whilst at high EcP the Cr content of the inner protective layer decreased and Ni-spinel oxide increased [30]. However, as intergranular SCC is thought to be associated with the fracture of grain boundary oxide, the influence of H<sub>2</sub> on PIO merits further investigation.

Oxidation studies of Alloy 600 in a superheated  $H_2$ -steam environment, which is used to accelerate the oxidation process [5,13,15,23,31], have shown that Alloy 600 is susceptible to PIO [16,18,20,32,33]. However, the majority of the  $H_2$ -steam oxidation experiments have been performed in a reducing environment with respect to the Ni/NiO transition [13,15,17,18,31,34,35], thus highlighting a knowledge gap in the literature.

Oxygen can preferentially diffuse along grain boundaries for several micron on samples exposed in more reducing conditions with respect to the Ni/NiO transition depending on the exposure time [13,15–18], with oxidation of the less noble metals in the vicinity of the grain boundaries as well as the formation in of an external Cr-rich oxide layer. It is also worth noting that during the surface oxidation process, the Cr diffusion can induce the grain to migrate laterally in a process called Diffusion Induced Grain Boundary Migration (DIGM) [36,37]. Several studies performed at various temperatures between 320 °C [16] and 480 °C [13,15,17–19,25] demonstrated the occurrence of PIO in Alloy 600 associated with DIGM. Further advanced analytical electron microscopy studies also revealed the presence of a local Al and Ti enrichments ahead the intergranular oxide that might act as possible accelerating factor and enhance the diffusion of oxygen along the new migrated area [14,15,19]. However, although there is increasing evidence of DIGM occurring at growing SCC cracks in both Ni-base alloys as well in stainless steels in high temperature hydrogenated water [38,39], a direct link between DIGM, PIO and SCC has not been identified.

Whilst it is known that the stress can affect the extent of intergranular oxidation [14], the aim of this paper was to investigate the oxidation mechanism reported to be associated with the early stages of Alloy 600 PWSCC. Thus, the oxidation behaviour of coupon specimens has been studied as function of oxidizing potential, which is controlled by the hydrogen partial pressure in the steam, and these experimental data have been correlated with SCC evolution as function of dissolved H<sub>2</sub> in primary water as reported in the literature [10]. The effect of stress on oxidation and the early stage of cracking is the subject of a future publication [40].

Using advanced microstructural characterization techniques, detailed analyses have been performed to assess the microchemical changes (including Al and Ti) along the GBs as a function of H<sub>2</sub> following exposure in low pressure H<sub>2</sub>-steam, a representative environment to PWR primary water [41] that has been shown to accelerate the oxidation process without changing its mechanism [3].

## 6.2. Experimental

#### 6.2.1. Material Preparation

The material used in this study was Alloy 600 (Heat no. 93510) manufactured by B&W Tubular Products Division and supplied by Westinghouse. The material was provided in the low temperature mill-annealed condition and the chemical composition is reported in Table 1. The material was Solution Annealed (SA) in air at 1100 °C for 30 minutes and water quenched within 10 seconds in order to minimize the formation of intergranular carbides [13]. Square coupon samples of dimensions of  $20 \times 20 \times 2 \text{ mm}^3$  were cut from the solution annealed material; these coupons were extracted several millimetres away from the external surfaces thus avoiding the possibility of oxide contaminations. The coupon samples were ground and metallographically polished with a 3 µm and a 1 µm diamond polishing suspension. The final polishing step was obtained with a 24 – 40 nm Silica Oxide Polishing Suspension (OPS) in order to remove any superficial deformed layer due to the previous grinding and polishing steps and have a surface representative of the bulk material. In fact, the surface finish and the final roughness has been shown to strongly influence the SCC susceptibility [42] and to affect the oxide evolution [5,43–45]. More details about the baseline characterization of this material can be found in [13].

Table 1: Chemical composition (wt%) for Alloy 600 used in this study

Heat no.	С	Mn	S	Р	Si	Cr	Ni	Cu	Al	Ti	Fe
93510	0.047	0.23	0.002	0.005	0.30	15.42	74.43	0.01	0.19	0.34	8.94

#### 6.2.2. H<sub>2</sub>-steam Environment

A low pressure super-heated H<sub>2</sub>-steam environment was used as a surrogate for a PWR primary water environment as it has the benefit of providing good control of the oxidizing potential with respect to the Ni/NiO transition [23]. The oxidizing potential of the system, and hence the oxygen partial pressure, can be modified by changing the ratio between the steam partial pressure over the hydrogen partial pressure. The environmental conditions in the H<sub>2</sub>-steam environment can be described by a parameter *R*, which is the ratio between dissociation pressure at the Ni/NiO transition  $(p_{O_2 Ni/NiO})$  and the  $p_{O_2}$  in the system (eq. (1)). Consequently, for *R* > 1 the Ni is stable, for *R* < 1 the NiO is stable.

$$R = \frac{p_{O_2 Ni/NiO}}{p_{O_2}}$$
(1)

Nine different  $H_2$ /steam ratios were used to examine the dependence of PIO susceptibility on the electrochemical potential. All the tests were conducted at 480 °C for 210 h and full details are reported in Table 2.

Test no.	Environment	$p_{o_2}$ atm	p <sub>02 Ni/Ni0</sub> atm	$R=\frac{p_{O_{2Ni/NiO}}}{p_{O_2}}$	<i>EcP</i> mV <i>vs</i> . Ni/NiO [40]	
1	NiO stability	5.9x10 <sup>-23</sup>	2.5x10 <sup>-24</sup>	1/24	52	
2	NiO stability	1.3x10 <sup>-23</sup>	2.5x10 <sup>-24</sup>	1/6	28	
3	Ni/NiO transition	2.5x10 <sup>-24</sup>	2.5x10 <sup>-24</sup>	1	0	
4	Ni stability	1.66x10 <sup>-24</sup>	2.5x10 <sup>-24</sup>	1.5	-7	
5	Ni stability	4.2x10 <sup>-25</sup>	2.5x10 <sup>-24</sup>	6	-28	
6	Ni stability	1.1x10 <sup>-25</sup>	2.5x10 <sup>-24</sup>	24	-52	
7	Ni stability	1.3x10 <sup>-26</sup>	2.5x10 <sup>-24</sup>	200	-86	
8	Ni stability	2.8x10 <sup>-27</sup>	2.5x10 <sup>-24</sup>	900	-110	
9	Ni stability	6.2x10 <sup>-28</sup>	2.5x10 <sup>-24</sup>	4000	-135	

Table 5: Summary of the experiments performed in the superheated low pressure H<sub>2</sub>-steam environment at 480 °C for 210 h

Experiments #1 to #6 were performed according to the procedure used in [13–15,23,25]: the deionized water was injected at a flow rate of 1.50 mL/min into an evaporator that was held at 200 °C using a high performance chromatography Shimadzu pump LC-20AT; the steam was mixed with a gaseous mixture of H<sub>2</sub> and Ar before being injected into the chamber which contained the samples. However, for experiments #7 to #9 (Table 2), which required significantly greater reducing conditions, steam was not generated via H<sub>2</sub>O evaporation but was "added" by bubbling an Ar/H<sub>2</sub> mixture through a container of H<sub>2</sub>O that was kept at 70 °C. The moist gas was then injected into the chamber that contained the samples. In all the experiments, as the H<sub>2</sub> flow rate was varied to produce the different oxidising potentials, and Ar was varied accordingly to maintain the total gas flow before being mixed with the steam at a constant rate of 40 cc/min. The flow rates of the gases were controlled with two independent Bronkhorst flow meters. More details about the thermodynamic of the low pressure superheated H<sub>2</sub>-steam system can be found in [23,41,46].

#### 6.2.3. Microstructural Characterization

The coupons samples were characterized after exposure to H<sub>2</sub>-steam environment with a range of conventional and advanced analytical microscopy techniques. A Zeiss Sigma field emission gun (FEG) – scanning electron microscope (SEM) equipped with an Oxford Instruments X-Max 150 silicon drift detector (SDD) for energy dispersive X-Ray (EDX) spectrum imaging and microanalysis and an Aztec analysis system was used to analyse the surface of the coupon samples after the exposure to H<sub>2</sub>-steam environment. The In-lens, secondary electron (SE), and annular backscattered electron (BSE) detectors were used at low accelerating voltage (3-5 kV) to analyse the of the surface of the coupons, with particular emphasis on the oxide morphology in the vicinity of the grain boundaries. A Zeiss Merlin FEG-SEM equipped with two Oxford Instruments X-Max 150 Silicon Drift Detector (SSD) and an Oxford Instruments X-Max Extreme 100 windowless SDD for low voltage EDX spectrum imaging and an Aztec analysis system for qualitative chemical analysis was used at low voltages to assess the composition after the high temperature H<sub>2</sub>-steam exposure.

FIB cross-sections were prepared from selected grain boundaries using a FEI Helios 660 and a FEI Quanta 3D Dual Beam SEM/FIB. Twenty FIB cross sections were evaluated from each sample in order to assess the extent of PIO penetration along the newly migrated GB. In order to study the DIGM effect on the morphology of the PIO, specific geometrical parameters of the migrated region, such as the depth (*d*), the width (*w*) and the area, were measured for over 50

grain boundaries on the SE-FIB cross sections by using the Fiji ImageJ software (version 2.0) [47,48].

The FEI Helios 660 FIB was also used to prepare six electron-transparent lift-out specimens for further analytical electron microscopy (AEM) analyses. TEM characterization was performed using an FEI Tecnai T20 LaB<sub>6</sub> analytical TEM/STEM operated at 200 kV and equipped with an Oxford Instruments X-Max 80 TLE SDD and Aztec analysis system, and a Philips CM20 TEM operated at 200 kV. Discrete STEM-EDX "spot" analyses were performed to analyse the local compositional variation along grain boundaries oriented parallel to the incident electron beam. These EDX spectra were quantified using the Aztec software (version 4.0) with theoretical "*k*-factors". More detailed analyses were performed using an FEI Talos F200 analytical FEG-S/TEM equipped with Super X (4 SDDs) for STEM-EDX spectrum imaging and microanalysis. The STEM-EDX spectrum image data acquisition was performed with a dwell time of 200 µs for a total live time of 30 min and whit a pixel size equal to 1.328 nm. STEM-EDX Spectrum Image (SI) datasets were analysed using Thermo Fisher Scientific Velox software (version 2.4).

## 6.3. Results

#### 6.3.1. SEM and FIB Characterization of the Oxidised Surfaces

Representative Secondary Electron (SE) and BackScattered Electron (BSE) micrographs illustrating the surface oxide morphologies of the coupons after exposure to the different H<sub>2</sub>-steam environments for 210 h at 480 °C are shown in Fig. 1. The SE images in Fig. 1a and b are representative of the sample surface exposed to R = 1/24 (oxidising condition). The grains appeared to be uniformly covered with a rough external oxide layer; moreover, along the GB, a narrow 1-2 µm region had a different contrast that might indicate the presence of a difference oxide morphology or oxide thickness. The micrographs of Fig. 1c and d are representative of the surface was covered with brightly-imaging nodules; the grain boundaries were also characterized by continuous and brightly imaging ridges/protrusions.

The surfaces shown in Fig. 1e and f are representative of the surface of samples oxidized at R = 1/24 (reducing conditions). The surface morphologies for these samples were similar to those characterized in previous studies [13,14,31] in a similar reducing superheated H<sub>2</sub>-steam environment; specifically, the surface was characterized by the presence of brightly imaging and

randomly dispersed features which had previously been identified via EDX to be metallic Ninodules [43].



Fig. 1: FEG-SEM observations of specimens exposed in H<sub>2</sub>-steam environment at 480 °C. (a, c, e) SE and (b, d, f) BSE images representative of the specimen surfaces after 210 h exposure under different oxidizing conditions: (a, b) R = 1/24; (c, b) R = 1; and (e, f) R = 24.

The SEM observations revealed that the majority of the grain boundaries exposed to the more oxidising environments (Fig. 1a and Fig. 1b) appeared to deviate from their original straight position and showed a wavy behaviour after the oxidation. Further low voltage (5 kV) SE and BSE images (shown in Fig. 2a and b) revealed pronounced undulated appearance of the grain boundaries after exposure in the more oxidising H<sub>2</sub>-steam environment. The dark and continuous "wavy line" is consistent with the presence of a surface oxide because features with a lower atomic number than the matrix appears darker when imaged using the backscattered

electron detector. Qualitative SEM-EDX analyses performed at a lower accelerating voltage (3.5 kV, see Fig. 2), which has the advantage of providing a limited interaction volume, indicated that the undulated GB feature was highly enriched in Al and O, suggesting the possible presence of aluminium oxide.

The undulation observed in Fig. 2 is not associated with a uniform migration of the GB in one direction but, as discussed by Balluffi *et al.* [36], the GB migration front can advance either side of the boundary. This observation has also been reported in previous studies on Alloy 600 exposed to  $H_2$ -steam environments [13].



Fig. 2: a) SEM-SE, b) SEM-BSE and c-h) corresponding SEM-EDX 3.5 kV maps for a sample oxidized in H<sub>2</sub>steam at R = 1/24.

Detailed FIB cross-sections were also produced to investigate the internal and intergranular oxidation behaviour in the vicinity of the grain boundary. FIB-SE micrographs of oxidized grain boundaries of samples exposed to R = 6, 200 and 4000 (reducing condition with respect to the Ni/NiO transition) are shown in Fig. 3d, e and f, respectively. Negligible PIO occurred along the GBs of the samples exposed to environments with R less than or equal to 1, and the surface of each sample was uniformly covered with an external and continuous oxide layer (Fig. 3d).

Conversely, significant PIO was observed for those samples exposed under more reducing conditions with respect to the Ni/NiO transition (Fig. 3e for R = 200 and Fig. 3f fo
4000); representative micrographs of samples exposed to environments with R = 200 and 900 are shown in Fig. 3c and d respectively. Interestingly, and irrespective of the oxidising condition, none of the examined grain boundaries were straight. Judging by the grain to grain contrast, they appeared to have undergone migration, however, it is worth noting that FIB cross section imaging alone is not sufficient to demonstrate the real occurrence of DIGM, but it can still provide a strong indication of this phenomenon. It was also noticed that the High Angle Grain Boundaries (HAGBs) in Fig. 3 were decorated with several darkly-imaging features that had been previously identified via electron diffraction in as  $M_{23}C_6$  intergranular carbides [13].



Fig. 3: overview of FIB-SE cross-section micrographs of samples exposed in H<sub>2</sub>-steam at: a) R = 1/24, b) R = 1, c) R = 1.5, d) R = 6, e) R = 200 and f) R = 4000.

The extent of PIO and DIGM for each sample was measured and the results are plotted as function of *R* in Fig. 4. Specifically, the average (blue dots, dash-dotted curve) and maximum (red squares, dotted curve) PIO is plotted in Fig. 4a, whilst the average migrated cross sectional area is reported in Fig. 4b. The extent of PIO showed a sharp transition and the highest susceptibility was identified in the reducing side of the Ni/NiO transition; in contrast, no PIO was detected in the NiO region. The maximum PIO of approximately 1.5 µm was occurred for *R* = 1.5 and, for a relatively wide range of reducing environments, the extent was approximately 300 – 400 nm. At *R* = 4000 the extent of PIO decreased to ≈60 nm, which was comparable to the measured value for *R* < 1. The average DIGM area (Fig. 4b) appeared to be almost independent on the oxidizing potential and, it was estimated from the FIB-SE micrographs to be between  $0.05\pm0.02 \mu m^2$  and  $0.09\pm0.03 \mu m^2$ .



Fig. 4: a) PIO as function of the oxidizing ratio *R*. The red, dotted line represents the maximum PIO detected whilst the blue, dotted curve is the average PIO. b) DIGM as a function of the oxidizing ratio *R*.

#### 6.3.2. Advanced TEM Characterization

Advanced AEM characterization focused on the samples exposed in the most oxidising environment at R = 1/24, since advanced AEM analyses of samples exposed in more reducing environments have been reported in previous studies by the present authors [13,14,31] as well as by other researchers [17–19,24,49].

The Bright-Field (BF) and Centred Dark-Field (CDF) image for a sample exposed at R = 1/24 for 210 h at 480 °C are shown in Fig. 5a and b, respectively. After exposure, TEM analysis revealed that the grain boundary was not straight but deviated laterally by  $\approx$ 500 nm from its original path into the adjacent grain. Very fine M<sub>23</sub>C<sub>6</sub> intergranular carbides (yellow arrow in Fig. 5b) formed during the water-quench and identified via selected area electron diffraction, were observed along the original grain boundary; these carbides served as a marker to identify the original position of the GB and the occurrence of DIGM. These carbides were imaged using the M<sub>23</sub>C<sub>6</sub> carbide reflections as shown in the inset in Fig. 5b.



Fig. 5: a) BF and b) corresponding CDF TEM images showing the migrated area at the GB of a sample tested in oxidizing conditions (R = 1/24). The inset in b) is the [100] selected area electron diffraction pattern that confirmed the presence of very fine  $M_{23}C_6$  carbides that formed during the quench (arrowed).

The surface of the sample was covered with an  $\approx 60$  nm thick external oxide layer comprised NiO, several Ni- and Fe-rich spinels and Cr<sub>2</sub>O<sub>3</sub> (identified by selected area electron diffraction). The various oxides are shown in the CDF images of Fig. 6, with corresponding selected area electron diffraction patterns.



Fig. 6: (a) SADP ([001] zone axis) acquired from the Alloy 600 SA grain boundary and the external oxide layer after exposure to R = 1/24 H<sub>2</sub>-steam environment showing several small reflections associate with the formation of incoherent oxides species on the surface. Several coloured dotted rings highlighting the reflections consistent with the presence of NiO, (Fe,Ni)Cr<sub>2</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> were added to the [001] SADP in (b). The high spatial resolution BF image (c) showed the morphology of the external oxide layer. The CDF image (d) was generated with the Fe<sub>3</sub>O<sub>4</sub> reflection (d reflection in the SADP (a)); whereas the CDF image (e) was formed with the contributions of FeCr<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> (e reflection in the SADP (a)).

Discrete FEG–STEM–EDX spot analyses revealed that the migrated region was strongly depleted in Cr (to  $\approx$ 5% wt) and Fe (to  $\approx$ 3% wt). EDX elemental maps extracted from the STEM-EDX spectrum image datasets obtained from the grain boundary migrated region are shown in Fig. 7. The newly migrated grain boundary was also associated with the presence of Al and Ti (Fig. 7f and g). No PIO was observed along the original or the newly migrated GB, confirming the FIB cross-section results reported in Fig. 3 which indicated a negligible intergranular oxide penetration ( $\approx$ 60 nm).



Fig. 7: a) HAADF image and b-g) corresponding STEM-EDX elemental maps acquired from a HAGB in a sample exposed under the most oxidising conditions (R = 1/24). Note the formation of Cr-rich inner oxide with associated enrichments of AI and Ti (despite the low levels of AI and Ti in the alloy).

#### 6.4. Discussion

PIO is considered to be one of the main processes leading to the initiation stage of PWSCC, and despite several decades of research [12–14,16,17,39,50], its role as a "precursor event" is still not fully understood. Thus, this study is focused on elucidating of the role of PIO as it relates to the initiation of PWSCC in Alloy 600. The Alloy 600 SA oxidation experiments in H<sub>2</sub>-steam at different oxidising potential were performed to understand: i) the possible relationship between the PIO and the SCC initiation time, ii) the evolution of PIO and DIGM for the different oxidizing potentials and iii) the role of the DIGM during the early stages of PWSCC.

#### 6.4.1. Correlation between the PIO with the SCC Initiation Time

The main objective of this work was to understand whether the PIO can be considered a precursor event associated with the formation of protocracks [1] leading to the initiation stage of PWSCC. However, this correlation is not feasible because there are no SCC data in H<sub>2</sub>-steam and, to the authors' knowledge, there are no systematic investigations of PIO as a function of potential in high temperature hydrogenated water in the literature. Therefore, the approach used in this study was to calculate the expected PIO that would develop within a fixed time from the Time to Initiation (*TTI*) experimental data from Molander *et al.* [10] and compare them with the results presented in this study.

Specifically, it was assumed that the intergranular oxidation penetration follows a parabolic law [9,12,51] and that the crack advance can be modelled as the repeated formation of a critical PIO depth (*i.e.* the "process zone" [9]) that fractures under the effect of a tensile stress [12]. Consequently, the time required to develop a "process zone"  $(t_1)$  can be calculated by using the Eq. (2), where D is the oxygen diffusion coefficient and b is the depth of the "process zone".

$$t_1 = \frac{b^2}{\mathcal{D}} \tag{2}$$

Under the hypotheses that the time required to obtain a macroscopic crack (*TTI*) is proportional to the time  $t_1$  required to develop the critical "process zone," it is possible to correlate *TTI* with  $t_1$  via a dimensionless constant k as shown in Eq. (3).

$$TTI \propto k \times t_1 \tag{3}$$

Since the crack advance process is governed by the supply rate of oxygen to the "process zone" [9], the diffusivity  $\mathcal{D}$  can be calculated from the depth of the PIO  $(d_{PIO})$  and the duration of the oxidation experiment, where *t* is equal to 210 h in this study (Eq. (4)):

$$\mathcal{D} = \frac{d_{PIO}^2}{t} \tag{4}$$

Therefore, substituting  $t_1$  from Eq. (2) into Eq. (3) and  $\mathcal{D}$  from Eq. (4) in Eq. (2), it is possible to obtain the relationship between *TTI* and  $d_{PIO}$  after at time *t*, according to Eq. (5).

$$TTI \propto k \times \frac{b^2}{D} \propto \frac{k \times b^2 \times t}{d_{PIO}^2} \propto \frac{A}{d_{PIO}^2}$$
(5)

In other words, the  $d_{PlO}$ , which is the depth of PIO that develops over a time t, is inversely proportional to the square root of TTI via a constant A.

Therefore, by using eq. (5) it is possible to calculate the dependence between the depth of PIO ( $d_{PlO}$ ) and the EcP from the *TTl vs.* EcP reported in [10]. Note that EcP depends on the dissolved value of H<sub>2</sub> in the water [52] and it is proportional to the ratio *R* [41]. This approach enabled a comparison of the results from Molander *et al.* [10] with those results obtained in this work in terms of PIO *vs.* corrosion potential.

The PIO and  $TTI^{-2}$  data have been plotted on two different scales due to the not unitary value of the constant A (Eq. (5)) as function of the ratio R (eq. (1)). The average PIO trend (blue circles, dashed line in the plot of Fig. 8) showed a very good correlation with the experimental  $TTI^{-2}$  data (green rhombus, line) from Molander *et al.* [10].



Fig. 8: Evolution of the average PIO as function of the oxidizing condition R (eq. (5)). The data from Molander *et al.* [10] is also plotted as square root of the initiation time (solid green line and green diamonds) so that the dependence of the time-to-initiation and the PIO as a function of the oxidizing condition can be compared.

Therefore, it appears that PIO can be considered to be the precursor event for SCC, and confirms that H<sub>2</sub>-steam is a valid accelerating environment to replicate PWR primary water as postulated in previous studies [13–16,25,31,41,43,53]. The sharp transition observed in the PIO trend was not observed in the  $TTI^{-2}$  plot (Fig. 8), possibly because applied stress can disrupt the protective oxide and modify the sharp transition that is otherwise seen for samples oxidized without stress. It is, however, worth noting the PIO is a complex process that is associated with local Al and Ti enrichments and DIGM; the implications of microchemical segregation and GB mobility are discussed in the following sections.

# 6.4.2. PIO and DIGM Behaviour as a Function of the Oxidising Potential

After the exposure to H<sub>2</sub>-steam environments under different oxidising potentials, a large number of grain boundaries were examined and a representative set is shown in the SE– FIB cross-sections in Fig. 3, where the PIO was observed to be strongly dependant by the oxidising conditions. The highest susceptibility to PIO for slightly reducing conditions (at R = 1.5 and 6) with respect to the Ni/NiO transition can be explained with the formation of a thin ( $\approx$ 10 – 20 nm) oxide layer that it did not protect the GB from oxygen diffusion [13,17,54]. In contrast, for the more oxidising conditions (R = 1/24), the PIO susceptibility was dramatically reduced because the external oxide (Fig. 3 and from Fig. 5 to Fig. 7) acted as protective layer and inhibited the oxygen diffusion along the GBs. The scattered values of the extent of PIO, especially for the samples exposed to the more reducing conditions (Fig. 4 to Fig. 6) might be explained by the different crystallographic orientations of the two adjacent grains that can induce a stress gradient, acting as supplementary driving force for the oxygen diffusivity along the GBs [55]. However, it is interesting to note that GB migration was observed irrespective of the occurrence of the PIO (Fig. 3 and from Fig. 5 to Fig. 7).

The GB migration mechanism associated with DIGM is based on local diffusion of the less noble alloying metals due to environmental conditions, where the grain laterally migrates leaving behind it a depleted region of the high diffusivity less noble elements [36,37,56]. The local depletion observed in the newly migrated area (Fig. 7) was comparable with the depletion observed in previous oxidation studies performed under more reducing condition in the same Alloy 600 SA heat [13]. However, the results by Langelier *et al.* [18] clearly showed that the migrated area was only depleted in Cr, thus suggesting that minor chemical differences associated with a specific heat may influence the oxidation behaviour of the Alloy in the proximity of the HAGBs. The occurrence of DIGM was previously believed to be strongly associated with PIO, because PIO was never observed without DIGM in Alloy 600 [13,14,16–19,21,39,57–60]. However, our findings clearly show that DIGM is not sufficient to promote PIO, and that it can occur independently from the PIO (Fig. 3).

Furthermore, it was observed that the measured extent of DIGM (area defined by the migrated versus original grain boundary locations) was similar for all environmental conditions, irrespective of the structure of the external oxide layer. In fact, DIGM was also observed in specimens tested under very reducing conditions (R = 4000, Fig. 3f). In this case, the formation of a thin external Cr-rich oxide layer acted as a driving force for the occurrence of DIGM, confirming the observations that Alloy 600 can easily form an external Cr-rich oxide with accompanying GB migration, as reported for Alloy 600 exposed under vacuum ( $\approx 10^{-5}$  mbar) at 340 °C [61]. Conversely, the sample exposed to R = 1/24 exhibited a well-developed external oxide layer consisting of Ni- and Fe-rich spinels and NiO with an inner Cr<sub>2</sub>O<sub>3</sub> layer containing Al-and Ti-rich oxides (Fig. 6 and Fig.7). Thus, the formation of the Ni- and Fe-rich oxides did not affect the extent of DIGM.

It is important to note that DIGM was not present prior into the sample exposure to H<sub>2</sub>steam as reported in [13], which investigated the same Alloy 600 heat used in this study. From the SE-FIB cross-section images of Fig. 3, it was observed that the migrated areas were either narrow and long or wide and shallow. This trend was confirmed in Fig. 9a, which shows an inverse relationship between the depth and width for the migrated areas. The plots in Fig. 9b and Fig. 9c illustrate the evolution of the aspect ratio d/w of the migrated area as function of R, where a schematic representation of these parameters is reported in the inset of Fig. 9a. Interestingly, the GBs that exhibited a narrow and elongated migrated region, (high d/w) were associated with the deepest PIO (at R = 1.5 and 6) whereas GBs with wide migrated areas (low d/w) exhibited no or shallow PIO (e.g. R = 1/24). It is therefore proposed that the PIO shielded the lateral GB migration, thus forcing the migration to develop in depth, rather than in width. It is proposed that the grain boundary is forced to laterally migrate with the formation of the advancing PIO along the newly migrated GB as long as the less noble metals are present in the proximity of the migration front (e.g. Cr and Fe) by intergranular diffusion of these solutes. However, as the supply of Cr and Fe near the migrating front is decreased, the Cr and Fe diffusion along the GB beneath the migrated region increases, forcing the "local non-migrated GB" to migrate to support the development of further and deeper PIO. The specific aspect ratio associated with the PIO evolution can explain why it was not possible to select SE-FIB images representative of both PIO and DIGM values (Fig. 3 and plots in Fig. 4a and b). Thus, it is clear that DIGM has an effect on the PIO evolution. Further considerations concerning the possible role of the chemical micro-segregation along the oxidised GB are discussed in the next section.



Fig. 9: a) the relationship between the width (w) and the depth (d) of the grain boundary migrated area defined for every FIB cross section; the schematic in the inset shows how width and depth were defined. b) the dependence between the aspect ratio of the grain boundary migrated region (depth/width) varies as function of the oxidising parameter R. c) PIO as function of the oxidizing parameter R showing that the deepest PIO also corresponds to the highest values of the aspect ratio depth/with of the migrated regions. Note that the legend in figures a and b are the same.

#### 6.4.3. Understanding the Role of DIGM and PIO

The DIGM has been observed to be adjacent to and ahead of the PIO and crack tips on samples exposed to the H<sub>2</sub>-steam environment [13–15,18,19,25,41] or simulated PWR primary water [21,39,59,60]; however, its contribution to the early stages of PWSCC is still not fully understood and at time contradictory. For instance, Shen *et al.* [60] proposed that DIGM is a retarding factor for SCC because it creates a more tortuous path for the advancing cracks. Conversely, oxidation studies [13,15,16] have proposed that DIGM enhances the O and Cr diffusivity and acts as an accelerating factor for PIO; this was supported by the fact that diffusion along moving grain boundaries was observed to be up to four orders of magnitude faster that on stationary ones [13,31,62,63].

Fig. 2h and Fig. 7f and g also showed the presence of Al- and Ti- enrichments that may correspond to  $Al_2O_3$  and  $TiO_2$ , since these oxides species are thermodynamically stable in these environmental conditions [64,65]. At conditions more oxidizing than Ni/NiO transition (R < 1), the presence of an external NiO layer (SADP in Fig. 6) prevented the formation of PIO, and the Al/Ti oxides were observed on the surface above the newly migrated area (Fig. 7). Conversely, under more reducing conditions (R > 6), PIO developed and Al/Ti-enriched oxides were detected along the migrated GB [14–17,19]. Therefore, DIGM and the Al/Ti enrichments can be considered to be secondary factors for the occurrence and evolution of PIO because they can support and enhance its evolution, although they do not appear to be rate controlling. Al/Ti oxides are incoherent with the FCC matrix and could enhance the mobility of O and Cr along the newly migrated GB [14–17,19,66]. It is worth noting that the experiments in this study were performed under conditions significantly more oxidizing for those required for the formation of Al, Ti, Fe and Cr oxides. However, their formation is dictated by the oxygen partial pressure of the protective oxide and not directly by the environment, which has an indirect role. In fact, as clearly shown from the Figs. 1 to 3 and from Figs. 5 to 7, the oxidizing conditions can affect the formation of the external layer and have implications on the evolution of Al-rich, Ti-rich, and Crrich oxides.

As shown in the graphical summary of Fig. 10, DIGM appeared in all the grain boundaries exposed to the different oxidising potentials. In the most oxidising condition (Fig. 10a) DIGM is caused by the formation of the external oxide layer that covered the surface and inhibited the material from preferential intergranular oxidation phenomena. Conversely, in the proximity of the Ni/NiO transition (Fig. 10b) the maximum oxide penetration occurs where the DIGM presented a narrower but deeper aspect, possibly due to a pinning effect from the advancing

PIO. Finally, in the most reducing conditions (Fig. 10c and d), the oxygen activity is too low for the formation of PIO and consequently DIGM develops laterally.



Fig. 10: schematics highlighting the evolution of PIO, DIGM, the external oxide layer and internal oxidation region as a function of the oxidizing conditions: a) R < 1, b)  $R \approx 1$ , c) R > 1.

### 6.5. Conclusion

Oxidation studies on Alloy 600 SA were performed in low pressure superheated H<sub>2</sub>steam environments at 480 °C for 210 h in order to understand the role of the preferential intergranular oxidation on SCC by using a range of complementary analytical microscopy techniques and the following conclusions can be drawn:

Alloy 600 SA is susceptible to PIO but only when it is exposed to a more reducing environment than the Ni/NiO transition. The maximum PIO penetration was found to be ≈1 µm in slightly reducing conditions (R = 1.5), whereas a penetration of ≈60 nm was found in the most oxidising environments (R = 1/24).

- The PIO data and the TTI for SCC in high temperature obtained from previous studies by Molander *et al.* [10] in water exhibited a similar dependence for more reducing conditions (*R* > 1). This confirms the dominant role of PIO development on SCC initiation. The slight difference observed for the more oxidizing conditions may be associated with the effect of the stress that was not present in the oxidation coupon samples examined in this study. However, these results provide evidence that the H<sub>2</sub>-steam environment is valid as an accelerated oxidation test for studying the PWSCC susceptibility of Ni-base alloys.
- The aspect ratio (d/w) of the migrated area varied accordingly with the susceptibility of
  PIO evolution. Oxidized GBs that exhibited the deepest PIO also presented the highest
  value of the aspect ratio and it was proposed that the oxide acts as chemical pinning
  and forced the grain to migrate in depth rather than in width.
- DIGM was shown to be a not sufficient condition for the development of PIO. Moreover,
   DIGM and the associated AI/Ti enrichments could accelerate the occurrence of PIO only when a non-protective external oxide layer is formed.

## 6.6. Acknowledgments

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# Introduction to Chapter 7.

Chapter 7, entitled "Correlation between Grain Boundary Migration and Stress Corrosion Cracking of Alloy 600 in Hydrogenated Steam", has been submitted for publication as a research paper in the journal Acta Materialia.

Alloy 600 strained samples were exposed to superheated H<sub>2</sub>-steam under different oxidising conditions representative of pressurized water reactor nuclear power plants and subsequently analysed using advanced electron microscopy techniques. It was experimentally proved that the SCC crack initiated within the preferential intergranular oxide developed along a newly migrated grain boundary. This chapter also demonstrates that SCC initiation involves the synergic interaction of the preferential intergranular oxide, the movable grain boundary coupled with a local Al- and Ti-enrichments, rather than one single mechanism.

The mechanistic understanding provided in this chapter can be used for ensuring safe operation of existing reactors and to inform the design of new generation reactors with the formulation of new and more advanced predictive models.

#### Author contributions:

L. Volpe is the principal author, he performed the experimental work, he analysed and processed the experimental data and he wrote the manuscript.

F. Scenini is the principal supervisor; he provided conceptual guidance and manuscript review.

M. G. Burke provided conceptual guidance and she contributed to the manuscript review.

# 7.Correlation between Grain Boundary Migration and Stress Corrosion Cracking of Alloy 600 in Hydrogenated Steam

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#### Abstract

Solution-annealed Alloy 600 samples were tested under applied load conditions in a superheated low pressure H<sub>2</sub>-steam environment over a range of oxidising potentials relevant to Primary Water Stress Corrosion Cracking (PWSCC). Increased SCC susceptibility was observed for potentials the more reducing than the Ni/NiO transition where a deeper Preferential Intergranular Oxidation (PIO) occurred. Advanced microstructural analysis clearly showed that SCC initiated along the grain boundaries that exhibited Diffusion-Induced Grain Boundary Migration (DIGM), as well as enrichments in Al and Ti. Rather than the result of a single dominant mechanism, the initiation of SCC in Ni-base alloys involves the synergistic interactions between DIGM and the formation of Al- and Ti-enriched oxides, promoting PIO that can fracture with applied stress.

Key words:

Preferential Intergranular Oxidation; Diffusion-Induced Grain Boundary Migration; Stress Corrosion Cracking; Alloy 600; AEM

### 7.1. Introduction

Primary Water Stress Corrosion Cracking (PWSCC) of Ni base alloys, such as Alloy 600, is one of the main issues associated with long-term operation of nuclear power plants [1–3]. Scott and Le Calvar proposed for the first time that PWSCC in Alloy 600 was associated with internal

oxidation phenomena selectively occurring at grain boundaries [4]. More recently, a more complex preferential intergranular oxidation (PIO) behaviour has been observed using advanced analytical microscopy techniques [5–11]: this preferential intergranular oxidation was shown to occur along a newly migrated GBs associated with Diffusion Induced Grain Boundary Migration (DIGM) driven by the outward intergranular diffusion of Cr. On this basis, PIO and DIGM have been proposed to be the "precursors events" [12,13] during the early stages of PWSCC for Nibase alloys. The DIGM can be described as the lateral motion of a grain boundary, resulting of the rapid diffusion of the less noble metals in the alloys to form oxides [5,14]. For Alloy 600, the lateral migration of the GB was associated with the outward diffusion of Cr and Fe in forming  $M_{3}O_{4}$  above the migrated GB and an external Cr-rich surface oxide layer [5,7,11,15]. These observations were reported for Alloy 600 samples exposed to low pressure H<sub>2</sub>-steam environment [5,6,7 - 11, 16 - 21] and later for both Alloy 600 and 690 samples exposed to simulated PWR primary water [22–26], thus confirming that the PIO and DIGM phenomena were related to the oxidation behaviour of the alloys under reducing conditions. Specifically, areas with a significant Cr-depleted region associated with DIGM were located immediately ahead of the crack tip [24,27] in Alloy 600 samples exposed to simulated PWR primary water environments.

Although, it is widely accepted that the PIO and DIGM can play an active role during the early stages of PWSCC, their contribution to the PWSCC initiation stages is still unclear. Several studies [5–8,10,11,20] have proposed that DIGM might act as an accelerating factor for O diffusion into the material and as well for enhanced mobility of Al and Ti [11] associated with "sweeping" these minor alloying elements by the migrating GB. On the other hand, Shen *et al.* [24] considered the DIGM to be a retarding factor for the crack propagation in that the more tortuous and longer path resulting from GB migration can retard the advancing intergranular crack.

Despite the work to date, the exact roles of PIO and DIGM have not been completely assessed, and a direct link between the PIO/DIGM "precursor events" and the SCC proto-cracks initiation sites in Alloy 600 has not yet been demonstrated. Therefore, the aim of this study was to evaluate the contribution of PIO and DIGM during the early oxidation stages associated with SCC of Ni-base alloys and to locate the initiation sites of proto-cracks along the oxidised grain boundaries.

The oxidation experiments were performed in a low pressure superheated H<sub>2</sub>-steam environment that has been shown to accelerate the oxidation rate of Ni-base alloys whilst maintaining the correct electrochemical corrosion potential with respect to the Ni/NiO

transition [16,18,19] and without changing the oxidation mechanism [8,28]. Solution-annealed (SA) Alloy 600 coupon samples were placed in a specially fabricated 4-point bending tool capable of applying an applied load on the samples during exposure over a range of different oxidising potentials close to the Ni/NiO transition. Analytical electron microscopy was used to study in detail the oxidation behaviour and crack development as function of the electrochemical conditions, and to obtain information regarding the initiation stages of SCC as function of PIO/DIGM and of the oxidising potentials.

#### 7.2. Experimental Procedures

#### 7.2.1. Material Preparation

The Alloy 600 (Heat no. 93510) used in this study was manufactured by B&W Tubular Products Division and provided by Westinghouse Electric Corporation. The material had chemical composition reported in Table 1 and it was provided in a low temperature mill annealed condition.

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Heat no.	С	Mn	S	Р	Si	Cr	Ni	Cu	Al	Ti	Fe
93510	0.047	0.23	0.002	0.005	0.30	15.42	74.43	0.01	0.19	0.34	8.94

Table 1: Chemical composition (wt%) of Alloy 600 SA used in this study

The material was solution annealed at 1100 °C in air for 30 min and then water quenched within 10 seconds to suppress intergranular carbides precipitation [5]. This resulted in a coarsegrained, fully recrystallized microstructure suitable for the investigation of the oxidation processes associated with PWSCC. A comprehensive baseline material characterization is reported in [46].

Rectangular coupon samples with dimension of  $28 \times 8 \times 2.2 \text{ mm}^3$  were extracted via electro discharge machining several millimetres away from the surfaces that were oxidized during the thermal treatment. All 6 surfaces of the sample were ground with SiC papers and then metallographically polished with 3 µm and 1 µm diamond polishing suspensions, respectively, to obtain samples with the dimension of  $25.5 \times 5.0 \times 1.4 \text{ mm}^3$ . During each step, the samples were rinsed with soapy water to remove any residual particle from the previous polishing process. The last polishing step was performed using a 24 - 40 nm silicon Oxide

Polishing Suspension (OPS) in order to remove the deformed layers induced by the previous grinding steps [18] because the surface finish can strongly affect the SCC behaviour of the material [18,29] and the surface oxide morphology [18,30–32]. After the OPS polishing the samples were ultrasonically cleaned in deionised water for 15 minutes, rinsed with ethanol and then dried in stream of hot air.

#### 7.2.2. Sample Loading

The coupon samples were placed in a specially made 4-point bending tool such as the surface of interest was on the extrados whilst loading. The whole apparatus was mounted in a superheated low pressure H<sub>2</sub>-steam system, as schematically shown in the Fig. 1.



Fig. 1: Schematic of the low pressure superheated H<sub>2</sub>-steam environment used to study the oxidation and cracking behaviour of the Alloy 600 SA coupon samples as function of the oxidising potentials. A schematic representation of the full apparatus used to strain the samples (blue) is shown in the inset

The sample was plastically strained by manually tightening the nut on the pull rod (inset of Fig. 1), which introduced a bending moment and consequent tensile straining on the extrados of the sample. The strain deformation ( $\varepsilon$ ) was calculated with the eq. (2), where  $\rho$  is the radius of curvature and y is the thickness of the sample. The parameters were visually measured by using the software ImageJ Fiji2 [34,35] at the end of the experiments.

$$\varepsilon = \frac{y}{2 \cdot \rho} \tag{2}$$

Prior to the experiments, the 4-point bending apparatus was calibrated with coupon samples exposed to air at 480 °C (same temperature of the oxidation experiments) and a relationship between the loading and the strain on the sample was obtained by measuring the deformation on the sample with the eq. (2).

A total of #4 oxidation experiments were performed by exposing the Alloy 600 SA samples to H<sub>2</sub>-steam at 480 °C for 120 h. For each experiment, the sample was preloaded at  $\varepsilon$  = 0.1%, then the entire 4-point bending apparatus was placed in the low pressure H<sub>2</sub>-steam reaction tube. The pull rod was periodically tightened by 250 µm, corresponding to  $\varepsilon$  = 0.4% every 7 hours to achieve a nominal deformation on the sample of the 7%. The full details for the oxidation experiments are reported in Table 2.

#### 7.2.3. H<sub>2</sub>-steam Environment

The Alloy 600 SA samples were exposed to low pressure superheated H<sub>2</sub>-steam environment. The low pressure system was originally developed by Scenini *et al.* [18,19] and has been used in subsequent studies [5,9–11,15–17,20,30,33]. The schematic of the system and the 4-point bending jig used for these experiments are shown in Fig. 1. The oxidising potential, and hence the oxygen partial pressure in the system  $(p_{O_2})$ , were set by adjusting the inlet flow rate of H<sub>2(g)</sub> and H<sub>2</sub>O<sub>(l)</sub>. For convenience, a parameter *R* (eq. (1)) was used to describe the thermodynamic conditions for the H<sub>2</sub>-steam environment. The ratio *R* represents the oxygen partial pressure at the Ni/NiO transition  $(p_{O_2 Ni/NiO})$  and the  $p_{O_2}$ , hence a *R* > 1 is representative of an environment more reducing than the Ni/NiO transition. A more detailed description of the thermodynamic of the superheated H<sub>2</sub>-steam environment can be found in [16,18].

$$R = \frac{p_{O_2 Ni/NiO}}{p_{O_2}}$$
(1)

The desired environmental conditions corresponding to a specific oxidising potential (Table 2) were created by injecting a mixture of  $H_2/Ar$ , preheated at 200 °C and mixed with deionized water in an evaporator.

Test no.	Environment	$p_{0_2}$ atm	p <sub>O2 Ni/NiO</sub> atm	$R=\frac{p_{O_{2Ni/NiO}}}{p_{O_2}}$	EcP mV <i>vs.</i> Ni/NiO [16]	Residual plastic deformation
1	NiO stability	5.9x10 <sup>-23</sup>	2.5x10 <sup>-24</sup>	1/24	52	7.9%
2	NiO stability	1.3x10 <sup>-23</sup>	2.5x10 <sup>-24</sup>	1/6	28	7.0%
3	Ni stability	1.7x10 <sup>-24</sup>	2.5x10 <sup>-24</sup>	2	-11	7.1%
4	Ni stability	1.1x10 <sup>-25</sup>	2.5x10 <sup>-24</sup>	24	-52	6.3%

Table 2: Summary of the experiments performed in the superheated low pressure H<sub>2</sub>-steam environment at 480 °C for 120 h under the effect of an applied loading

A High-Performance Shimadzu Pump LC-20AT was used to pump the water into the evaporator with a feeding rate of 1.50 mL/min. The gaseous mixture composed by H<sub>2</sub>/Ar and steam was then injected into the stainless steel reaction tube at 480 °C. The H<sub>2</sub>/Ar mixture was set to be constant and equal to 40 cc/min via two independent Bronkhorst flowmeters, where the H<sub>2</sub> flow rate was varied to obtain the desired oxidising potential and the Ar was used as inert gas to have a consistent flow rate for the different oxidation experiments. For this study, four oxidising environments were selected: two in slightly more oxidising conditions (R = 1/24 and 1/6), and two in slightly more reducing conditions (R = 2 and 24) with respect to the Ni/NiO transition (Table 2).

#### 7.2.4. Microstructural Characterization

After exposure to the low pressure H<sub>2</sub>-steam environment, the samples were analysed by a variety of complementary microscopy techniques. The surfaces of the samples were evaluated using a Field Emission Gun (FEG) – Scanning Electron Microscope (SEM) Zeiss Merlin equipped with two Oxford Instruments X-max 150 Silicon Drift Detector (SDD) and an Oxford Instruments Extreme 100 windowless SDD Energy Dispersive X-Ray (EDX) Aztec analysis system for low voltage (less than 5 kV) EDX analysis. An FEI Helios 660 Nano Lab FEG Focused Ion Beam (FIB)/SEM was used to prepare site-specific cross sections, including at least one oxidized and cracked grain boundary, and to prepare electron-transparent FIB lift-out specimens for detailed Analytical Transmission Electron Microscopy (ATEM) characterization.

For each sample, 20 FIB cross-sections were prepared and analysed using a low voltage (5 kV) Immersion lens to obtain data set regarding the PIO and crack penetration. The Secondary

Electron (SE)-FIB cross section images were also analysed with Fiji ImageJ software (version 2.0) [34,35] to measure the cracks length and the migrated area between 100K X and 150K X of magnification.

Statistical analyses were performed with the software OriginPro 2017 [36]. Histogram charts with a varying bin size were chosen to accurately describe the distribution of the cracks length and migrated area as function of the different oxidising conditions for 20 High Angle Grain Boundaries (HAGBs) analysed, as observed from the SE-FIB cross sections. The overall data for both crack length and migrated areas are also reported in a summary chart showing the survival cumulative probability function.

In addition, six (6) FIB specimens, each containing one cracked grain boundary were extracted with the *in-situ* lift out technique for the sample exposed at R = 24, milled to electron transparency and polished at 2 kV to minimise the ion damage induced by the Ga<sup>+</sup> ion beam. TEM analyses were performed in a Philips TEM CM20 LaB6 operated at 200 kV and a FEG-TEM FEI Talos F200X S/TEM with an X-FEG and Super X (4 SDD detectors) for improved Scanning Transmission Electron Microscopy (STEM)–EDX spectrum imaging and microanalysis. Analytical TEM was used to characterize the microstructural modification and chemical compositional variation in the region near the oxidised grain boundary and to locate the crack initiation site after the exposure to the H<sub>2</sub>-steam environment. The STEM-EDX spectrum image data acquisitions were performed with a dwell time of 200 µs for a total live time of 30 min and with a pixel size equal to 1.875 nm. STEM-EDX Spectrum Image (SI) datasets were analysed using Thermo Fisher Scientific Velox software (version 2.8) and the data were shown as background subtracted and as weight%.

#### 7.3. Results

# 7.3.1. SEM and FIB Characterization after Exposure under Bending Conditions to H<sub>2</sub>-Steam

Representative SE micrographs, presented in Fig. 2, show the surface oxide morphologies of the strained samples exposed to the  $H_2$ -steam environment at 480 °C for 120 h for the different oxidising potentials.



Fig. 2: a, c, e, g) low magnification SE micrographs and b, d, f, h) high magnification SE representative micrographs of the surface for the samples under 4 point bending test after exposure to H<sub>2</sub>-steam environment. The micrographs show the marked differences between the surface morphology for the oxidising environments: a, b) R = 1/24, c, d) R = 1/6, e, f) R = 2, g, h) R = 24.

Irrespective of the oxidizing potentials examined, emergent slip steps were visible on all extrados surfaces because the samples had been plastically strained. The micrographs in Fig. 2a – d are representative of the surface of the samples exposed to more oxidising conditions (R = 1/24 and 1/6). The surfaces were uniformly covered with a continuous oxide layer on all extrados surfaces and small intergranular cracks could be observed in the high magnification images (red arrows in Fig. 2b and d). Transgranular cracks were also visible in Fig. 2b and d (white arrows); however, these cracks appeared to be associated with a fracture of the external oxide layer only and were thus not related with any preferential intergranular oxidation process.

The surface sample exposed to more reducing conditions are shown in Fig. 2e – h. The surfaces were decorated with protruded features. Higher magnification SE micrographs (Fig. 2f and h) showed that the faceted features mainly decorated the slip steps. The morphology of these features is similar to those observed in previous studies, which were identified as pure Ninodules [5–7,9,10,17–20]. Clear intergranular cracks were identified on both samples exposed to R = 2 and 24 (as indicated with red arrows in Fig. 2e – h; a pronounced undulated and "wavy" morphology of the intergranular cracks was observed from the surface for the sample exposed to R = 24 (Fig. 2g).

FIB cross-sections were prepared to investigate the intergranular oxidation and crack behaviour along the grain boundaries for each of the samples tested, as shown in Fig. 3. As shown from the SE-FIB micrographs in Fig. 3, the cracks initiated and developed at GBs where PIO occurred along the newly-migrated GBs. Conversely, the original GB was straight (dotted yellow lines in Fig. 3) and did not oxidize. This behaviour was very clear for the samples exposed to R = 2 and 24 (Fig. 3c and d), where the cracks were located in the PIO on the newly migrated GB. However, it is worth noting that FIB cross-section imaging alone cannot provide a conclusive indication of the occurrence of DIGM. Therefore, more detailed advanced ATEM characterization was performed to assess the occurrence of DIGM. More comprehensive data are presented in Section 7.3.2.

From the SE-FIB images, a marked difference in SCC susceptibility was observed for the samples exposed to the various H<sub>2</sub>-steam environments. In particular, the samples exposed to more oxidising conditions (Fig. 3a and b) with respect to the Ni/NiO transition exhibited a very low susceptibility to cracking [37] whereas the samples exposed to more reducing environments (Fig. 3c and d) showed much greater SCC susceptibility, with the maximum susceptibility located at R = 2 (Fig. 3c) [30].

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Fig. 3: SE-FIB cross sections showing the region close to the GB of the strained samples tested at the different oxidising conditions: a) R = 1/24, b) R = 1/6, c) R = 1.5 and d) R = 24. The SE-FIB in c) was acquired at lower magnification due to the length of the crack and the inset in c) was acquired at the same magnification of the other SE-FIB micrographs. The dotted, yellow line represents the original GB.

The plots in Fig. 4 and Fig. 5 show the statistical distribution of the crack length and of the migrated areas for the four oxidising environments. Specifically, the plot of Fig. 4a shows the crack length left-skewed distribution for the sample exposed to R = 1/24; with the data ranging from 0.02 µm to 0.40 µm with the mode located at 0.11 µm. The crack length distribution in the plot of Fig. 4b is representative for the sample exposed at R = 1/6. The distribution was roughly symmetric, spanning from 0 µm to 0.5 µm with the mode occurring at 0.20 µm. On contrary, the plot of Fig. 4c shows a strongly left-skewed distribution associated with the crack length of the sample exposed to R = 2. The data were ranging from 0 µm to 6 µm with the mode at 1.23 µm. The plot of Fig. 4d shows the distribution of the cracks for the sample exposed at R = 24; in this case the crack length data are slightly left-skewed distributed within a range from 0 µm to 1.5 µm and with the mode located at 0.6 µm. The all crack length data are summarized in the cumulative survival probability plot of Fig. 4e where the evolution of the SCC susceptibility for the samples exposed to the four oxidising potentials is shown. In fact, by considering a

cumulative survival probability of the 95%, the crack length value was  $\approx 0.2 \,\mu$ m for R = 1/24 (blue, line),  $\approx 0.4 \,\mu$ m for R = 1/6 (red, dashed line),  $\approx 1.1 \,\mu$ m for R = 24 (purple, double pointed, dashed line) and  $\approx 3.2 \,\mu$ m for R = 2 (green, pointed and dashed line), thus showing the highest susceptibility to SCC under reducing conditions and close to the Ni/NiO transition.



Fig. 4: Statistical analyses of the crack depth as function of the different oxidising potential are shown in a) R = 1/24, b) R = 1/6, c) R = 2, d) R = 24. In e), the relationship between the crack depth and the cumulative survival probability of observation for the different oxidising potential is plotted.

The distribution of the DIGM areas associated with the samples exposed to different oxidising environments is shown in the histogram plots in Fig. 5a – d. Specifically, the plot of Fig. 5a, representative of the sample exposed to R = 1/24, shows a left-skewed distribution, where the data ranged from 0.02  $\mu$ m<sup>2</sup> to 0.11  $\mu$ m<sup>2</sup>, with the mode located at 0.05  $\mu$ m<sup>2</sup>. A similar range distribution (0.1  $\mu$ m<sup>2</sup> – 0.09  $\mu$ m<sup>2</sup>) was observed for the DIGM areas associated with the sample exposed to R = 1/6 (Fig. 5b), where the distribution appeared to be symmetric and the mode occurred at 0.055  $\mu$ m<sup>2</sup>. The DIGM areas data for sample exposed at R = 2 (Fig. 5c) are right-skewed distributed ranging from 0.03  $\mu$ m<sup>2</sup> to 0.3  $\mu$ m<sup>2</sup> and the mode located at 0.18  $\mu$ m<sup>2</sup>. A left skewed DIGM area distribution was found for the sample exposed to R = 24. Specifically, the data ranged from 0.01  $\mu$ m<sup>2</sup> to 0.025  $\mu$ m<sup>2</sup> and the mode was located at 0.08  $\mu$ m<sup>2</sup>. These data are summarized in the cumulative survival probability plot of Fig. 5e: by considering a probability of the 95%, the value of the DIGM areas was  $\approx$ 0.07  $\mu$ m<sup>2</sup> for R = 1/24 (blue, line),  $\approx$ 0.08  $\mu$ m<sup>2</sup> for R = 1/6 (red, dashed line),  $\approx$ 0.19  $\mu$ m<sup>2</sup> for R = 24 (purple, double pointed, dashed line), and  $\approx$ 0.22  $\mu$ m<sup>2</sup>



Fig. 1: Statistical analyses of the migrated area labelled as DIGM as function of the different oxidising potential are shown in a) R = 1/24, b) R = 1/6, c) R = 2, d) R = 24. In e), the relationship between the migrated area (DIGM) and the cumulative survival probability of observation for the different oxidising potential is plotted.

# 7.3.2. ATEM characterization after Exposure under Bending Conditions to H<sub>2</sub>-Steam

TEM analysis of the sample exposed to R = 24 confirmed the presence of cracks along the newly-migrated GB. This characterization was performed on the sample exposed to R = 24because the more reducing condition prevented the formation of an external Ni oxide layer, thereby eliminating what in the analysis of the PIO/DIGM "precursor events" in crack formation [5–11,16–20]. In addition, this environmental condition also readily facilitated identification of the crack initiation sites as opposed to the analysis for the R = 2 (Fig. 3) condition.

The bright-field (BF) TEM image in Fig. 6a shows a shallow PIO penetration/crack (yellow arrows) along a newly-migrated GB. To confirm that the PIO/crack developed along the newly-migrated GB, the fine intergranular  $M_{23}C_6$  served as a marker to identify the original position of the grain boundary prior to migration, and this is indicated with red arrows in the centred-dark field (CDF) TEM image in Fig. 6b. The [ $\overline{1}12$ ] selected area electron diffraction pattern (SADP) in Fig. 6c shows the reflections used to generate the CDF TEM image of Fig. 6b [5]. The BF TEM image in Fig. 7a shows the initiation site of a crack developed in PIO (dotted, green line) along

the newly migrated GB (red, dotted line) and the original and straight GB is indicated with a yellow, dashed line.



Fig. 6: (a) BF TEM and (b) CDF TEM micrographs showing the advancing preferential intergranular oxide and a small embryo crack (yellow arrow in (b)) along a newly migrated grain boundary for the sample exposed to R = 24 H<sub>2</sub>-steam environment. The original grain boundary was identified by using fine residual M<sub>23</sub>C<sub>6</sub> intergranular carbides (red arrow in (b), and the (c) corresponding [ $\overline{112}$ ] SADP with the M<sub>23</sub>C<sub>6</sub> reflections used to generate the CDF TEM image in (b).

A second BF TEM image is shown in Fig. 7b with associated CDF TEM images, generated with the reflections consistent with the presence of Fe<sub>3</sub>O<sub>4</sub> (c), Cr<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (d), Cr<sub>2</sub>O<sub>3</sub> (e), Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (f) are shown from Fig. 7c – f. The [ $\overline{1}12$ ] SADP (Fig. 7g) shows the reflections used to generate the CDF TEM images, highlighted with red circles and identified with the same letters used to label the CDF TEM images. A second [ $\overline{1}12$ ] SADP (Fig. 7h) was added to show the discrete rings associated with the several oxide species found along the newly oxidised and cracked GB.



Fig. 7: (a) BF TEM image showing the migrated GB after exposure to 480 °C H<sub>2</sub>-steam environment for the strained sample at R = 24. The BF TEM image and the corresponding CDF TEM images (c-f) were generated with the reflections c to f in the  $[\overline{1}12]$  SADP (g). For clarity, a second  $[\overline{1}12]$  SADP (h) was added to highlight the discrete rings formed with the reflections associated with the several oxide species formed in the PIO.

High-Angle Annular Dark Field (HAADF) STEM image (Fig. 8a) and the corresponding elemental maps extracted from the STEM-EDX spectrum imaging data-cube showed that the oxidised grain boundary was enriched in Fe and Cr whilst the associated DIGM region was depleted in Cr and Fe (Fig. 8). Al and Ti enrichments were observed in the PIO core and these enrichments appeared to follow the newly-migrated grain boundary, as shown in the Al Kα and Ti Kα elemental maps of Fig. 8. A second HAADF STEM image (Fig. 8b) was added for clarity to

show in detail the location of the original GB (yellow, dashed line) that was decorated with small Cr- rich  $M_{23}C_6$  (Cr K $\alpha$  elemental maps) [5,15] and the PIO/crack (green, dotted line) developed along the newly-migrated boundary (red, dotted line).



Fig. 8: HAADF STEM image and corresponding STEM-EDX elemental maps of the advancing PIO and crack on the newly migrated grain boundary after exposure to R = 24 H<sub>2</sub>-steam environment. The HAADF STEM image in b shows in detail the original GB (yellow, dashed line), the advancing PIO/crack (greed, dotted line) along the newly migrated GB (red, dotted line). Note the evident curtaining effect due to the different milling rates of the matrix/oxide/crack is visible as vertical darkly imaging "scars" in the (a) HAADF STEM image and in the Ni K $\alpha$  and Cr K $\alpha$  elemental maps.

The overlayered elemental maps in Fig. 9a obtained from the Cr K $\alpha$  (blue), Al K $\alpha$  (light blue) and Ti K $\alpha$  (purple) elemental maps of Fig. 8, show the PIO/crack occurred along the newly migrating GB, with the flanks of the cracks highly enriched in Al and Ti. The HAADF STEM image of Fig. 9b and the corresponding STEM EDX elemental maps (Fig. 9c – g) show the chemical redistribution at the crack tip. Al- and Ti- oxides were observed in the PIO core at the crack tip, as shown in the Al K $\alpha$  and Ti K $\alpha$  elemental maps of Fig. 9e and g and in the overlayered elemental map of Fig. 9c.

It is worth noting that due to the nature of the oxide and the presence of the intergranular crack, significant curtaining effect, as shown in the HAADF STEM images and their corresponding elemental maps of Fig. 8 and Fig. 9, was developed during the preparation of the TEM specimen, despite the use of low kV of the Ga<sup>+</sup> ion beam during the final polishing stages. Therefore, the supporting HAADF image and corresponding STEM EDX Pt L $\alpha$  and Ga K $\alpha$  elemental maps in Fig. S1 show the contribution of the Pt and Ga in the correspondence of the oxidised and cracked GB, thus providing a better understanding of the vertical darkly imaging

marks visible in the HAADF STEM and STEM EDX elemental maps in Fig. 8 and Fig. 9. These marks were enriched in Pt and Ga, thus explaining the different imaging contrast, especially evident in the HAADF STEM images (Fig. 8 and Fig. 9) and in the Ni K $\alpha$  elemental maps (Fig. 8). However, the EDX spectra (supporting Fig. S2) acquired from the oxide formed at the crack tip does not show any significant contribution of these elements to the elemental maps of Fig. 8 and Fig. 9.



Fig. 9: (a) overlayered Cr Al Ti K $\alpha$  elemental maps extracted from the STEM EDX spectrum imaging dataset shows the PIO with Al and Ti along the flanks of the intergranular crack. (b) the high magnification HAADF STEM image and the corresponding (c – g) STEM-EDX elemental maps shows the chemical redistribution at the crack tip with the enrichment of (f) Al and (g) forming the (e) core of the PIO surrounded by the Cr-rich oxide, along the newly migrated GB. Evident curtaining effect due to the different milling rates of the oxide nature, the matrix and the development of the cracks matrix/oxide/crack as the vertical darkly "scars", especially visible in the (a) HAADF STEM image and in the Ni K $\alpha$  and Cr K $\alpha$  elemental maps.

# 7.4. Discussion

The aim of this study was to understand the role of PIO, DIGM, local elemental segregation and applied stress/strain on the early stages of intergranular SCC. In order to evaluate the initiation sites, advanced electron microscopy techniques have been used to characterize the resulting surface morphology and crack evolution as function of the PIO and DIGM for the four oxidising potentials.

# 7.4.1. Surface Morphology and Crack Behaviour as Function of the Oxidising Potential

The top view micrographs showed different oxide morphologies depending on the oxidising potential, although they all had visible slip steps which were associated with the plastic deformation during the straining process (Fig. 2). When the samples were tested under oxidizing conditions, the surface oxide (Fig. 2a – d) was consistent with an NiO layer [16,38,39]. Conversely, reducing potentials (R = 2 and 24) promoted the formation of discrete features decorating the surface (Fig. 2e – h); in particular, emergent slip steps were highly decorated with Ni nodules (Fig. 2g). Nodule formation is proposed to be associated with the rejection of the most noble solute in the alloy [5,10,19] so that Ni is expelled to the surface to counteract internal stresses generated from the increased volume of internal particle oxides [18]. Specifically, Ni is proposed to use short-circuit diffusion paths along linear defects extending to the surface, and is then expelled on the surface [5,6,18,20,40] in the form of Ni nodules. This mechanism can explain the high proportion of the Ni-nodules detected along the slip steps.

The highly undulated appearance of the cracks as observed from a surface view of the sample tested at R = 24 (Fig. 2g and h) suggests that the cracks developed along the newly-migrated GBs. In fact, previous oxidation studies performed on the same material (Heat 93510) in the same H<sub>2</sub>-steam environment (R = 24) have shown that the undulated GBs were associated with PIO that had occurred along migrated GBs [5,15]. The initiation of the cracks along the newly migrated GBs was confirmed using FIB-prepared cross-section samples (Fig. 3) and ATEM analyses (Fig. 6 – Fig. 8). These analyses, especially for the samples exposed to R = 2 and 24, clearly showed the development of an intergranular crack within the preferentially oxidised region along the newly migrated GB. These new results highlight the role of DIGM during the early stages of SCC for Alloy 600.

The SE images of the FIB cross-section samples (Fig. 3) and the statistical analyses (Fig. 4 and Fig. 6) showed the effect of different oxidising environments on the evolution of SCC in which the highest SCC susceptibility was found to occur at R = 2 and 24 [5,37]. Conversely, the SCC susceptibility was drastically reduced for the samples at R = 1/24 and 1/6 where the formation of the external oxide layer [15,17,41,42] protected the surface and inhibited the GBs from further preferentially oxygen penetration and reduced the cracking susceptibility.

The crack morphology seems to be affected by the environment, in fact, the more reducing conditions promoted significant PIO and internal oxidation (Fig. 3 and Fig. 4) and the

crack, as well as the corresponding migrated area, appeared to be narrow and deep; this finding suggests that the cracks developed concurrently with the intergranular oxide formation (Fig. 3c and d). On contrary, the cracks observed in the samples exposed to oxidizing potentials (R = 1/24 and 1/6, Fig. 3a and b) appeared to be wide and shallow. This can be associated to a delayed cracking initiation that developed only when the external oxide layer and the associated newly grain boundary were formed [15]. Moreover, the highly scattered values of the crack length, especially for the more reducing conditions, can be explained by the GB orientation with the respect to the loading direction [43] and GB character [44]. It is also important to note that, although the applied strain was higher on the samples exposed to more oxidising conditions, the highest susceptibility to cracking was still observed in the samples exposed under more reducing conditions (Table 2).

The DIGM area distributions as function of *R* in Fig. 5b exhibited an influence from the oxidising environments, in contrast to what was observed in previous studies [15] in which the size of the migrated area associated with DIGM was practically independent of the environmental conditions in the absence of stress. This discrepancy can be explained considering that when the crack advances, it exposes the underneath material and it promotes a PIO with associated a further GB migration.

From this work it is clear that the stages of oxidation associated with the early stages of SCC for Alloy 600 involved the synergistic occurrence of PIO, which is accelerated by the occurrence of DIGM, and segregation of minor alloying elements, and that the oxide fractures under the effect of applied stress. The roles of DIGM and oxidation in the early (precursor) stages are discussed in more detail in the next section.

# 7.4.2. Accelerating Factors: Role of DIGM, Al/Ti Enrichment and Strain on the PIO and SCC

The Diffusion-Induced Grain Boundary Migration is one of the main characteristic phenomenon associated with the precursor stages of SCC of Ni-base alloys, as visible in Fig. 3 and from Fig. 6 to Fig. 8. DIGM can be described as the lateral motion of the grain boundary associated with solute diffusion (*e.g.* Cr and Fe in forming an external oxide layer) [45,46], and it has been observed in both Alloy 600 and 690 exposed to H<sub>2</sub>-steam [5–7,10,11,16,17] as well as in simulated PWR primary water environments [23–25,47].
It is believed that DIGM can provide an accelerating factor for the O and Cr diffusivity [15]; in fact, it has been observed that elemental diffusion along movable GBs is higher that stationary grain boundaries [48–52]. Specifically, it has been reported a four times faster diffusion in Fe-Zn Alloy [48] and of "several order of magnitude" in Ni-Cr-Al alloys [49,50]. An enhanced diffusivity was also observed along oxidised grain boundaries in Alloy 600 [51] and the DIGM phenomenon was believed to be responsible for the faster diffusion of oxygen and chromium [52]. The data presented in our study are consistent with what required to explain the accelerating factor and an enhanced O and Cr diffusivities [6,7,11,15] and it may be used to improve the latest model that predicts the evolution of the SCC in Ni-base alloys [53].

In contrast, Shen *et al.* [24] have proposed that DIGM can be a retarding parameter for the crack development as the migration creates a longer and more tortuous path. However, it is possible that DIGM may have a dual role in SCC: it can accelerate the development of PIO and nucleation of the "proto-cracks" during the initiation of SCC, and it may retard the development of the crack during the propagation stages, since the observations of Shen *et al.* [24] have been made on crack tip and on well-develop cracks.

DIGM has also been proposed to be an accelerating factor for the diffusion of minor alloying elements, such as AI and Ti, that are swept along the newly migrating GB [11]. These alloying elements were significantly enriched along the newly migrated GB [6,7,11,15], and from the current observations, they were found to be at the crack tip (Fig. 8 and Fig. 9). The AI and Ti enrichment can provide a further accelerating factor for oxygen diffusion, as these elements are readily oxidised to AI<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> [38,39] and create additional short-circuit diffusional paths [7,11,15,54], thereby further enhancing O diffusion. Moreover, from the observation of the location and morphology of the PIO including the AI/Ti- oxides along the GB, it is suggested that the AI and Ti oxides may contribute to the preferential site for the incubation and initiation of the proto-cracks that eventually develop into SCC.

Another additional accelerating factor can be associated with the applied stress and plastic deformation; in fact, a plastic deformation can promote a strain gradient across the GB, that can strongly affect the initiation and propagation and increase the intergranular oxidation susceptibility of Alloy 600 and austenitic alloys [6,55,56]. Moreover, the applied stress can generate a stress gradient along the crack flank with its maximum at the crack tip [23,57–59]. It has been observed that this stress gradient can accumulate dislocations and promote the formation of vacancies that can enhance the inward intergranular oxygen diffusion [23].

An improved mechanism describing in detail the early stages of SCC for Alloy 600 SA is proposed and schematically shown in Fig. 10. A representative cross section of a HAGB for an OPS Alloy 600 SA before exposure to the oxidising environment is shown in Fig. 10a, where intergranular M<sub>23</sub>C<sub>6</sub> carbides, represented as tiny black features, decorate the original HAGB. During the early stage of exposure to H<sub>2</sub>-steam environment, an external Cr-rich oxide layer is formed (blue feature); the diffusion of Cr induces the GB to laterally migrate (Fig. 10b). Minor elements such as Al and Ti are shown as the light blue feature in Fig. 10b. Due to the nonprotective nature of the external Cr-rich oxide, oxygen can preferentially diffuse along the newly migrated GB and it can oxidize Al, Ti and Cr, forming the PIO (Fig. 10c). PIO may be "enhanced" by the synergic effect of GB mobility, promoted by the Cr oxidation, and of the formation of an incoherent oxide enriched in Al and Ti (Fig. 10c). Under the applied tensile stress, the oxide can fracture in a brittle manner and expose the metal to further oxidations and cracking (Fig. 10d and e).



Fig. 2: Schematic of the cracking evolution stages of Alloy 600 SA: (a) a representative GB before the exposure to the more reducing H<sub>2</sub>-steam environment with respect to the Ni/NiO transition, (b) the environment induced the formation of an outer Cr-rich oxide which induces the GB to laterally migrated with associated the enrichment of Al and Ti. (c) due to the non-protective nature of the external Cr-rich oxide, oxygen may preferentially diffuse along the GB, causing oxide formation and incoherent surfaces and PIO. (d-e) the brittle preferential intergranular oxide under the effect of externally applied tensile stress can fracture and exposing the underneath material that will discontinuously oxide and fracture.

## 7.5. Conclusion

Alloy 600 SA samples were exposed under the effect of an applied stress to low pressure superheated H<sub>2</sub>-steam environment at 480 °C for 120 h to investigate role of PIO and DIGM during the early stages of SCC in an environment that is relevant to PWSCC. By using a range of complementary analytical microscopy techniques, the following conclusions can be drawn:

- Alloy 600 SA is susceptible to SCC when exposed to  $H_2$ -steam under more reducing environmental conditions with respect to the Ni/NiO transition; where the highest susceptibility to intergranular cracking were observed close to the phase transition (R = 2).
- Intergranular cracks were observed to initiate and propagate in the PIO along newlymigrated grain boundaries, thus showing a synergistic effect between PIO and DIGM during the early stages of SCC initiation.
- STEM-EDX analyses identified a AI/Ti oxide "core" along the intergranular SCC "proto-crack" and along the non-cracked migrated GB. This local segregation with the synergic effect of the movable grain boundary may be responsible of an enhanced O and Cr diffusivities and could also promote oxide fracture for the crack initiation.

## 7.6. Acknowledgments

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## 7.8. Supplementary Images



Fig. S1: (a) HAADF STEM image and (b, c) supporting STEM EDX elemental maps showing the Pt and Ga location along the oxidised and cracked GB. The curtaining effect associated with the different milling rates of the matrix/oxide/crack caused the redistribution of the Pt and Ga in the proximity of the darkly vertical "scars", thus altering the STEM-EDX elemental maps showed in the Fig. 8. The high magnification (d) HAADF STEM image of the crack tip and the corresponding Pt Lα and Ga Kα elemental maps show a negligible curtaining effect as also reported in Fig. 9.



Fig. S2: The (b) EDX spectrum extracted from the area circled in red, dotted line in the HAADF STEM image in (a), shows the elements located at the crack tip of the intergranular crack developed in the PIO along the newly migrated GB. The insets (c) and (d) clearly show that the peaks of the Ga (Ga-L $\beta$  and Ga-K $\alpha$ ) and Pt (Pt-M $\alpha$ , Pt-M $\beta$ ) are not overlapped with the Al-K $\alpha$ , thus confirming the negligible effect of the FIB curtaining on the crack, (please refer to the Fig. 8, Fig. 9 and Fig. S1). Similar results were also observed from the (f) EDX spectrum extracted from the area circled in red, dotted line from the high magnification HAADF STEM image in (e) of the crack tip. The insets (g) and (h) clearly show that the corresponding peaks of Pt as Pt-M $\alpha$  and Pt-M $\beta$  and Ga as Ga-L $\alpha$  and Ga-K $\alpha$  are not overlapped with the Al-K $\alpha$ .

## Introduction to Chapter 8.

Chapter 8, entitled "Oxidation Behaviour of Solution-Annealed and Thermally-Treated Alloy 690 in Low Pressure H<sub>2</sub>-Steam", has been submitted for publication as a research paper in the journal Scripta Materialia.

Alloy 690 is a structural material used in nuclear power plants and despite its excellent in-service performance, many laboratory experiments have shown that it can undergo stress corrosion cracking. It is therefore important to understand whether Alloy 690 can initiate to crack in real nuclear power plants.

Advanced electron microscopy techniques showed that Alloy 690 was almost immune to preferential intergranular oxidation, although it was susceptible to grain boundary migration which was induced by the formation of an external and protective Cr-rich oxide layer. It was observed that grain boundary migration can occur irrespective of the formation of the intergranular oxide, thus suggesting that the migration of the grain boundary is a not sufficient condition for the development of the intergranular oxide and subsequent cracking, as already shown in the Chapter 6. for Alloy 600.

The mechanistic understanding provided in this chapter can be used for ensuring safe operation of existing reactors and to inform the design of new generation reactors with the formulation of predictive models.

#### Author contributions:

L. Volpe is the principal author, he performed the experimental work, he analysed and processed the experimental data and he wrote the manuscript.

F. Scenini is the principal supervisor; he provided conceptual guidance and manuscript review.

M. G. Burke provided conceptual guidance and she contributed to the manuscript review.

# 8.Oxidation Behaviour of Solution-Annealed and Thermally-Treated Alloy 690 in Low Pressure H<sub>2</sub>-Steam

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### Abstract

Oxidation experiments were performed on Alloy 690 in a low pressure H<sub>2</sub>-steam environment to investigate the effects of the microstructure and thermal treatment on the "precursors events" associated with Primary Water Stress Corrosion Cracking (PWSCC). Advanced analytical electron microscopy characterisation revealed that the Alloy 690 did not exhibit Preferential Intergranular Oxidation (PIO) but rather only Diffusion-Induced Grain Boundary Migration (DIGM) promoted by the formation of an external Cr<sub>2</sub>O<sub>3</sub> oxide layer for both material conditions (solution-annealed, SA *vs.* thermally-treated, TT). These data demonstrate that for Alloy 690 the DIGM is a not sufficient condition for the occurrence of PIO.

Key words:

Alloy 690; PWSCC; Preferential Intergranular Oxidation; Internal Oxidation; Diffusion-Induced Grain Boundary Migration.

### 8.1. Main Text

Ni-base alloys have been widely employed for the construction of structural components in nuclear power systems due to their high resistance to localized corrosion. However, since Alloy 600 (Ni-15Cr-10Fe) is known to be very susceptible to Primary Water Stress Corrosion Cracking (PWSCC), it has been replaced with the higher Cr Alloy 690 (Ni-30Cr-9Fe). Although Alloy 690 has demonstrated a significant improved resistance [1] to PWSCC with no instances of SCC in service, laboratory experiments have shown that, under some conditions, Alloy 690 is not immune to PWSCC [2–6]. Therefore, it is important to study the early stages of PWSCC to understand whether its occurrence is possible in nuclear power plants.

In the case of Alloy 600, a significant effort has been invested to understand the degradation mechanism via extensive testing and analysis programs. More recently, particular attention has focused on elucidating the early pre-initiation stages of PWSCC. The Preferential Intergranular Oxidation (PIO) model [7–11], which is based on the "internal oxidation" model of Scott and Le Calvar [12], has been used to describe the "precursors events" [13,14] to PWSCC initiation. In fact, the intergranular cracks were observed to form within the oxide that preferentially developed along newly migrated grain boundaries (GBs) [15] as a consequence of a Diffusion-Induced Grain Boundary Migration (DIGM) process. In Alloy 600 it was also observed that DIGM occurred when the less noble alloying elements (e.g. Cr and Fe) diffused to form an oxide [16,17]. The DIGM is believed also to accelerate the formation of the intergranular oxidation process, although it is not its cause [10]. However, in the case of Alloy 690, the roles of PIO [18] and DIGM on the PWSCC resistance are yet to be clarified. Thus, the aim of this study was to investigate the evolution of PIO and DIGM in solution-annealed (SA) and in thermallytreated (TT) coupons to relate these processes to the early / "precursor" events for PWSCC. Alloy 690 is used in the thermally-treated condition in PWRs since the precipitation of an extensive and "semi-continuous" network of intergranular carbides was shown to improve the PWSCC resistance in Alloy 600 [19].

The material used in this study was an Alloy 690 Sumitomo Heat No. 670743 with chemical composition (wt.%) of 59.9Ni, 29.6Cr, 9.9Fe, 0.4Al, 0.3Ti, 0.3Mo, 0.27Mn, 0.24Si, 0.02C and 0.007P. A portion of the material was solution annealed at 1100 °C in air for 30 minutes and then water-quenched within 10 seconds to minimize the formation of the intergranular carbides. Rectangular samples of 20 × 15 × 2 mm<sup>3</sup> for both SA and TT (as-received condition) were cut with a grinding wheel and the surface of interest was metallographically prepared and finally polished with a SiO<sub>2</sub> Oxide Polishing Suspension (OPS). The surface of interest was exposed to a low pressure superheated H<sub>2</sub>-steam environment for 120 h at 480 °C, under conditions more reducing than the Ni/NiO transition, similar to those described in [7]. This system was selected because it is capable of performing accelerated oxidation tests on Ni-base alloys whilst reproducing the correct electrochemical conditions relevant to PWR primary water [20,21]. The full thermodynamic details and the experimental set-up of this system are described in [20,22].

Prior to and after the exposure in the H<sub>2</sub>-steam environment, the coupons were characterized in detail using advanced electron-optical techniques. A Zeiss Sigma Field Emission Gun (FEG) – Scanning Electron Microscope (SEM) equipped with an Oxford Instruments X-Max

150 Silicon Drift Detector (SDD) for Energy Dispersive X-Ray (EDX) spectrometry with an Aztec analysis system was used to characterize the surface of the coupon samples. An FEI NanoLab Helios 660 Focus Ion Beam (FIB)-SEM was used to image the surface of the sample before exposure to  $H_2$ -steam and to prepare site-specific cross-section specimens (15 per sample) including at least one High Angle Grain Boundary (HAGB) before and after environmental exposure. The FIB was also used to prepare electron-transparent specimens for advanced Analytical Transmission Electron Microscopy (ATEM) analyses. For each sample, 4 TEM FIBprepared specimens were extracted via the in-situ lift-out technique and thinned to the electron transparency. The TEM analyses were conducted with a Philips CM20 operated at 200 kV, and AEM characterization was performed using an FEI Tecnai T20 operated at 200 kV and equipped with an Oxford Instruments windowless SDD for EDX microanalysis for discrete STEM-EDX "spot" analyses in the proximity of the newly-migrated grain boundary region in the FIB-produced specimens. More detailed advanced AEM analyses were performed using the FEI Talos F200 analytical FEG-S/TEM equipped with X-FEG and Super X (4 SDDs) for Scanning Transmission Electron Microscopy (STEM)-EDX analyses to characterize the microstructure and the microchemical segregation in the proximity of the oxidized HAGBs. STEM-EDX "spot" analyses and STEM-EDX Spectrum Image (SI) datasets were acquired using the same data acquisition parameters reported in [10].

Representative backscattered electron (BSE) images of the Alloy 690 microstructures from the SA and TT conditions prior to exposure in the H<sub>2</sub>-steam environment are shown in Fig. 1. For both heat treatments the grains were equiaxed and contained numerous twins; the grain size ranged from 4 to 117  $\mu$ m (average of 24±16  $\mu$ m) for the SA condition (Fig.1a and b) and from 4 to 151  $\mu$ m (average of 36±24  $\mu$ m) for the TT condition (Fig.1d and e). The as-solution-annealed alloy contained randomly-dispersed darkly-imaging features, as shown in Fig. 1b. The TT microstructure was characterized by the presence of spheroidal randomly-dispersed darklyimaging precipitates (red arrows in Fig. 1e and f) in addition to extensive intergranular precipitation (white arrows in Fig. 1e and f). SEM-EDX microanalysis confirmed these to be TiN inclusions [23] whereas the limited intergranular precipitates were identified as Cr-rich M<sub>23</sub>C<sub>6</sub> by Selected Area Electron Diffraction (SAD) and STEM-EDX microanalysis, as shown in the Fig. S1. These observations were confirmed by FIB cross-sections micrographs (Fig. 1c and f), where the HAGB for the Alloy 690 SA coupon sample showed a straight appearance with no apparent intergranular precipitates detected via SEM imaging (Fig. 1c) and the HAGBs for Alloy 690 TT were decorated with intergranular M<sub>23</sub>C<sub>6</sub> carbides (white arrows in Fig. 1f).



Fig. 1: (a, b) BSE-SEM and (c) BSE-FIB micrographs showing the microstructure and the morphology of the grain boundaries in the Alloy 690 SA. (d, e) BSE-SEM and (f) BSE-FIB micrographs showing the microstructure and the morphology of the grain boundaries in the Alloy 690 TT.

The Secondary Electron (SE) micrographs in Fig. 2 show the surface morphology for the Alloy 690 SA (Fig. 2a and b) and TT (Fig. 2d and e) after exposure to H<sub>2</sub>-steam environment. Irrespective of the heat treatment (SA *vs.* TT) the coupons oxidized in a similar way in hydrogenated steam: the majority of the grains were covered with several shiny faceted features; these features were associated with the formation of Ni-nodules and developed on a finer particle layer that uniformly covered the surface of the grains (Fig. 2a, b, d and e). These surface Ni-nodules are believed to form to counteract the compressive stresses associated with classical internal oxidation processes [22], and they have been already observed in previous oxidation studies performed on Alloy 600 [7,11,22,24].

In the proximity of the GB, a Nodule-Free Zone of  $\approx 1.5 \,\mu$ m wide was detected for both heats, as shown from the top view SE images in Fig. 2a, b, d and e. Moreover, these regions devoid of nodules, were covered with a very thin oxide layer. In the Alloy 690 SA samples the HAGBs were decorated with several darkly-imaging elongated features adjacent the original GB as indicated with the white arrows in the BSE image of Fig. 2a, that may be associated with surface oxidation processes. For the TT sample, the intergranular carbides decorating the HAGBs and directly exposed to the  $H_2$ -steam environment, appeared to be locally consumed/oxidised (red arrows in Fig. 2d and e).

Despite the differences from the surface observations (Fig. 2a, b, d, e) in the proximity of the GB regions after the exposure to the H<sub>2</sub>-steam environment, site-specific FIB cross-section samples of Alloy 690 SA (Fig. 2c) and TT (Fig. 2f) show that both materials responded similarly to the elevated temperature oxidation environment.

Specifically, the surfaces were covered with a thin oxide layer, visible as a continuous darkly-imaging feature in Fig. 2c and f and no or negligible PIO was observed in either heat. However, in both heats, the HAGBs appeared to laterally migrate by  $\approx$ 300 nm. Within the grains, a highly interconnected and fine internal oxide with an average penetration of  $\approx$ 400 nm was observed for both SA and TT conditions (Fig. 2c and f). These darkly-imaging features were identified by electron diffraction and STEM-EDX SI analyses to be highly interconnected Cr<sub>2</sub>O<sub>3</sub> internal oxide that surrounded pure Ni zones and sporadically scattered Fe-rich oxide islands (see complementary SADP and STEM-EDX analyses in Fig. S2).



Fig. 2: (a, b, c) SE micrographs of Alloy 690 SA showing (a) and (b) the surface morphology, and (c) the cross-section after exposure to H<sub>2</sub>-steam. (d, e, f) SE micrographs of Alloy 690 TT showing (d) and (e) the surface morphology, and (f) the FIB cross-section morphology after exposure to H<sub>2</sub>-steam.

Conventional TEM analyses were performed on FIB-prepared cross-section specimens for both Alloy 690 SA and TT to evaluate the oxidation behaviour in the proximity of the GB region after exposure to H<sub>2</sub>-steam environment and to confirm the occurrence of DIGM.

The bright field (BF) TEM image in Fig. 3a shows a representative HAGBs for the Alloy 690 SA after exposure to H<sub>2</sub>-steam. The oxidized GB experienced local GB migration, which was confirmed by using Convergent Beam Electron Diffraction (CBED) patterns oriented along the [013] zone axis acquired from the matrix (Fig. 3b) and the newly-migrated region (Fig. 3c). The STEM-EDX data indicated that the migrated region was Ni enriched ( $\approx$ 77.1 wt%) and Cr depleted ( $\approx$ 12.8 wt% *vs.*  $\approx$ 30 wt%). In addition, the migrated area was covered with a  $\approx$ 10 nm oxide layer, highly enriched in Cr, Fe and Ni, which is most likely Cr<sub>2</sub>O<sub>3</sub> and (Ni,Fe)(Ni,Cr)<sub>2</sub>O<sub>4</sub> spinels [25]. Along the newly migrated GB, very limited intergranular oxidation ( $\approx$ 50 nm) was observed with localised enrichments in Al and Ti, as visible in the STEM-EDX elemental maps of Fig. 3.



Fig. 3: (a) BF TEM showing a migrated HAGB for the Alloy 690 SA. (b), (c) [013] CBED patterns obtained from the 2 regions identified with the red dots in (a) confirming that the regions have the same orientation. (d) HAADF STEM image and elemental maps for Ni, Cr, Fe, O, Al and Ti extracted from the STEM-EDX SI dataset. Note the enrichment of Al and Ti at the metal/oxide interface above the migrated region and the very shallow intergranular oxidation (≈50 nm) along the newly migrated GB.

A similar GB oxidation behaviour was observed for the Alloy 690 TT sample (Fig. 4), in fact no preferential intergranular oxidation was detected on the HAGB, as shown in the BF TEM image in Fig. 4b. The [ $\overline{1}12$ ] SADP (Fig. 4a) contains reflections from both the matrix M<sub>23</sub>C<sub>6</sub> intergranular carbide, as shown in the Centred Dark-Field (CDF) TEM image of Fig. 4e formed using the reflections circled in the SADP in Fig. 4a. Although the coarse intergranular carbide shown in Fig. 4 would have been expected to pin the original GB, the electron diffraction data obtained from the "adjacent grains" on either side of the carbide indicated that DIGM had occurred [7,10,15]. CBED coupled with SAD confirmed that the orientation of the matrix on either side of the coarse M<sub>23</sub>C<sub>6</sub> was the same ([ $\overline{1}12$ ]), as shown in Fig. 4c and d. This result appeared to be in contrast to the behaviour observed in reducing H<sub>2</sub>--steam environments for Alloy 600 TT [8,26]; in those studies, the coarse intergranular M<sub>7</sub>C<sub>3</sub> carbides in Alloy 600 TT acted inhibited DIGM, but rather resulted in an apparent carbide "decomposition" [8]. The STEM-HAADF image and the corresponding elemental maps of Fig. 4 showed that the migrated area was highly enriched in Ni (~74.9 wt%) and significantly depleted in Cr (~14.8 wt%). Enrichments in Al and Ti were also detected on the surface (elemental maps in Fig. 4).



Fig. 4: (b) BF-TEM and (c) complementary CDF TEM images of an oxidised and migrated GB containing  $M_{23}C_6$  carbides for the Alloy 690 TT. The image in (a) shows the  $[\overline{1}12]$  SADP of the grain and the semicoherent  $M_{23}C_6$  intergranular carbide. (c) and (d)  $[\overline{1}12]$  CBED patterns obtained from the 2 regions identified as the red dots in the BF TEM image in (b) confirming that the regions have the same orientation. (f) HAADF STEM image and elemental maps for Ni, Cr, Fe, O, Al and Ti extracted from the STEM-EDX SI dataset. Note the enrichment of Al and Ti at the metal/oxide interface above the migrated region. For both samples, a hole was found to occur in the proximity of the newly migrated GB (ATEM images in Fig. 3 and Fig. 4). The presence of this hole is not completely understood and it may be associated with a locally thermal etching due to the exposure to the H<sub>2</sub>-steam.

Despite the fundamental microstructural differences between the Alloy 690 SA and TT microstructures (Fig. 1), the oxidation behaviour of the samples in the H<sub>2</sub>-steam environment was similar for both material conditions in contrast to the behaviour of Alloy 600 SA and TT specimens, where this latter exhibited "decomposition" of the coarse intergranular carbide at the sample surface [8,26,27]. The results of this study showed that PIO was not promoted in Alloy 690 (Fig. 2 to Fig. 4), independently from the alloy heat treatment/microstructure.

The intergranular  $M_{23}C_6$  carbides did not appear to act as a Cr "reservoir" to assist in formation of the  $Cr_2O_3$  surface oxide; in fact, they were not consumed if not directly exposed to the surface, differently as reported for the  $M_7C_3$  of Alloy 600TT tested in similar environmental conditions [8,26,27]. It is possible that the increased Cr content in the Alloy 690 ( $\approx$ 30 wt%) compared to Alloy 600 ( $\approx$ 15 wt%), combined with the different nature of the carbides, promoted the formation of external Cr-rich oxide layer as shown in Fig. 3 and Fig. 4 [18,28] that protected the alloy, including the intergranular carbides, from further oxidation.

It is proposed that the formation of this external oxide layer induced the DIGM. In fact, grain boundary migration occurs when the less-noble alloying elements in the alloy diffuse to form an external oxide layer [16,17]. Specifically, the local compositional asymmetry of Cr in the near GB region was responsible for the occurrence of DIGM as shown in Fig. 3 and Fig. 4. Surprisingly, the DIGM occurred despite the presence of a rather large intergranular  $M_{23}C_6$  carbide. This is different to what was observed for Alloy 600 TT, in which the extensive network of intergranular carbides pinned the GBs and drastically reduced their migration [8,26]. However, for Alloy 690, it is plausible that the driving force responsible for DIGM (Cr diffusivity) is stronger because the alloy formed an external oxide layer as shown in Fig. 3b and e.

DIGM has already been observed in both Alloy 600 and Alloy 690 [7,29], and can be an accelerating factor for O and Cr diffusion. It has been reported that the diffusivity along mobile grain boundaries was at least 4 times higher than stationary GBs [30–33]. This accelerating factor could be further enhanced by Al and Ti that are "swept up" by the migrating GB [34]. These Al and Ti enrichments will enhance new incoherent oxide formation and short circuit diffusion paths, thus accelerating the oxygen diffusion [35]. However, this accelerating effect can only be "active" only if the environmental conditions can promote the inward diffusion of O

[10,25], as observed on Alloy 600 SA exposed to more oxidising conditions with respect the Ni/NiO transition [10]. Conversely, Alloy 690 TT and SA were exposed to an environment where PIO should be promoted [7,8,10,11,15,24,26,34,36–38]; however, this higher Cr alloy formed an external Cr-rich oxide layer that promoted DIGM and inhibited PIO, thereby creating a migrated GB similar to those observed for "oxidised" Alloy 600 [10,38]. Thus, DIGM alone is a not sufficient condition for the occurrence of PIO also for the Alloy 690.

From this study, the following conclusions are drawn:

- Alloy 690 exhibited similar oxidation behaviour, irrespective of the thermal treatment, in correspondence of the GB and within the grain, where a high interconnected Cr<sub>2</sub>O<sub>3</sub> internal oxide was identified.
- Alloy 690 showed a high resistance to PIO due to the formation of a thin and dense protective Cr<sub>2</sub>O<sub>3</sub> layer above the migrated GB that inhibited further inward oxygen diffusion and it ceased to PIO.
- DIGM occurred in both TT and SA conditions of Alloy 690. In addition, Al and Ti enrichments were detected at the surface corresponding to the zone created by the migrating GB.
- These results showed that the dense Cr<sub>2</sub>O<sub>3</sub> surface layer promoted by the 30 wt% Cr Alloy 690 induced the GB migration but prevented the PIO, thus demonstrating that DIGM is a not sufficient signature for the development of PIO in Alloy 690.

### 8.2. Acknowledgments

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## 8.3. References

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## 8.4. Supplementary Images



Fig. S1: (a) Bright-Field (BF) and (b) corresponding Centred Dark-Field (CDF) TEM images of a typical grain boundary in thermally-treated Alloy 690 containing numerous M<sub>23</sub>C<sub>6</sub> intergranular carbides identified via selected area electron diffraction, as shown in the [001] SADP inset. (c) HAADF STEM image and corresponding STEM-EDX elemental maps of GB triple point, with intragranular TiN and intergranular M<sub>23</sub>C<sub>6</sub> carbides. (d) BF TEM image and (e) HAADF STEM image showing typical as-solution-annealed microstructure for Alloy 690. The micrographs show GBs with several pile-up dislocations formed during the fast water quenching. The STEM-EDX elemental maps associated with the HAADF STEM image in (e) show that the main elements were homogeneously distributed with discrete TiN precipitates formed during thermomechanical processing of the original alloy.



Fig. S2: (a)  $[\overline{112}]$  SADP containing reflections from both the grain and the internal oxide formed in the Alloy 690 after exposure to H<sub>2</sub>-steam environment at 480 °C for 120 h under reducing conditions. The internal oxide and the corresponding several surface oxides and pure Ni nodules are shown in the Bright Field (BF) TEM image in (b) and in the HAADF STEM images in (e) and (f). The Centre Dark Field (CDF) TEM images of the oxide (formed using the reflections circled in the SADP in (a)) show the high interconnectivity of the oxide. The combined STEM-EDX elemental map in (g) and the O K $\alpha$  elemental map associated with the HAADF STEM image in (f) show that the internal oxide was a Cr<sub>2</sub>O<sub>3</sub> surrounding pure Ni and sporadic Fe-rich oxide zones.

## 9. Final Conclusions and Future Work

#### 9.1. Conclusions

This work focused on the understanding of the early stages of SCC of Ni-base alloys with particular emphasis on the role of the "precursor events" Preferentially Intergranular Oxidation (PIO) and Diffusion Induced Grain Boundary Migration (DIGM), relevant to PWSCC studies for Alloy 600 and Alloy 690.

Prior the oxidation experiments, the low pressure superheated H<sub>2</sub>-steam system was validated and the environmental conditions reproducing the Ni/NiO transition in the H<sub>2</sub>-steam were identified at 372 °C, 400 °C, 430 °C and 480 °C by using an *in-situ* electrochemical analysis performed with an Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> solid-state reference and *ex-situ* XRD characterization of Ni-200 coupons and pure Ni powder at 480 °C. The Gibbs free energy associated with the formation of NiO and decomposition of H<sub>2</sub>O was dependent on the media considered. The experimental data were found to be in good agreement with the literature thus confirming that the thermodynamic approach and the assumption that the partial pressures ratio was equal to the volume ratio at atmospheric pressure of steam and H<sub>2</sub> was correct. Therefore, this study clearly provided experimental evidence that the system can be used as surrogate to perform oxidation experiments relevant to PWSCC.

Once the thermodynamic of the H<sub>2</sub>/steam ratio was established, a systematic characterization of the coupon sample of Alloy 600 SA exposed to the H<sub>2</sub>-steam at 480 °C was performed. The results from the unstrained coupon samples showed that the environmental conditions could strongly influence the PIO evolution, in fact Alloy 600 SA was observed to be susceptible to PIO but only when it was exposed to a more reducing environment than the Ni/NiO transition. The maximum PIO penetration was found to be  $\approx 1 \ \mu m$  in slightly reducing conditions (R = 1.5), whereas a penetration of  $\approx 60 \ nm$  was found in the more oxidising environments (R = 1/24) with a sharp "PIO-threshold" in the proximity of the Ni/NiO transition.

The PIO presented a similar evolution to the time to initiation for SCC in high temperature obtained from previous studies as function of the potential (or H<sub>2</sub> partial pressure) and it confirmed the dominant role of PIO during the early stages of SCC initiation. Moreover, these results consolidated the electrochemical characterization and confirmed the possibility to

use the H<sub>2</sub>-steam environment as surrogate system to perform accelerated oxidation test to study the PWSCC susceptibility of Ni-base alloys.

The strained coupon samples showed that the material was susceptible to SCC independently from the oxidising conditions, however the highest susceptibility to crack was observed to more reducing conditions with respect to the Ni/NiO transition. The intergranular cracks were found to initiate and propagate in the PIO along a newly migrated grain boundary thus suggesting a strong synergic role of the PIO/DIGM associated with a local AI/Ti enrichment during the early stages of SCC.

DIGM was shown to be a required condition, although not sufficient, for the development of PIO and it is believed to play an accelerating role for Cr and O diffusivity, due to the migrating GBs as well as the generation of incoherent phase such as Al and Ti oxides, that provide as short-circuit paths for oxygen diffusion. The Al and Ti oxides can be also responsible of an enhanced O and Cr diffusivity and could also act as a preferential site for the crack initiation. However, it is also necessary that the environmental conditions must promote the inward diffusion. In fact, DIGM and Al/Ti enrichments were observed to occur also in the samples exposed to the most oxidising conditions, however the oxide layer inhibited the penetration and cease the formation of PIO, thus explaining also the less susceptibility to crack for the samples exposed to the more oxidising conditions.

It was also noticed that PIO can affect the morphology of the DIGM migrated area, in fact oxidized GBs that exhibited the deepest PIO also presented the narrow and deep migrated areas and therefore it was proposed that the oxide can act as chemical pinning and forced the grain to migrate in depth rather than in width.

Oxidation experiments of Alloy 690 TT and SA after exposure to H<sub>2</sub>-steam at 480 °C showed that the alloys exhibited high resistance to PIO, irrespective of the thermal conditions. Moreover, the GB morphology after oxidation showed a further confirmation of the secondary role of the DIGM and the Al/Ti minor segregation during the early stages associated with the PWSCC for Ni-base Alloys. In fact, the material exhibited the morphology of DIGM despite the PIO was almost totally absent. In this case, the limiting oxygen diffusion factor might be associated with the dense and protective oxide Cr-rich layer, formed in the correspondence of the newly migrated area thanks the higher Cr content of the Alloy 690 than the Alloy 600. Therefore, these results show that also for the Alloy 690 the DIGM is a not sufficient condition for the PIO occurrence, thus corroborating that PIO can occur only if the environmental condition or the chemical composition of the alloy can promote its formation.

As overall conclusion, an improved mechanism describing in detail the early stages of SCC for Alloy 600 SA is proposed. It is believed that during the very early stages of exposure to H<sub>2</sub>-steam environment, the formation of an external Cr-rich layer is observed, where the diffusion of Cr induced the GB to laterally migrate and minor element such as Al and Ti are swept and enrich along the newly migrated GB. Oxygen can preferentially diffuse along the newly migrated GB and it can oxides the Al and Ti enrichment and the Cr in forming the PIO. The PIO can undergo to an "acceleration" by the synergic effect of the movable GB and of the formation of an incoherent oxide enriched in Al and Ti. Under the applied tensile stress, the oxide can brittle fracture and expose the metal to further oxidations and cracking. However, it is worth reminding that the environmental conditions (*e.g.* exposure under oxidising conditions) or the chemical composition (*e.g.* higher Cr content in Alloy 690) can lead to the by formation a dense and protective oxide barrier layer which suppress the oxygen diffusion along GBs.

#### 9.2. Future Work

Despite the experimental work performed that showed a better understanding of the role of DIGM/PIO and the identification of the occurrence site of the early cracks, there are still several research aspects/open questions that require more studies. Therefore, the possible future experimental challenges are briefly discussed in the current chapter.

# Quantification of the DIGM effect on the PIO evolution rate and development of an *advanced predictive model*

The quantification of the accelerated oxygen and chromium diffusion associated with the DIGM and the local segregation of Al and Ti is one of the principal open challenge to be addressed. These data and in general the development of a better mechanistic understanding of the PWSCC early stages of Ni-base alloys can be can be used for ensuring safe operation of existing reactors and to inform the design of new generation reactors with the formulation of new and more advanced predictive models.

Specifically, Alloy 600 SA with an OPS surface can be exposed to H<sub>2</sub>-steam under oxidising conditions in order to form DIGM associated with an external oxide layer. A further surface OPS polishing can remove the oxide layer and expose both original and newly migrated

grain boundary that can be used to quantify the preferential oxygen and chromium diffusion by exposing the sample under reducing conditions (that can promote the occurrence of PIO).

#### Understanding the role of an external oxide layer to the SCC susceptibility of Alloy 600

The sample exposed under the most oxidising condition presented an external and protective double oxide layer ( $Cr_2O_3$  and NiO rich). New experiments can be performed to understand the role of the pre-oxide film and of the DIGM on the oxygen diffusion, thus contributing on the development of new and more precise *advanced predictive models*. Specifically, Alloy 600 SA can be tested under oxidising and then reducing conditions under an active loading in order to identify and quantify the development of the cracks.

#### Understanding of the effect of the surface finishing on the oxidation behaviour

New oxidation and accelerated SCC studies can be performed on machined Alloy 600 and Alloy 690 in order to develop better advanced predictive models that can take in account machined materials that are used in nuclear power plants. These experiments can help the understanding of the early oxidation stages occurring in real NPPs and informing the design of new generation reactors.

#### Understanding of oxidation evolution during the early stages of the Alloy 690

One challenge that has been raised from this work was associated with the formation of the external oxide on Alloy 690. Further analyses can be performed to understand the oxide growth evolution (*e.g.* linear, parabolic) and the corresponding highly interconnected internal oxide. These data can be used for the Specifically, Alloy 690 SA and TT can be exposed to the superheated low pressure H<sub>2</sub>-steam environment under reducing condition at different time exposures.

## Appendices

Due to the alternative format of this thesis, some useful information was not included in the papers due to the criteria and limits set by the journals. Therefore, the full calculations regarding the (A.I) thermodynamic and the (A.II) electrochemistry of the superheated H<sub>2</sub>-steam environment used during this study are reported in this section.

### A.I. H<sub>2</sub>-Steam Environment Calculation

The low pressure superheated H<sub>2</sub>-steam environment can be set by knowing the oxygen partial pressure  $(p_{O_2})$  and the dissociation pressure at the Ni/NiO transition  $(p_{O_2Ni/NiO})$  for a given temperature.

The dissociation pressure at the Ni/NiO transition can be calculated from the Gibbs free energy of formation (A.2) for the reaction (A.1).

$$Ni_{(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NiO_{(s)} \tag{A.1}$$

$$\Delta G_{f,NiO} = \Delta G_{f,NiO}^{\Phi} + RT \ln \left[ \frac{a_{NiO}}{a_{Ni} a_{O_2}^{\frac{1}{2}}} \right]$$
(A.2)

where  $\Delta G_{f,NiO}$  represents the Gibbs free energy of formation for NiO,  $\Delta G_{f,NiO}^{\phi}$  the standard Gibbs free energy of formation, R the universal gas constant, T the absolute temperature and  $a_i$  is the activity of the species involved in the reaction. At the Ni/NiO transition phase,  $\Delta G_{f,NiO}$  is zero, because the phases are at the thermodynamic equilibrium. Assuming that the activity of a solid can be considered equal to 1 ( $a_{Ni} = a_{NiO} = 1$ ) and for a gas, the activity is equivalent to its partial pressure ( $p_i$ ) over the standard partial pressure ( $p^{e}$ ), the equation (A.2) can be written as (A.3):

$$0 = \Delta G_{f,NiO}^{\Theta} + RT \ln \left[ \frac{1}{\left( \frac{p_{O_2 Ni/NiO}}{p^{\Theta}} \right)^{\frac{1}{2}}} \right]$$
(A.3)

The equation (A.3) can be rearranged to give to oxygen partial pressure at the Ni/NiO transition:

$$p_{O_{2Ni/NiO}} = exp\left[-\frac{2\Delta G_{f, NiO}^{*}}{RT}\right]$$
(A.4)

The  $p_{O_2}$  in steam can be extrapolated from the Gibbs free energy (A.6) of the equation (A.5) likewise the calculation of the  $p_{O_2 Ni/NiO}$ 

$$H_2 O_{(g)} \rightleftharpoons H_{2(g)} + \frac{1}{2} O_{2(g)}$$
 (A.5)

$$\Delta G_{d,H_2O} = \Delta G_{d,H_2O}^{\Theta} + RT \log \left[ \frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right] = \Delta G_{d,H_2O}^{\Theta} + RT \ln \left[ \frac{p_{H_2}}{p_{H_2O}} \cdot \left( \frac{p_{O_2}}{p^{\Theta}} \right)^{\frac{1}{2}} \right]$$
(A.6)

where  $\Delta G_{d, H_2O}$  represents the Gibbs free energy of the decomposition for the reaction,  $\Delta G_{d, H_2O}^{\Phi}$ the standard Gibbs free energy of decomposition, R the universal gas constant, T the absolute temperature and p the partial pressure. The equation can be rearranged to give the oxygen partial pressure  $(p_{O_2})$ , as follow, by considering that the system is at equilibrium (*i.e.*  $\Delta G_{d, H_2O} = 0$ ):

$$p_{O_2} = p^{\bullet} \cdot \left(\frac{p_{H_2O}}{p_{H_2}}\right)^2 exp\left[-\frac{2\Delta G_{d,H_2O}^{\bullet}}{RT}\right] = \left(\frac{1}{PPR}\right)^2 exp\left[-\frac{2\Delta G_{d,H_2O}^{\bullet}}{RT}\right]$$
(A.7)

Where *PPR* (Partial Pressure Ratio) represents the ratio of hydrogen over steam.

The values of  $\Delta G_{f,i}^{\phi}$  of formation for NiO and H<sub>2</sub>O, associated with the equations (A.1) and (A.5) can be calculated with the equation (A.8).

$$\Delta G_{f,d}^{\Theta} = A + BT \log T + CT \tag{A.8}$$

where the values A, B and C are reported in

Table A.6.

Table A.6: Values for the standard Gibbs free energy of formation for NiO and H<sub>2</sub>O [101], expressed as the *energetic values A*, *B* and *C*. Specifically, the value B for the standard Gibbs free energy of NiO and H<sub>2</sub>O is equal to 0 cal·mol<sup>-1</sup>·K<sup>-1</sup>.

A, cal·mol<sup>-1</sup> B, cal·mol<sup>-1</sup>
$$K^{-1}$$
 C. cal·mol<sup>-1</sup> $K^{-1}$ 

NiO	56010	0	-20.37
H₂O	-58900	0	-13.10

#### PPRs and Flow Rates

Assuming that the ratio of flow rates is equivalent to the ratio of the pressures, the flow rates at the operating temperature can be calculated from the equations (A.9) and (A.10).

$$F_{steam} = \frac{F_{H_2O} \cdot \rho_{H_2O}}{\rho_{steam}} \tag{A.9}$$

$$F_{H_{2,HT}} = \frac{F_{H_{2,RT}} \cdot T_{HT}}{T_{RT}}$$
(A.10)

where  $F_{steam}$  represents the flow rate of steam,  $F_{H_2O}$  the input flow rate of water,  $\rho_{steam}$  the density of the steam and  $\rho_{H_2O}$  the density of water at the input temperature.  $F_{H_2,HT}$  is the hydrogen flow rate at high temperature,  $F_{H_2,RT}$  is the hydrogen input flow rate,  $T_{HT}$  is the operating temperature and  $T_{RT}$  is the input temperature, hence 1/PPR is equal to:

$$\frac{1}{PPR} = \frac{F_{steam}}{F_{H_{2,HT}}} = \frac{F_{H_{2}O} \cdot \rho_{H_{2}O} \cdot T_{RT}}{F_{H_{2,RT}} \cdot T_{HT} \cdot \rho_{steam}}$$
(A.11)

#### Equivalency between Different Environmental Systems

Several oxidation and SCC experiments have been performed at different temperature, however, conducting tests at constant dissolved hydrogen but at different temperatures implies different oxidising conditions. For examples, 20 cc/kg of dissolved hydrogen at 280 °C represents a reducing environment with respect to the Ni/NiO transition, but it is an oxidizing environment for tests conducted at 360 °C. Therefore, in order to compare different experiments, it is important to maintain the same oxidizing conditions, irrespective of the temperature. This is particularly important for Ni base Alloys, which are very susceptible to SCC close to the Ni/NiO transition. Furthermore, different environments are employed to simulate the PWR primary water environments, namely i) autoclave experiments in high pressure high temperature hydrogenated water, ii) low pressure superheated H<sub>2</sub>-steam environment, and iii) high pressure hydrogenated steam. It is therefore important to obtain an equivalence in terms of oxidizing conditions in order to be able to compare the results obtained from different systems and temperatures.

The approach used to identify an equivalence for experiments at different conditions is to assume that the ratio of  $p_{O_2}$  over the  $p_{O_2 Ni/NiO}$  is the same, as shown in eq. (A.12).

$$\frac{p_{O_2}}{p_{O_2 Ni/NiO}} = const_1 \tag{A.12}$$

Moreover, a similar equivalence can be obtained considering the ratio between the fugacity of  $H_2$  in the environments and the one corresponding to the Ni/NiO transition  $([H_{2 Ni/NiO}])$  (eq. (A.16)). The value of the  $[H_2]_{Ni/NiO}$  for high temperature water conditions is calculated by using eq. (A.14) reported in the EPRI 1015288 document [7]. It is worth noting that with this assumption, the environmental conditions at different temperatures are equivalent.

$$\frac{[H_2]_{Ni/Ni0}}{[H_2]} = const_2 \tag{A.13}$$

$$cc/kg H_2 at Ni/NiO boundary = 10^{(0.0111 \cdot T(^{\circ}C) - 2.59)}$$
 (A.14)

A similar consideration can be made in order to compare autoclave test conditions with low pressure superheated H<sub>2</sub>-steam. However, the ratio of the [H<sub>2</sub>] for the autoclave is replaced with the H<sub>2</sub> partial pressure ratio (ratio of fugacities) for the case of low-pressure H<sub>2</sub>-steam system (eq. (A.15)).

$$\frac{[H_2]_{Ni/Ni0}}{[H_2]} = \frac{p_{H_2Ni/Ni0}}{p_{H_2}}$$
(A.15)

By substituting the values of the  $p_{H_{2Ni/NiO}}$  and  $p_{H_2}$ , it is possible to obtain the eq. (A.16).

$$\frac{[H_2]_{Ni/NiO}}{[H_2]} = \frac{p_{H_2Ni/NiO}}{p_{H_2}} = \sqrt{\frac{p_{O_2}}{p_{O_2Ni/NiO}}} = \frac{1}{PPR} \cdot \sqrt{\frac{exp\left(-\frac{2\Delta G_{d, H_2O}^{\Phi}}{RT}\right)}{exp\left(-\frac{2\Delta G_{f, NiO}^{\Phi}}{RT}\right)}}$$
(A.16)

By substituting the equations (A.7) and (A.11) in the equation (A.16), the relationship between the ratio of the hydrogen concentrations in autoclave and *PPR* in the  $H_2$ /steam system can be calculated.

By rearranging the eq. (A.16), the  $H_2$  flow rate at room temperature can be calculated as follow (eq. (A.17)):

$$F_{H_2 RT} = \frac{[H_2] \cdot F_{H_2 O} \cdot \rho_{H_2 O} \cdot T_{RT}}{[H_2]_{Ni/NiO} \cdot {}^{\circ}\!\!{}^{$$

The parameters used in equation (A.17) have been already listed in the equations (A.4), (A.6), (A.11) and (A.14).

### A.II. Calculating the Ni/NiO Transition

The oxidation of pure nickel in gas phase can be written according the equation (A.18), that can be split in the two semi-reactions (A.19) and (A20):

$$Ni_{(s)} + H_2 O_{(g)} \rightleftharpoons Ni O_{(s)} + H_{2(g)}$$
 (A.18)

$$Ni_{(aq)}^{2+} + \frac{1}{2}O_{2(g)} + 2e^{-} \rightleftharpoons NiO_{(s)}$$
 (A.19)

$$H_2 O_{(g)} \rightleftharpoons \frac{1}{2} O_{2(g)} + 2H_{(g)}^+ + 2e^-$$
 (A.20)

the EcP of  $NiO_{(s)}$  can be calculated from the equation (A.18), using the Nernst equation and it can be expressed, as follow:

$$E_{eq} = E_{NiO}^{\Phi} + \frac{RT}{2F} \ln \left[ \frac{a_{NiO} a_{H^+}^2}{a_{Ni} a_{H_2O}} \right]$$
(A.21)

where  $E_{eq}$  represents the equilibrium potential of the half-cell and  $E_{NiO}^{\Phi}$  is the standard equilibrium potential of NiO. As already mention above, the activity of a solid can be considered equal to 1, so the equation (A.21) can be written as follow:

$$E_{eq} = E_{NiO}^{\bullet} - \frac{RT}{2F} \ln a_{H_2O} + \frac{RT}{2F} \ln H^+ = E_{NiO}^{\bullet} - \frac{RT}{2F} \ln a_{H_2O} - \frac{RT}{F} pH \qquad (A.22)$$

For the dissolution of  $H_2O_{(I)}$  in  $O_{2(g)}$  and  $H_{2(g)}$ , the Nernst equation associated with the second semi-reaction cell (A.19) is shown in the equation (A.23).

$$E_{eq} = E_{H_2O}^{\bullet} + \frac{RT}{2F} \ln \left[ \frac{a_{H^+}^2 a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right]$$
(A.23)

where  $E_{eq}$  represents the equilibrium potential of the half-cell and  $E_{H_2O}^{\phi}$  is the standard equilibrium potential of H<sub>2</sub>O. Rearranging the terms, the EcP can be written as:

$$E_{eq} = E_{H_2O}^{\Theta} - \frac{RT}{2F} \ln a_{H_2O} - \frac{RT}{F} pH + \frac{RT}{4F} \ln \frac{p_{O_2}}{p^{\Theta}}$$
(A.24)

At Ni/NiO transition, the  $p_{O_2}$  is equal to the oxygen partial pressure at the Ni/NiO transition, hence the  $p_{O_2}$  can be substituted with the  $p_{O_2 Ni/NiO}$ :

$$E_{eq} - E_{Ni0}^{\theta} = E_{H_20}^{\theta} - \frac{RT}{2F} \ln a_{H_20} - \frac{RT}{F} pH + \frac{RT}{4F} \ln \left[ \frac{p_{O_2}}{p^{\theta}} \right] - E_{H_20}^{\theta} + \frac{RT}{2F} \ln a_{H_20} + \frac{RT}{F} pH - \frac{RT}{4F} \ln \left[ \frac{p_{O_2 Ni/NiO}}{p^{\theta}} \right]$$
(A.25)

Rearranging:

$$E_{eq vs. Ni/NiO} = E_{eq} - E_{NiO}^{\bullet} = \frac{RT}{4F} \ln p_{O_2} - \frac{RT}{4F} \ln p_{O_2,Ni/NiO} = \frac{RT}{4F} \ln \left[ \frac{p_{O_2}}{p_{O_2 Ni/NiO}} \right] \quad (A.26)$$

Because the maximum PWSCC susceptibility is located in the proximity of the Ni/NiO transition, it is convenient to refer the electrochemical potential with respect to the Ni/NiO  $(E_{eq vs. Ni/NiO})$ .

$$E_{eq vs. Ni/NiO} = \frac{RT}{4F} \ln \left[ \frac{p_{O_2}}{p_{O_2 Ni/NiO}} \right]$$
(A.27)

By substituting the  $p_{O_2}$  and  $p_{O_2Ni/NiO}$  into the equation (A.26), the  $E_{eq vs. Ni/NiO}$  can be expressed as the ratio of the *PPRs* (A.28 and A.29):

$$E_{eq vs. Ni/NiO} = \frac{RT}{4F} \ln\left[p^{\varphi} \left(\frac{1}{PPR}\right)^2 exp\left[-\frac{2\Delta G_{d, H_2O}^{\varphi}}{RT}\right]\right] - \frac{RT}{4F} \ln\left[p^{\varphi} \left(\frac{1}{PPR}\right)^2_{Ni/NiO} exp\left[-\frac{2\Delta G_{d, H_2O}^{\varphi}}{RT}\right]\right] (A. 28)$$

Rearranging:

$$E_{eq vs. Ni/NiO} = \frac{RT}{4F} \ln \left[ \frac{\left(\frac{p_{H_2O}}{p_{H_2}}\right)^2}{\left(\frac{p_{H_2O}}{p_{H_2}}\right)^2_{Ni/NiO}} \right]$$
(A. 29)

Combining the two  $E_{eq vs. Ni/NiO}$  in the equations (A.27) and (A.29), a direct relationship between the ratio of the oxygen partial pressures and the *PPRs* was obtained.

$$\frac{p_{O_2}}{p_{O_2 Ni/Ni0}} = \frac{\left(\frac{p_{H_2 O}}{p_{H_2}}\right)^2}{\left(\frac{p_{H_2 O}}{p_{H_2}}\right)^2_{Ni/Ni0}}$$
(A.30)

By substituting the equations (A.4) and (A.7) into the eq. (A.26) and (A.27), the dependence of the  $E_{eq vs. Ni/Ni0}$  from the standard Gibbs free energy of formation was obtained (A.31).

$$E_{eq vs. Ni/Ni0} = \frac{1}{2F} \cdot \left[ \left( \Delta G_{f, Ni0}^{\Theta} - \Delta G_{d, H_20}^{\Theta} \right) + \text{RT} \cdot \ln \left( \frac{p_{H_20}}{p_{H_2}} \right) \right]$$
(A.31)

Rearranging:

$$\frac{1}{PPR} = \left(\frac{p_{H_2O}}{p_{H_2}}\right) = exp\left[\frac{2F \cdot E_{eq\,vs.\,Ni/NiO} - \left(\Delta G_{f,\ NiO}^{\Phi} - \Delta G_{d,\ H_2O}^{\Phi}\right)}{RT}\right]$$
(A. 32)

In the particular case that the system is at Ni/NiO transition, the eq. (A.32) can be written as:

$$\frac{1}{PPR} = \left(\frac{p_{H_2O}}{p_{H_2}}\right) = exp\left[\frac{\Delta G^{\Theta}_{f,H_2O} - \Delta G^{\Theta}_{d,NiO}}{RT}\right]$$
(A.33)

By substituting the standard enthalpy and entropy of formation [98], the eq. (A.33), can also be expressed as function of two parameters *A* and *B* (A.34). In an Arrhenius plot, the slope of the best fit will be equal to  $\Delta A_i/R$ , that corresponds to the difference of standard enthalpy between H<sub>2</sub>O and NiO ( $\Delta H_i^{\Theta} = \Delta H_{d, H_2O}^{\Theta} - \Delta H_{f, NiO}^{\Theta}$ ) and the intercept is equal to  $\Delta B_i/R$  that correspond to the difference of standard entropy between H<sub>2</sub>O and NiO ( $\Delta S_i^{\Theta} = \Delta S_{d, H_2O}^{\Theta} - \Delta S_{f, NiO}^{\Theta}$ ).

$$\ln\left(\frac{1}{PPR}\right)_{Ni/Ni0} = \frac{A_{\Delta G^{\Theta}_{d, H_2O}} - A_{\Delta G^{\Theta}_{f,NiO}}}{R} \cdot \frac{1}{T} + \frac{B_{\Delta G^{\Theta}_{d, H_2O}} - B_{\Delta G^{\Theta}_{f,NiO}}}{R}$$
(A.34)
## A.III. Fabrication of the Ni/NiO Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> SSRE

The components and the fabrication of the Ni/NiO  $Y_2O_3$ -ZrO<sub>2</sub> solid state reference electrode used to monitor the corrosion potential of the low pressure superheated H<sub>2</sub>-steam environment are reported in this section.

## Materials and Suppliers

- Ceramic tube in Yttria Stabilized Zirconia 8 mm OD x 5 mm ID x 250 mm long, one end closed (Alfa Aesar, Part Number (PN): 99517-PC).
- 2. Conax fittings (Conax Buffalo Corporation, PN: EG-125-A-SS-T).
- 3. Sensor body and nut (High Pressure Equipment Co., PNs: 210591 and 210590).
- 4. Ni wire (99.98%), diameter of 0.75 mm.
- 5. Au wire (99.95%), diameter of 0.75 mm.
- 6. Fiberglass wool
- 7. Ni powder (99.999%)
- 8. NiO powder (99.96%)
- 9. Teflon tube, ID (0.9 1.0 mm)
- 10. Belleville spring washers (www.mcmaster.com, PN: 91235A108).
- 11. Teflon rod diameter 12.7 mm.
- 12. Rulon LR rod diameter 12.7 mm.
- 13. Stainless Steel (SS) A316 rod, diameter 12.7 mm

## **Machined Components**

- Machine a SS washer with 1.9 mm thick x 11.0±0.1 mm OD x 8.1 mm ID (this should fit within the Conax fitting and around the ceramic tube).
- 2. Machine a SS follower with 15.9 mm long x 12.6 (+0.0 and -0.1) mm OD x 3.2 mm ID (drill a hole in centre).
- 3. Machine a SS follower with the top part equal to 12.7 OD x 6.4 mm long and the low part equal to 11.2 mm OD x 6.4 mm long with 3.2 mm drilled hole in centre.
- 4. Machine a Rulon LR disc\_1 of 11.23mm DIA x hole 1 mm x 3.2 mm thickness.
- 5. Machine a Rulon LR disc\_2 of 11.23mm DIA x hole 1 mm x 1.3 mm thickness.

- 6. Machine a Rulon LR collar of 11.25mm DIA x ID 8.10 mm x 10mm long (this should fit within the Conax fitting and around the ceramic tube).
- 7. Machine a Vespel disc of 11.23mm x hole 1 mm x 3.2 mm thickness.

## Fabrication of the SSRE

- 1. Insert the ceramic tube through the Conax fitting.
- 2. Slide the stainless steel washer on the ceramic tube.
- 3. Cut a piece of gold wire that fits around the ceramic tube.
- 4. Slide the gold wire and the Rulon LR collar on the ceramic tube, and then push into the Conax fitting.
- 5. Weight the metal and oxide powder and mix them with the weight ratio of 1:1.
- 6. Purge out the ceramic tube with argon gas for few minutes to remove the air inside the ceramic tube.
- 7. Cut a 500 mm long piece of Ni wire. Stretch the wire to make it straight. Clean off a 75 mm long section of the end that will go into the ceramic tube with steel wool. Then use acetone to remove any residue. Put a small hook shape on the clean end to help prevent it from pulling out of the ceramic tube.
- 8. Put a small amount of Ni/NiO powder in the tube to prevent the Ni wire from touching the ceramic tube.
- 9. Place the Ni wire into the ceramic tube and purge again with argon.
- 10. Place a small amount of Ni/NiO powder into the ceramic tube and then tap the tube to make sure the powder settled to the bottom. Pack the powder with a 1/16" diameter rod. Purge again with argon for a few minutes and repeat the procedure until there are 25 mm of the mixed powder in the ceramic tube.
- Purge the tube again and then put in the fiberglass wool and push to the powder with the 1/16" diameter rod. The fiberglass wool should be about 12.7 mm long.
- 12. Cut a piece of Teflon tube that will cover the copper wire from the fiberglass wool to the top of the ceramic tube. Purge with argon again.
- Slide on the Rulon LR disk\_2, the Vespel disk, the Rulon LR disk\_1 and a second Vespel disc and push into the Conax fitting.
- 14. Torque the assembly to 100 in-lbs (11.3 Nm) using a stainless-steel follower and a nut to push the stainless steel follower. Let it sit for 2 minutes and re-torque to 100 in-lbs. Repeat

this operation 4 times. Then, let it sit for about 30 minutes and re-torque to 100 in-lbs. Let it sit for another 30 minutes and unload the torque from the assembly. Check to see if the ceramic tube is tight in the fitting by trying to rotate the ceramic tube. If it is not tight, re-torque to 150in-lbs (16.95 Nm) as described above. In between each step, place the Conax fitting at the temperature in between 70 and 90 °C to facilitate the relaxation of the Rulon disks.

- 15. After the tube is tight in the assembly, put the sensor body on the Conax fitting.
- 16. Insert the Belleville spring washers, no. 88 placed 2 in series and 2 in parallel.
- 17. Insert the top stainless-steel follower in the body.
- Put on the nut and finger-tight until it makes contact with the top stainless-steel follower.
  Then tighten 4.5 turns to set the load on the Belleville washers.
- Cover the Ni wire with Teflon tube into the body out to 25 mm from the end of Ni wire to keep the wire from making contact with the body and other items.