SELF-HEALING BEHAVIOUR OF MAX PHASE CERAMICS STUDIED BY COMPUTED X-RAY TOMOGRAPHY

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SCHOOL OF MATERIALS
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Abstract

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Self-healing behaviour of MAX phase ceramics studied by computed X-ray tomography

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MAX phase ceramics are promising candidates as high temperature materials. The self-healing capabilities of these materials may further improve their reliability and reduce maintenance costs during service. However, previous two dimensional research on their healing behaviour is either inadequate or sometimes even biased, because crack healing is essentially a three dimensional process. In this study, the self-healing behaviour of two MAX phase ceramics: Ti$_2$AlC and Cr$_2$AlC were investigated in three dimensions using high resolution synchrotron and laboratory X-ray tomography.

The Ti$_2$AlC showed remarkable healing ability of repeatedly repairing cracks at 1150 °C for three healing cycles with each healing cycle lasting less than 66 minutes. The healing kinetics of Ti$_2$AlC was revealed to have a strong dependence on crack location, which deviates from a previously proposed uniform healing model. The Ti$_2$AlC maintains its healing kinetics when the post-healing crack propagation follows a different growth path to the original crack. While a decreased healing kinetics was observed if the crack grows through a previous healed zone. The strength recovery is closely related to the healing percentage, where a full strength recovery was achieved with a healing percentage of over 90 %.

In comparison, the Cr$_2$AlC showed a much slower healing kinetics, with a parabolic constant of 4.3×10$^{-3}$ μm$^2$·s$^{-1}$. The healing process of Cr$_2$AlC was revealed to be more or less independent of crack location, where crack tip is always healed first. The crack gap is filled by purely Al$_2$O$_3$ after healing without the formation of Cr$_2$O$_3$. The composition of the healed area varies along the crack. A Cr$_7$C$_3$ sublayer beneath the Al$_2$O$_3$ layer was found at the healed zone of crack root, while missing in the healed zone at crack tip. The influence of impurity Cr particles on healing kinetics was investigated through a correlative microscopy study, combining X-ray tomographic slices with SEM images. The existence of Cr particles was found to accelerate the healing rate. However, this was always accompanied by the formation of large pores, which may be detrimental to the strength recovery after healing.
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Dedication

To my mother and my father,

To my wife Yuanyuan Liu,

To my son Dongda Pei
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Chapter 1 Introduction

1.1 MAX phase: A metal-like ceramic

For a long time, ceramics and metals have occupied more or less two parallel disciplines in materials science. They are intrinsically often very different from each other. Ceramics are usually hard, elastically stiff and lightweight. They exhibit excellent oxidation resistance, corrosion resistance and maintain their mechanical strength even at high temperatures. However, their applications are largely restricted due to their low toughness and difficulty of machining them to high precision. Metals, on the other hand, are known for their damage tolerance and easy machinability. However, they are susceptible to severe oxidation and corrosion in harsh environments at elevated temperatures. Therefore, it would be ideal if a material could possess the advantages of both ceramics and metals.

In the past two decades, a relatively new discovered ceramic family (MAX phase ceramics) are arousing more and more attention due to their unusual combination of properties from both ceramics and metals [1-3], shown in Figure 1.1. MAX phase ceramics constitute a family of ternary layered compounds with the general formula: \( M_{n+1}AX_n \), where \( n \) is 1, 2 or 3, \( M \) is an early transition metal, \( A \) is an A-group (mostly IIIA and IVA) element and \( X \) is either C or N [4-5]. They exhibit typical ceramic properties of high stiffness, high strength at elevated temperature, as well as excellent resistance to oxidation and corrosion [6-8]. Yet, they are very different from traditional ceramics. MAX phase ceramics are good conductors of electricity and heat, are damage tolerant and can be readily machined using conventional cutting tools [9]. This unique combination of properties creates new possibilities for technology improvements and makes them suitable to be used under high temperature circumstances.
Figure 1.1 MAX phase ceramics combining properties from both ceramics and metals.

1.2 Self-healing: From damage prevention to damage management

MAX phase ceramics can exhibit damage tolerance to some extent. However, as a ceramic, their structural integrity will be significantly compromised by the existence of cracks or surface flaws [10]. In fact, low toughness is the major drawback of any ceramic. Therefore, endless efforts have been made to prevent damage from happening in the past few decades. Although the mechanical properties of ceramics have been greatly improved in this way, there may be a more advanced methodology in terms of material design.

Over millions of years’ evolution, nature seems to have developed its own strategies in material design. Instead of adopting the damage prevention paradigm, it prefers to keep the damage at a certain level followed by an autonomous repairing process [11]. This can be best seen in the healing process of a bone or skin [11-12], where the formation of damage (scratch on a skin or crack in a bone) automatically triggers the healing process. Inspired by this “self-healing” concept, a lot of healing materials or healing systems have been developed in the past ten years, including self-healing polymers, metals and ceramics [13-14]. The development of these self-healing materials marks a transformation of material design concept from damage prevention
to damage management, which may greatly increase materials’ reliability and reduce maintenance costs [15], shown in Figure 1.2.

![Figure 1.2 Schematic diagram of damage development in self-healing materials and conventional materials. In conventional materials, damage level is either constant or increasing. In self-healing materials damage level could be reduced through various self-healing mechanisms. Adapted from Sybrand [15].](image)

### 1.3 Self-healing in MAX phase ceramics

Given their potential application as high temperature components, it would be desirable if MAX phase ceramics could autonomously repair themselves during service. In 2008, Song reported that a crack with average width of 5 µm in Ti₃AlC₂ was healed by heat treatment in air at 1100 °C for 2 hours [16]. The crack healing of Ti₃AlC₂ is by an oxidation process, where crack gaps are filled by oxides (mainly Al₂O₃ and rutile TiO₂) at high temperature. Considering that MAX phase ceramics perform a more or less similar oxidation process, this self-healing ability could be universal for any MAX phase ceramics.
CHAPTER 1

INTRODUCTION

Until now the studies on self-healing behaviour of MAX phase ceramics are mainly focused on Al-containing phases, such as Ti$_3$AlC$_2$, Ti$_2$AlC and Cr$_2$AlC [16-21]. This is due to the fact that the oxidation products of Al-containing MAX phase ceramics are usually composed of primarily α-Al$_2$O$_3$, which is not only beneficial for their oxidation resistance, but also provides good strength recovery after healing. Previous research shows that the strength recovery is closely related to the healing percentage (damage repair level) [19]. Therefore, it would be very important to understand the healing kinetics. Current studies on healing kinetics are based on either indirect or two dimensional (2D) measurements, such as thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) on plane surface oxidation [19, 22-23]. However, defects especially cracks are actually three dimensional in nature. As a result, the information from indirect or 2D measurements is limited and biased to extreme conditions. The recent development of computed X-ray tomography (CT) provides new possibilities to directly observe this 3D dynamic healing process with a resolution high enough to obtain quantitative information.

1.4 Goals and outline

The major goal of this thesis is to understand the healing kinetics of MAX phase ceramics (Ti$_2$AlC and Cr$_2$AlC are chosen) by three dimensional (3D) measurements using high resolution synchrotron and laboratory X-ray tomography.

This thesis has been prepared in alternative format. Two chapters are manuscripts and will be submitted as Journal Publications to relevant scientific journals in the ceramic area. The structure of the thesis and content of each chapter are listed below.

Chapter 2 introduces basic understandings of MAX phase ceramics, including their brief history, crystal structure and mechanical properties. Their oxidation behaviours are also summarized, which provide clues to their healing capability. The current studies concerning self-healing behaviour of both Ti$_2$AlC and Cr$_2$AlC are reviewed with their limitations discussed.

Chapter 3 investigates the cyclic healing behaviour of Ti$_2$AlC through high resolution synchrotron X-ray tomography. Ti$_2$AlC exhibited cyclic healing capabilities for at least three healing cycles at 1150 °C in air. The healing kinetics in
both 2D and 3D are quantified. The healing kinetics of Ti$_2$AlC seemed to have a strong dependence on oxygen partial pressure and could be greatly retarded due to previously formed oxides.

Chapter 4 studies the self-healing behaviour of Cr$_2$AlC through high resolution laboratory X-ray tomography. The healing kinetics of Cr$_2$AlC is much slower than that of Ti$_2$AlC and proved to follow a parabolic law with rate constant of $4.3 \times 10^{-3} \mu m^2 s^{-1}$. The influence of impurity Cr particles on healing behaviour was revealed by combining results from tomographic slices with SEM images.

Chapter 5 summarizes the major findings of this thesis, together with a prospective view of future work concerning the crack healing behaviour of MAX phase ceramics.
1.5 Reference


Chapter 2 Literature review

MAX phase ceramics constitute a family of ternary layered compounds with the general formula: $M_{n+1}AX_n$, where $n$ is 1, 2 or 3, $M$ is an early transition metal, $A$ is an A-group (mostly IIIA and IVA) element and $X$ is either C or N [1]. It combines some typical properties of both ceramics and metals [2]. Like ceramics, they exhibit high strength and stiffness both at room and high temperatures [3]. They have superior oxidation resistance at high temperature than their counterpart intermetallics, carbides or nitrides [4-5]. Like metals, they are electrical and thermal conductive, thermal shock resistant and plastically deformable at high temperatures [6]. Due to this unusual combination of properties, MAX phase ceramics have great potential to be used as a high temperature structural material. Recent discoveries of self-healing capability of this material add new credits to its high temperature applications [7-9].

The following section 2.1 gives a brief review of the history of MAX phase ceramics. The crystal structures, bonding (as well as vacancies) are also included to provide a clue to their unusual properties. Section 2.2 deals with their mechanical properties which are of vital importance for a potential candidate for high temperature components. Section 2.3 and 2.4 review their thermal stability and oxidation behaviour under high temperature, which are not only critical for any high temperature application but also closely related to their self-healing capability. Section 2.5 summarizes current studies and some challenges for understanding self-healing behaviour of both Ti$_2$AlC and Cr$_2$AlC. Section 2.6 provides a basic overview of Computed X-ray tomography, a technique that formed the basis of the experimental work of the thesis as it can shed new light and improve our knowledge on the self-healing behaviour of these materials.

2.1 Introduction to MAX phase ceramics

2.1.1 History of MAX phase ceramics

The research of MAX phase dates back to the 1960s, when Nowotny and his group discovered more than 100 new carbides and nitrides [10-11]. The term “$T_xM_yX_z$”
was firstly used by Nowotny to describe the complex carbides and nitrides, where T is a transitional metal, M is a group of 12-16 elements or another transitional metal, and X is either C or N [12]. Among them are the so called “H-phases”, which have a chemical formula of $M_2AX$ (X is either C or N). These H-phases consist of octahedral $M_2X$ interleaved by purely A atoms [13].

In 1967, the same group discovered $Ti_3SiC_2$ and $Ti_3GeC_2$, both having a similar structure to the H-phases, in which $M_3C_2$ are separated by A layers [14-15]. The $Ti_3SiC_2$ synthesized by Nowotny were through chemical reaction by sintering $TiH_2$, Si, and graphite at 2000 °C. However, impurity phases such as TiC and SiC were usually found in the $Ti_3SiC_2$ matrix. In 1972, pure $Ti_3SiC_2$ was made by Nickl and his group by chemical vapour deposition [8]. They described the $Ti_3SiC_2$ to be “anomalously soft” for a transitional carbide [16].

The real breakthrough came in 1996, when Barsoum and El-Raghy successfully synthesized high purity bulk $Ti_3SiC_2$ by hot pressing Ti, SiC and graphite at 1600 °C for 4 hours [17]. The properties of $Ti_3SiC_2$ were revealed to be relatively soft (Vickers hardness of 4 GPa), reasonably stiff (Young’s modulus of 326 GPa), stable thermally, good conductivity ($4.5 \times 10^6 \ \Omega^{-1} \cdot m^{-1}$), and readily machinable. These unusual combinations of metallic and ceramic properties were later shown to be typical for MAX phase ceramics.

In 1999, Barsoum identified the structure to be $Ti_4AlN_3$ through high resolution TEM, whereas it was previously proposed to be $Ti_3Al_2N_2$ [18-19]. The structure of $Ti_4AlN_3$ is similar to the “H-phase”, with four layers of Ti atoms separated by a layer of Al atoms, as shown in Figure 2.1.
With the confirmation of the 413 phases and its structure, it became clear that a family of ternary layered compounds was discovered. In a review paper in 2000, Barsoum introduced the name “$M_{n+1}AX_n$” phase ($n = 1, 2, \text{ or } 3$) to describe these layered ternary compounds, where “$M$” is an early transitional metal, “$A$” is an A group element (mostly in group 13 and 14) and “$X$” is either C or N [1].

The members of the MAX phase family have been fast growing in the last two decades. At present, 59 MAX phase ceramics have been discovered, including 48 $M_2AX$ phases, 6 $M_3AX_2$ phases and 5 $M_4AX_3$ phases. Table 2.1 lists the MAX phases currently known.

**Figure 2.1** HRTEM image along the [1120] zone. Adapted from Barsoum et al. [18].
Table 2.1 MAX phases known to exist. The 312 and 413 phases are highlighted in green and yellow, respectively. Adapted from Barsoum and Radovic [20].

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2.1.2 Crystal structure and bonding

The $\text{M}_{n+1}\text{AX}_n$ phase ceramic belongs to the space group of $\text{P6}_3/\text{mmc}$ and shares a similar crystal structure, with two formula units per unit cell, as shown in Figure 2.2.

![Figure 2.2 Crystal structure of 211, 312 and 413 MAX phase ceramics. Adapted from Barsoum and Radovic [20].](image)

Near close packed $\text{M}_{n+1}\text{X}_n$ layers are interleaved with layers of pure A-group element, while X atoms fills the octahedral sites. The differences between these three $\text{M}_{n+1}\text{AX}_n$ phase crystal structures are the number of M layers separating the A layers. In 211 phases, there are two; in 312 phases, there are three and in 413 phases, there are four [16].

In 211 phases, there are three inequivalent atoms. In 312 phases, there are four inequivalent atoms, with two kinds of M sites: Those adjacent to A layers and those further away from A layers. In 413 phases, there are five inequivalent atoms. In addition to the two kinds of M sites, there are two kinds of X sites in the crystal structure [16].
The first theoretical calculation of the structure was conducted by Medvedeva in 1998 through an \textit{ab initio} calculation on Ti$_3$SiC$_2$ \cite{21}. Since then, a number of such theoretical studies had been carried out by other researchers and a review paper published in 2000 made a summarization of these studies \cite{1}.

According to density of state calculations, the bonding of MAX phase ceramics is a combination of covalent, metallic and ionic bonds \cite{2}. The M-X bonds in MAX phase ceramic are similar to its binary counterparts, where the p-d orbital interactions between the M and X atoms are quite strong, leading to strong covalent bonds, with calculated energy state located around -2 to -5 eV below the Fermi energy, $E_f$ \cite{23}. The M-A bonds in MAX phase ceramic are weaker than those of M-X bonds, with interactions between the d electrons of M atoms and p electrons of A atoms located around -1 eV below $E_f$. The charge transfer in MAX usually has a tendency from the Al toward the C while the M elements remain more or less neutral \cite{24}.

\subsection*{2.1.3 Vacancy}

Although the crystal structure determines the basic physical properties of MAX phase ceramics, point defects, especially vacancies, not only play an important role in the mechanical, oxidation and corrosion response of MAX phase ceramic, but also have an influence on its structural stability \cite{25}. There are three kinds of vacancies in MAX phase ceramics. For example, vacancies in Ti$_2$AlC include $V_{Ti}$, $V_{Al}$ and $V_{C}$. Although the direct observation for vacancies in MAX phase is scarce, Liao performed \textit{ab initio} calculations for the formation and migration of monovacancy in Ti$_2$AlC \cite{26}.

The formation energies for $V_{Al}$, $V_{Ti}$ and $V_{C}$ are 6.336, 11.180 and 10.714 eV, respectively \cite{27}. However the energy barriers for the vacancy migrations in Ti$_2$AlC were calculated to be 0.83, 2.38 and 3.00 eV, respectively, for $V_{Al}$, $V_{Ti}$, and $V_{C}$ \cite{28}. The relatively lower formation and migration energy of $V_{Al}$ implies that A-group elements have the propensity to selectively react with their surroundings. This has been confirmed by many subsequent studies and is especially true for the oxidation process of MAX phase ceramics \cite{29-30}. The preferential oxidation of MAX phases occurring at high temperature will be discussed later in detail.
The influence of Al vacancies on the phase stability of Ti$_2$AlC was studied by Wang in 2008 [25]. An electronic structure analysis was performed on defective Ti$_2$AlxC ($x<1$) under Al sub-stoichiometry. The diffusion barrier for Al atoms along the (0001) plane was further confirmed to be relatively small (0.83 eV), which implies that Al has rapid diffusive mobility. The formation of Al vacancies result in an elimination of Ti-Al bonds, which leads to the redistribution of unbonded Ti d-electrons in space. The unbonded Ti d-electrons will firstly fill the Ti-Ti d-d metallic bonding stages. Therefore, the phase stability was calculated to be retained down to an Al sub-stoichiometry of Ti$_2$Al$_{0.5}$C. Further depletion of Al (Ti$_2$AlxC ($x<0.5$)) results in a saturation of unbonded Ti d-electrons in the Ti-Ti d-d metallic bonding state. Thus, an occupation of Ti-Al antibonding state occurs, rendering the crystal structure to be unstable and decomposition to twinned TiC$_{0.5}$ and Al.

2.2 Mechanical properties of MAX phase ceramics

2.2.1 Elastic properties

Theoretical and experimental bulk and Young’s moduli have been reviewed and compared by Barsoum and Radovic and the comparison shown in Figure 2.3 [20].

![Figure 2.3](image.png)

**Figure 2.3** Comparison of theoretical and experimental bulk and Young’s moduli. Adapted from Barsoum and Radovic [20].
As noted from the Figure 2.3, the MAX phases containing heavy elements such as Sn, Pb and In, have lower stiffness than those containing lighter elements like Al and S. For example, Ti$_2$SnC has a Young’s modulus about 138 GPa, while that of Ti$_2$AlC is around 277 GPa [31].

Another factor that plays a role in the MAX phase’s bulk moduli is the concentration of vacancies. This phenomenon is best seen in Ti$_2$AlN, where the addition of N increases the bulk moduli values, because more vacancies on the Al and N sites were formed [32].

Compared to other materials with a layered structure, whose elastic properties are highly anisotropic, MAX phase ceramics are more elastically isotropic. For example, the values of $c_{11}$ and $c_{33}$ of Ti$_3$SiC$_2$ are almost equal. As for Ti$_2$AlC, it is a little more anisotropic with 308 GPa for $c_{11}$ and 270 GPa for $c_{33}$ [20].

2.2.2 Response to compressive and tensile stresses

The compression strength of MAX phase ceramic is usually a function of both grain size and strain rates [33]. In all cases, coarse-grained specimens tend to fail at a lower load than their fine-grained counterparts. When loaded at high strain rates, MAX phase ceramics undergo a sudden catastrophic failure in a brittle mode. However, if the strain rate is low, the stress-strain curve exhibits a V-shape rather than a sharp drop at ultimate compressive stress [34], as shown in Figure 2.4.

Shear fracture always occurs when the strain rate is low in compression [35], as shown in Figure 2.5. Features characteristic of various energy absorbing mechanisms such as delamination, grain bending and pull-out, and crack deflection, were found on the fractured surface. These mechanisms prevented the material from failing in a catastrophic manner.

In contrast to large numbers of papers published on compressive behaviour of MAX phase ceramics, the references on tensile behaviour of these materials are scarce. Perhaps the main reason is that performances of these materials under tensile loads are poor, like many ceramics, meaning that the tests are difficult to perform. The failure is always brittle with almost no ductility.
Figure 2.4 Stress-displacement curves obtained when Ti$_2$AlX samples are loaded in compression. Note that various curves are shifted for clarity’s sake. Adapted from Barsoum et al. [34].

Figure 2.5 SEM images of the microstructure of Ti$_3$AlC$_2$ deformed up to failure at room temperature: (a) fatal crack after compression; (b) deformed microstructures near crack. Adapted from Bei et al. [35].
2.2.3 Fracture toughness and damage tolerance

Fracture toughness describes the materials’ resistance to propagate a pre-existing flaw. It is a very important property for material design and this is especially true for ceramic materials, as fracture toughness in a ceramic is usually low.

The fracture toughness of MAX phase ceramics falls into the range from 5 to 9 MPa·m$^{1/2}$, which is considerably higher than its MX counterpart. For instance, the fracture toughness of Ti$_2$AlC and Ti$_3$SiC$_2$ are 6.5 and 6.2 MPa·m$^{1/2}$, while those of TiC and SiC are 3.8 and 3.3 MPa·m$^{1/2}$, respectively [20]. This result is not surprising, considering the various energy absorbing mechanisms observed in Figure 2.5.

Another direct consequence of these various energy absorbing mechanisms is the high damage tolerance of MAX phase ceramics. This property is best shown in the Vickers and nano-indentation test as shown in Figure 2.6, where damage was confined to a small local area around the indentations by plastic deformation [36-37].

![Image of Ti$_3$SiC$_2$ after (a) vickers indentation test, adapted from El-Raghy et al. [36]; (b) nano-indentation test, adapted from Kooi et al. [37].]
2.2.4 High temperature mechanical behaviour

All MAX phase ceramics undergo a brittle-to-plastic-transition at a characteristic high temperature. For example, for many Al-containing phases, the temperature is between 1000 °C and 1100 °C [38-39].

Zhou studied the mechanical behaviour of polycrystalline Ti$_2$AlC both at room temperature and at high temperature up to 1200 °C [39], as shown in Figure 2.7.

![Figure 2.7 Compression test of polycrystalline Ti$_2$AlC at room temperature and high temperatures up to 1200 °C. Adapted from Zhou and Wang [39].](image)

The stress-strain curve at room temperature deviated from linearity and there were a number of loading-relaxation-reloading processes before failure, which indicates that Ti$_2$AlC is not completely brittle. By comparison, the material deformed more or less plastically at temperatures above 1050 °C. Similar results were found on the deformation process of Ti$_3$SiC$_2$, where a strain of over 15 % was achieved when Ti$_3$SiC$_2$ samples were compressed at 1300 °C.

As outlined before, the dominant fracture mechanism of MAX phase ceramics was by shear at room temperature, when the strain rate was small. The damage was usually confined to a small area near the critical crack through the formation of voids, cavities and delamination. However, at high temperatures above the brittle to plastic
transformation temperature, the damage was more widely distributed due to a better mobility of dislocations. The pile-up of dislocations against grain boundaries produced many microcracks as shown in Figure 2.8 [40].

![Figure 2.8 Deformed surface of Cr<sub>2</sub>AlC at 800 °C. Adapted from Tian et al. [40].](image)

### 2.3 Thermal stability

Given their potential application at high temperatures as well as their nano-laminated structure, the thermal stability of MAX phase ceramic is of vital importance. It is generally accepted that the MAX phase ceramics do not melt but decompose at high temperature [41]. For instance, Ti<sub>2</sub>AlC becomes unstable at temperatures above 1400 °C in vacuum and begins to decompose via sublimation of Al [42]. The decomposition of Cr<sub>2</sub>AlC under Ar atmosphere happens at temperature above 1500 °C [43]. Due to the weak bond between A and MX blocks, the decomposition process follows the general equation:

\[
M_{n+1}AX_n \rightarrow M_{n+1}X_n + A
\]  

(2-1)

Therefore, the decomposition process is normally accelerated if the M<sub>n+1</sub>X<sub>n</sub> or A is consumed. Given the high mobility of A atoms, the reaction between A atoms and the atmosphere usually results into a decreased decomposition temperature [41].
The actual decomposition process, however, is more complex. Take Ti$_2$AlC as an example. Zhou observed an intermediate decomposition route, where Ti$_2$AlC was first transformed to Ti$_3$AlC$_2$ by losing half of its Al layers in accordance with the equation below [44]:

$$2Ti_2AlC = Ti_3AlC_2 + TiAl_x + (1 - x)Al \text{ with } x < 1 \quad (2-2)$$

Further depletion of Al resulted in the formation of TiC and pure Al:

$$Ti_3AlC_2 = TiC + Al + Ti \quad (2-3)$$

Similar intermediate products are also found in the decomposition process of Ta$_2$AlC, Nb$_2$AlC and Ti$_2$AlN, where Ta$_4$AlC$_3$, Nb$_4$AlC$_3$ and Ti$_4$AlN$_3$ phases are firstly formed before the final decomposition product of MX and A [45-47]. Therefore, it could be concluded that the decomposition of a MAX phase with a lower n, typically 1, usually follows a two-step reaction, where it is firstly transformed to its relative MAX phase with a higher n and then continued to decompose to MX and pure A. For 211 MAX phases that do not have a higher n counterpart, for instance, Cr$_2$AlC, a direct formation of MX and pure A is thus expected.

2.4 Oxidation behaviour of MAX phase ceramics

MAX phase ceramics are potential materials for high temperature applications. Therefore, oxidation resistance is considered to be one of the most important factors in evaluating their performance at high temperatures. Due to the ease of fabrication of pure bulk materials, the oxidation behaviour of Ti$_3$SiC$_2$ was the first to be extensively studied [48-49].

In 1994, Racault synthesized high purity Ti$_3$SiC$_2$ through a solid-state method and by TGA measurements determined that the oxidation of Ti$_3$SiC$_2$ starts at around 400 °C [49]. The oxidation process has a rapid rate in the initial 20 mins, followed by a much slower rate afterwards, as shown in Figure 2.9a.
Ti$_3$SiC$_2$ exhibits a much better oxidation resistance than its MX counterpart TiC, as shown in Figure 2.9b. Considering the same TiO$_2$ is formed after the oxidation of both Ti$_3$SiC$_2$ and TiC, the production of SiO$_2$ should be the main reason for a better oxidation resistance.

**Figure 2.9** (a) Oxidation percentage of Ti$_3$SiC$_2$ as a function of time in temperature range of 450 °C to 1250 °C. (b) Oxidation percentage of Ti$_3$SiC$_2$ and TiC as a function of time at 750 °C. Adapted from Racault et al. [49].

A typical SEM image after oxidation of Ti$_3$SiC$_2$ is shown in Figure 2.10. The oxidation of Ti$_2$SiC$_2$ resulted in the formation of an outer coarse-grained TiO$_2$ scale and an inner fine-grained scale comprised of SiO$_2$ and TiO$_2$ [50].
Figure 2.10 Back scattered SEM image of cross-section of Ti$_3$SiC$_2$ after oxidation at 1200 °C for 20 h. Adapted from Sun et al. [50].

A Pt marker experiment conducted by Sun implied that the outer layer of TiO$_2$ is formed by the outward diffusion of Ti, while the inner layer of TiO$_2$ and SiO$_2$ grows by the inward diffusion of oxygen [51]. The improved oxidation resistance of Ti$_3$SiC$_2$ (compared to TiC) is due to the formation of SiO$_2$, which hinders the inward diffusion of oxygen.

Figure 2.11 Back scattered SEM image of cross-section of Ti$_3$SiC$_2$ after oxidation at 1200 °C for 100 hours with a Pt marker. Adapted from Sun et al. [51].

The oxidation kinetics of Ti$_3$SiC$_2$ were first determined by Barsoum to be parabolic with parabolic constant of $2\times10^{-8}$ and $2\times10^{-5}$ kg$^2$·m$^4$·s$^{-1}$ at temperatures of 1000 °C.
and 1400 °C, respectively [48]. The weight gain per unit area could be described by the equation below:

\[
\left( \frac{\Delta w}{A} \right)^2 = k_p \cdot t
\]  

(2-4)

Where \(\Delta w\) is the weight gain during the oxidation process; \(A\) is surface area; \(k_p\) is the parabolic constant; \(t\) is oxidation time.

Similar experiments on the oxidation kinetics of Ti\(_3\)SiC\(_2\) were undertaken by other researchers to consider the effect of longer oxidation times. Radhakrishnan found a parabolic-linear law for the oxidation of Ti\(_3\)SiC\(_2\) at 1000 °C for 50 hours [52]. While Sun observed a parabolic kinetics for the oxidation of Ti\(_3\)SiC\(_2\) in temperature range of 900 °C to 1100 °C for 22 hours [50]. However, the oxidation kinetics exhibited a linear law at 1200 °C for 22 h. Therefore, it can be concluded that the short time oxidation of Ti\(_3\)SiC\(_2\) followed a parabolic relationship. At higher oxidation temperatures and for longer oxidation times, the oxidation kinetics of Ti\(_3\)SiC\(_2\) transformed to a linear one. This suggests that the long-time oxidation resistance of Ti\(_3\)SiC\(_2\) is questionable.

Until now, the reason for this parabolic-to-linear transformation is unclear. However, one of the possible explanations could be the formation of large voids (as shown in Figure 2.12) or cracks during long term oxidation, due to the gradual build-up of internal stress [48]. Such voids and cracks could provide a channel for the inward diffusion of oxygen, thereby adversely affecting the oxidation resistance of Ti\(_3\)SiC\(_2\).

Ideally, a dense void- and crack-free oxide layer is required for better oxidation resistance. So far Al containing MAX phases, for instance, Ti-Al-C and Cr-Al-C system, are the most promising candidates in the MAX phase family due to the formation of a dense continuous Al\(_2\)O\(_3\) layer [5, 29, 53-54].
2.4.1 Oxidation of Ti$_2$AlC

The oxidation behaviour of Ti$_2$AlC was first reported by Barsoum in 2001 [4]. The isothermal oxidation behaviour of Ti$_2$AlC was studied in the temperature range of 1000-1100 °C for 20 hours. Ti$_2$AlC showed a better oxidation resistance than its intermetallic counterparts such as Ti$_3$Al. Subsequently, a lot of research has been focused on this material due to its excellent oxidation resistance at high temperatures [29, 53, 55].

2.4.1.1 Oxidation kinetics of Ti$_2$AlC

In the original paper of Barsoum, Ti$_2$AlC was found to obey a parabolic law at temperatures above 900 °C in air through oxide scale thickness measurements [4]. The corresponding activation energy was calculated to be 458.7 kJ/mol. Sundberg reported a similar parabolic law, when bulk Ti$_2$AlC was exposed at 1100-1300 °C in air for 8 hours by continuous thermogravimetric analysis (TGA) [56]. However, using the same testing method, Wang in 2003 reported a cubic law for the isothermal oxidation behaviour of Ti$_2$AlC in temperature range of 1000-1300 °C for 20 hours in air [53], shown in Figure 2.13.
Basu conducted a long-time isothermal oxidation experiment on Ti$_2$AlC [29]. Weight gain during oxidation of Ti$_2$AlC for 120 hours in temperature range of 1000-1300 °C was measured and the results confirmed a cubic law for long-time oxidation of Ti$_2$AlC.

Perhaps it is now reasonable to say that Ti$_2$AlC obeys a parabolic kinetic for short time oxidation and transfers to a cubic kinetic for long-time oxidation at high temperatures. One possible explanation is that the oxidation process for relatively short times is mainly controlled by lattice diffusion. While that for long time diffusion is dominated by grain boundary diffusion, due to an increased thickness of oxides.
2.4.1.2 Oxidation microstructure of Ti$_2$AlC

The microstructure of Ti$_2$AlC is less controversial. The oxide scale is usually composed of a continuous inner layer of $\alpha$-Al$_2$O$_3$ and a discontinuous outer layer of rutile TiO$_2$ [57]. Note that the inner Al$_2$O$_3$ is dense without any large pores or voids. The excellent oxidation resistance of Ti$_2$AlC at high temperatures in air could be attributed to this protective oxide layer.

![Cross section back scattered SEM image of Ti$_2$AlC after oxidation at 1200 °C for 12 hours.](image)

**Figure 2.14** (a) Cross section back scattered SEM image of Ti$_2$AlC after oxidation at 1200 °C for 12 hours. (b) Top view of oxide scale. Adapted from Byeon et al. [57].

2.4.1.3 Oxidation mechanism of Ti$_2$AlC

The oxidation mechanism of Ti$_2$AlC could be generally described as a process of inward diffusion of oxygen and outward diffusion of both Al and Ti [53].

The oxidation process of Ti$_2$AlC could be divided into two stages:

I. **Initial stage**

In this stage, oxygen partial pressure on surface of Ti$_2$AlC is high enough for simultaneous oxidation of both Al and Ti. Rao conducted an oxidation
experiment on Ti$_2$AlC at 1200 °C and confirmed the existence of both Al$_2$O$_3$ and TiO$_2$ after 3 minutes heat treatment [58], as shown in Figure 2.15.

Figure 2.15 Bright field TEM image of Ti$_2$AlC after oxidation at 1200 °C in air for 3 minutes. Adapted from Rao et al. [58].

II. Second stage

With increasing time, more and more oxides are formed. The oxygen partial pressure at the Ti$_2$AlC-oxide scale interface decreases. Eventually, the oxygen partial pressure will be smaller than that required to form TiO$_2$. However, due to a much lower oxygen partial pressure for the formation of Al$_2$O$_3$, Al$_2$O$_3$ layer will continue to grow. Ti atom will need to diffuse through the formed Al$_2$O$_3$ layer to react with oxygen. As a result, Al$_2$O$_3$ is present in the inner part and TiO$_2$ in the outer part of the oxide scale [55].

2.4.2 Oxidation of Cr$_2$AlC

Cr$_2$AlC was discovered together with other “H-phases” in the 1960s by Nowtony [10]. However, after that, it was largely neglected due to the big challenge of fabricating a single phase bulk Cr$_2$AlC.

2.4.2.1 Oxidation kinetics

In 2005, Lin synthesized bulk Cr$_2$AlC with high purity through an in situ hot pressing solid-liquid reaction [59]. The oxidation start temperature was measured to be around 800 °C by TG-DSC experiment, as shown in Figure 2.16. This
temperature is around 400 °C higher than other ternary metal aluminium carbides such as Ti₃AlC₂ [60], implying a better oxidation resistance of Cr₂AlC. The same author further determined that the oxidation behaviour of Cr₂AlC followed a parabolic law, with a parabolic constant of 6.8×10⁻¹⁰ kg²·m⁻⁴·s⁻¹, which was 3-4 orders magnitude lower than Ti₃SiC₂ (6.58×10⁻⁷ kg²·m⁻⁴·s⁻¹) [48], as shown in Figure 2.17.

**Figure 2.16** Simultaneous TG-DSC measurements for oxidation of Cr₂AlC powders at a heating rate of 10 °C/min in air. Adapted from Lin et al. [54].
Due to its excellent oxidation resistance at high temperatures, Cr$_2$AlC is attracting more and more attention. In addition to Lin’s initial work, various synthesis methods have been developed and the oxidation behaviour of Cr$_2$AlC investigated [61-66]. A summary of these studies is given in Table 2.2. Although the methodology they used was identical (weight gains of polished Cr$_2$AlC bars were measured by TGA experiments), there are still some uncertainties concerning the oxidation kinetics of Cr$_2$AlC. It can be seen that most authors argue that the oxidation kinetics of Cr$_2$AlC obeys a parabolic law, similar to that of Ti$_3$SiC$_2$ [48]. However, instead of the continuous weight gain caused by take-up of oxygen during oxidation, Lee observed a weight loss for Cr$_2$AlC after 10 hours heat treatment at 1200 °C [66]. In addition, Li investigated the oxidation of both fine and coarse grained Cr$_2$AlC at 1100 and 1200 °C for 100 hours [67]. He pointed out that Cr$_2$AlC obeyed a cubic oxidation law rather than a parabolic one at 1200 °C for both fine and coarse grained Cr$_2$AlC. At 1100 °C, the fine grained Cr$_2$AlC deviated from both parabolic and cubic laws, while the coarse grained Cr$_2$AlC sample followed a cubic law [8].

Despite of these inconsistencies in the oxidation kinetics, it is generally accepted that the formation of a dense $\alpha$-Al$_2$O$_3$ is critical for its excellent oxidation resistance.
Table 2.2 A summary of oxidation kinetics of Cr$_2$AlC at various temperatures reported in journal publications.

<table>
<thead>
<tr>
<th>temperature/ °C</th>
<th>oxidation time/h</th>
<th>kinetic</th>
<th>kinetic constant/kg$^2$m$^{-3}$s$^{-1}$</th>
<th>grain size/ μm</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>100</td>
<td>neither parabolic or cubic</td>
<td>-</td>
<td>2</td>
<td>S. B. Li, X. D. Chen, et al (2013)</td>
</tr>
<tr>
<td>1100</td>
<td>100</td>
<td>cubic</td>
<td>-</td>
<td>60</td>
<td>S. B. Li, X. D. Chen, et al (2013)</td>
</tr>
<tr>
<td>1200</td>
<td>50</td>
<td>weight loss after 10 h</td>
<td>-</td>
<td>17</td>
<td>D. B. Lee, S. W. Park (2007)</td>
</tr>
<tr>
<td>1200</td>
<td>100</td>
<td>cubic</td>
<td>-</td>
<td>60</td>
<td>S. B. Li, X. D. Chen, et al (2013)</td>
</tr>
</tbody>
</table>
2.4.2.2 Oxidation microstructure of Cr$_2$AlC

The microstructure of Cr$_2$AlC after oxidation in air is usually composed of an outer layer of Al$_2$O$_3$ and an inner layer of Cr$_7$C$_3$ [54], as shown in Figure 2.18. Unlike other MAX phases (such as Ti$_2$AlC, Ti$_3$AlC, Ti$_3$SiC$_2$, where a large amount of TiO$_2$ or SiO$_2$ are formed after oxidation), Cr$_2$O$_3$ is rarely found in the oxide scale. The reason for this unusual oxidation behaviour is still unclear at the moment and needs to be further addressed.

![Figure 2.18](image)

**Figure 2.18** Cross section SEM image of Cr$_2$AlC after oxidation in air for 20 hours at: (a) 1100 °C; (b) 1200 °C. Adapted from Lin et al. [54].

2.4.2.3 Oxidation mechanism of Cr$_2$AlC

The oxidation mechanism was first revealed by Lee through a Pt marker experiment by depositing a thin Pt film on the surface of Cr$_2$AlC before oxidation [68]. An Auger Electron Spectroscopy (AES) study was conducted after oxidation at 1100 °C.
for 5 mins in air, as shown in Figure 2.19. The fact that the $\text{Al}_2\text{O}_3$ scale and $\text{Cr}_2\text{AlC}$ matrix were on the same side of the Pt film suggested that the formation of $\text{Al}_2\text{O}_3$ is due to inward diffusion of O. In addition, a small amount of Cr was also seen in the oxide scale, indicating $\text{Cr}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ were formed simultaneously during the initial oxidation stage.

![Figure 2.19 AES profile of Cr$_2$AlC after oxidation at 1100 °C for 5 mins in air. The penetration rate is 18 nm/min for reference SiO$_2$. Adapted from Lee et al. [68].](image)

Later, Yang conducted an annealing experiment on a Cr$_2$AlC specimen, which had been oxidized at 1100 °C for 40 hours [69]. A wedge-shaped specimen was prepared by focused ion beam slicing before further heat treatment. The newly formed $\text{Al}_2\text{O}_3$ ridges were found along the grain boundaries of the existing $\text{Al}_2\text{O}_3$. This result implied that the outward grain boundary diffusion of Al became the dominant oxidation mechanism after the formation of an $\text{Al}_2\text{O}_3$ layer. Thus, the oxidation mechanism of Cr$_2$AlC could be described as a combination of inward diffusion of oxygen and outward diffusion of Al.
Based on the previous discussion, the oxidation process of Cr₂AlC can be divided into two stages [54]:

I. An early stage before the dense continuous Al₂O₃ layer is formed

In this stage, the oxygen partial pressure is high enough for the formation of both Al₂O₃ and Cr₂O₃, following the reaction below:

\[ 4\text{Cr}_2\text{AlC} + 13\text{O}_2 = 4\text{Cr}_2\text{O}_3 + 2\text{Al}_2\text{O}_3 + \text{CO}_2 \uparrow \]  \hspace{1cm} (2-5)

II. A second stage after the dense continuous Al₂O₃ layer is formed

In this stage, the oxygen partial pressure is reduced. Due to a relative weak Cr-Al bond and a strong Cr-C bond, selective oxidation of Al will occur. The depletion of Al within the Cr₂AlC results into the formation of Cr₇C₃, following the reaction below:

\[ 28\text{Cr}_2\text{AlC} + 23\text{O}_2 = 8\text{Cr}_7\text{C}_3 + 14\text{Al}_2\text{O}_3 + 4\text{CO}_2 \uparrow \]  \hspace{1cm} (2-6)

As previously discussed, the Al depletion induced sub-stoichiometry of Ti₂Al₃C could be as high as \( x = 0.5 \). Considering a similar crystal structure of Cr₂AlC, the
stability of Cr\textsubscript{2}Al\textsubscript{x}C is expected to be maintained when x is smaller than 0.5. Therefore, a secondary reaction at the beginning of the second stage could follow the equation below:

\[
Cr_2AlC + 0.75(1 - x)O_2 = 0.5(1 - x)Al_2O_3 + Cr_2Al_xC
\] (2-7)

For long term oxidation at high temperature, Cr\textsubscript{7}C\textsubscript{3} has the tendency to react with O and the formed Cr\textsubscript{2}O\textsubscript{3} may further transform to CrO\textsubscript{3} [70], which has a high volatile pressure. The evaporation of CrO\textsubscript{3} results in a weight loss during the oxidation process.

\[
2Cr_7C_3 + 16.5O_2 = 7Cr_2O_3 \uparrow + 6CO_2 \uparrow
\] (2-8)

\[
Cr_2O_3 \rightarrow CrO_3 \uparrow
\] (2-9)

In reality, the two oxidation stages are usually intertwined with each other. The secondary reactions as well as the evaporation of Cr\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{7}C\textsubscript{3} further increase the complexity of this process. Therefore, the indirect measurement of weight gain during oxidation of Cr\textsubscript{2}AlC may not reflect its true kinetics and a direct observation of the oxidation process, in this case, is more beneficial.

### 2.5 Self-healing in materials

"Look deep into nature, and then you will understand everything better" is a quote by Albert Einstein. This is especially true when it comes to the design of modern materials. The properties of materials in nature are optimized for their intended purpose through millions of years’ natural selection. As material scientists, we can learn from these evolutionary refinements and improve the performance of man-made materials [71]. One of their outstanding characteristics is “self-healing” capability, where damage is autonomously repaired or healed to keep functional or structural integrity. The self-healing in nature is a very common mechanism and happens in various scales, from repair of a DNA to healing of broken bones [72]. It
is obviously a more economical way to repair something rather than completely replace it.

Bring this automatic healing concept to material design marked a transfer from traditional “damage prevention paradigm” to advanced “damage management concept” and could be revolutionary [73].

2.5.1 Self-healing in polymers and ceramics

The self-healing concept was first introduced to polymers by White in 2001. Healing agents contained within microcapsules were embedded in a structural composite containing a catalyst capable of polymerizing the healing agent [74], as shown in Figure 2.21. The healing agent is released when a crack passes through the microcapsules. The contact of healing agent and catalyst triggers a polymerization process, bonding the crack surfaces together. Therefore, a key factor that determines self-healing process is the continuous transportation of a healing agent and this is also true for self-healing mechanisms in other materials.

![Figure 2.21](image)

**Figure 2.21** Self-healing in polymer a composite: (a) cracks form in matrix; (b) crack propagates through microcapsules, releasing healing agent into the crack plane; (c) the healing agent contacts the catalyst, triggering polymerization that bonds crack surfaces together. Adapted from White et al. [74].
By far, polymer composites are the most studied self-healing materials because they are easy to modify [75]. However, the adoption of self-healing concept is more demanding in other materials such as ceramics. Ceramic materials usually have a higher strength than metals, however, their application is largely narrowed due to their sensitivity to defects and cracks. Once such flaws are initiated, the structure of a ceramic is significantly compromised [76]. Therefore, such automatic healing ability has the potential to greatly increase their reliability while reducing maintaining costs.

There are three self-healing mechanisms for ceramics, including re-sintering, stress relaxation, and oxidation mechanisms [77-79]. Among these three self-healing mechanisms, the oxidation mechanism is the most promising because the crack surface is usually bonded by the formed oxide and filled through volume expansion. The re-sintering mechanism, however, is often accompanied by void formation in the matrix, thereby reducing the strength, while the relaxation mechanism increases the strength of material but does not actually repair the crack.

Oxidation induced self-healing in ceramics occurs when the material are exposed to high temperature in an oxidizing environment. SiC ceramic or ceramic composite embedded with SiC particles or whiskers exhibit self-healing capabilities at temperature above 1000 °C through the oxidation of SiC [80].

\[
SiC + 2O_2 \rightarrow SiO_2 + CO_2 \uparrow \quad (2-10)
\]

Given the potential application as high temperature structural materials, the oxidation process of MAX phase ceramics could also be used as a crack healing mechanism.
Figure 2.22 Crack healing of SiC embedded ceramic: (a) before crack healing; (b) crack gap is filled by SiO$_2$ after healing. Adapted from Madhan and Probhakaran [75].

2.5.2 Self-healing in MAX phase ceramics

Song reported that a crack with average width of 5 µm in Ti$_3$AlC$_2$ was healed by oxidizing the cracked sample at 1100 °C in air for 2 hours [9]. The crack healing of Ti$_3$AlC$_2$ is an oxidation process where crack gap was filled by oxidation products composed of α-Al$_2$O$_3$ and rutile TiO$_2$, as shown in Figure 2.23. The healed area had a sandwich structure; two Al$_2$O$_3$ layers were found adjacent to the crack surface with a TiO$_2$ layer in between.

Another thing worth noting is that the composition varies according to the crack width. The healed area tends to have a higher TiO$_2$ content with increasing crack width. A crack opening less than 1 µm is found to be filled by mainly Al$_2$O$_3$. This result is not surprising since previous oxidation experiments on Ti$_3$AlC$_2$ showed that Al is always preferentially oxidized due to a weaker Ti-Al bond [81].

The overall oxidation reaction of Ti$_3$AlC$_2$ could be written as:

$$4Ti_3AlC_2 + 23O_2 = 12TiO_2 + 2Al_2O_3 + 8CO_2 \uparrow$$  \hspace{1cm} (2-11)

Considering that the mass densities of Ti$_3$AlC$_2$, TiO$_2$ and Al$_2$O$_3$ are 4.25, 4.27 and 3.99 g/cm$^3$ [9], respectively. Therefore, if fully oxidized, one unit volume Ti$_3$AlC$_2$
will yield 1.22 unit volume TiO$_2$ and 0.28 unit volume Al$_2$O$_3$. The total volume expansion is around 50%.

The strength recovery after healing is strongly dependent on the microstructure of the healed area. The Al$_2$O$_3$ formed was dense with a smaller grain size, while some pores could be observed in the coarse TiO$_2$ phase. An adhesion test between the Al$_2$O$_3$ scale and Ti$_3$AlC$_2$ substrate demonstrated a strong adhesive strength of over 85 MPa [82]. However, the existence of porous TiO$_2$ phase largely reduces the recovered strength.

One simple way of solving this problem is to increase the amount of Al in the material. Therefore, a better strength recovery is expected in the 211 Al containing MAX phase ceramic such as Ti$_2$AlC and Cr$_2$AlC.

**Figure 2.23** Cross section of the microstructure of Ti$_3$AlC$_2$: (a) secondary SEM image; (b) Ti map; (c) Al map and (d) O map. Adapted from Song et al. [82].
2.5.2.1 Self-healing in Ti$_2$AlC

I. Healing of surface cavities

The healing of surface cavities in Ti$_2$AlC ceramics was studied by Yang [83]. The healed cavities were composed of a bottom Al$_2$O$_3$ layer and a top rutile TiO$_2$, as shown in Figure 2.24. The thickness of Al$_2$O$_3$ in the cavity is a function of the original cavity width. When the cavity is wider than 6 µm, the thickness of Al$_2$O$_3$ could be 1.5 times larger than that formed on a flat surface.

In addition, the microstructure of the oxide formed in cavity and that on flat surface is different. The Al$_2$O$_3$ formed on the flat surface are composed of an inner columnar layer and an outer equiaxed layer. However, the cavity is filled by equiaxed fine grained Al$_2$O$_3$.

The favourite growth direction of Al$_2$O$_3$ is always perpendicular to the surface, as this has the largest compositional gradient. As a result, the growth direction of the oxide on a flat surface is parallel to each other. In a cavity, the favourite oxide growth direction varies with different positions, as shown by the white arrows in Figure 2.24. Therefore, the growth of Al$_2$O$_3$ grains in a cavity will leave space between themselves, which provides fast channels for the outward diffusion of Al and Ti atoms.

To sum up, the surface curvature has an effect on both the microstructure and growth rate of the oxide. This model may also be applied to the healing of a crack, as crack propagation in MAX phase ceramics follows a zigzag route. The crack surface roughness is expected to be very high.
Figure 2.24 Back scattered SEM image of Ti$_2$AlC after oxidation for 16 hour: (a) surface morphology; (b-c) local cross sections made by FIB sectioning at position b and c. Adapted from Yang et al. [83].

Figure 2.25 Schematic model of the healing process in a cavity. The arrows indicate the fastest growth directions of Al$_2$O$_3$ grains. Adapted from Yang et al. [83].
II. Self-healing of cracks

Due to the nature of the oxidation healing mechanism, healing is assumed to happen wherever there are cracks and available oxygen. Li reported the multiple healing capability of Ti$_2$AlC, when it is exposed in air at 1200 °C [7]. A total healing cycle of seven times was achieved in their experiment, as shown in Figure 2.26.

The first crack was healed completely after 2 hours at 1200 °C in air. The second crack became wider in width, but was again healed completely under the same conditions. As the healing cycle increases, the crack width increased each time. After sixth cycle, crack opening part was no longer fully healed.

Another thing worth noting is that with increasing healing cycles, the oxides formed in the previous healing cycles retard the oxide growth rate. This is similar to the oxidation protection provided by oxides formed in an isothermal oxidation process of this material.

![Figure 2.26](image)

**Figure 2.26** Back scattered SEM image of fracture and healing of Ti$_2$AlC samples at 1200 °C in air. Adapted from Li et al. [7].
2.5.2.2 Self-healing in Cr$_2$AlC

Despite its impressive properties at high temperature, such as high stiffness and high oxidation resistance, the research on the healing behaviour of Cr$_2$AlC is scarce. Part of the reason for this is that the high oxidation resistance acts as a negative factor when it comes to the healing of a crack. The greatly reduced oxide growth rate indicates that a longer healing time will be needed to completely heal a crack.

Li studied the influence of crack length on recovered strength [8], shown in Figure 2.27. It can be seen that the recovered flexural strength decreases with increasing crack length, when same heat treatment condition is applied. For samples with initial crack length less than 0.5 mm, the recovered flexural strength rises up to around 600 MPa. This value is even higher than the original flexural strength, implying that healing mechanism repairs not only introduced cracks but also some flaws in the original sample.

![Figure 2.27](image.png)

**Figure 2.27** Residual flexural strength and recovered flexural strength as a function of crack length after oxidation at 1100 °C for 4 hours in air. Adapted from Li et al. [8].

For cracks with length in the range of 1.8~2.5 mm, increased healing time results in a higher recovered flexural strength, as shown in Figure 2.28. The recovered strength reached 40~70 MPa after 2 hours healing at 1100 °C. It continues to rise up to
80~100 MPa and 120~180 MPa after 4 and 100 hours healing respectively at 1100 °C. Note that the increased recovery strength between 2 and 4 hours healing is almost equal to that between 4 and 100 hours healing. This means that the healing efficiency in terms of recovered strength decreases with increasing healing time, which is consistent with the oxidation kinetics of Cr₂AlC in an isothermal heat treatment experiment.

![Recovered flexural strength as a function of crack length and healing time. Adapted from Li et al. [8].](image)

**Figure 2.28** Recovered flexural strength as a function of crack length and healing time. Adapted from Li et al. [8].

Although the strength recovery of Cr₂AlC seems to be dependent on crack length and healing time, the fundamental deciding factor is likely to be the healing percentage (the degree of completion for crack healing). As mentioned above, the oxidation rate of Cr₂AlC is much slower than other MAX phase ceramics such as Ti₃AlC₂ and Ti₂AlC. A small increase in crack width will significantly increase the time needed for complete healing.

### 2.6 Computed X-ray tomography

Computed X-ray tomography, also known as CT, is a non-destructive powerful technique to characterize internal structure of an object, such as density and defects. Originally, it was designed for medical imaging. With the improvements of spatial
resolution as well as image collection and reconstruction time, it is now widely used in various fields, such as geology, biology, materials science, etc [84-86]. In materials science, for example, it is of great interest to obtain 3D information of internal defects such as voids and cracks, which are crucial for materials mechanical properties and usually unattainable through traditional 2D surface characterization techniques. The following section will cover some of the basic principles of this technique.

2.6.1 Basic physics of X-ray tomography

The Greek word “tomo” means to cut or to section [87]. Fundamentally, the problem of Computed X-ray tomography could be described as reconstructing series of cross sections or slices mathematically from X-ray projections taken at various angles around an axis through an object [88-89]. As an X-ray travels through an object, it will be absorbed or scattered, a process called attenuation. In X-ray photon energy range below 200 keV, there are three dominant interaction mechanisms:

I. Photoelectric absorption:

The photoelectric effect was first described by Albert Einstein in 1905. When the X-ray photon has energy greater than the binding energy of an electron, the entire X-ray photon energy can be absorbed. The kinetic energy of the electron of the inner shell will be increased and it will be liberated from the atom. The vacancy left by the free electron will be filled by outer shell electrons with simultaneous energy radiation (Figure 2.29), known as characteristic fluorescence.

![Figure 2.29 Illustration of photoelectric absorption. Adapted from Jiang Hsieh [85].](image)
Tightly bound electrons in materials with a higher atomic number are more likely to be involved in this photoelectric absorption due to the closer binding energies to that of X-ray photons. This is best described as [90-91]:

\[ u = k \frac{\rho}{A} \frac{Z^4}{E^3} \]  

(2-12)

Where \( u \) is linear absorption coefficient, \( k \) is a constant that depends on the shell involved, \( \rho \) is the density of material, \( A \) is the atomic weight, and \( E \) is the incident X-ray photon energy.

II. Compton scattering:

The Compton effect was discovered by Arthur Holly Compton in 1923. When the X-ray photon has energy significantly higher than the binding energy of an electron, it collides with an electron and frees it from the atom. The X-ray photon is scattered with partial loss of its initial energy, therefore it is inelastic scattering. The probability of Compton scattering depends on the electron density rather than the atomic number of materials.

![Compton scattering illustration](image)

**Figure 2.30** Illustration of Compton scattering. Image adapted from Jiang Hsieh [85].

III. Coherent scattering

Coherent scattering is also known as Rayleigh or Thomson scattering. It is an elastic scattering process, where the scattered and incident X-ray has equal energy. However, the angle of the scattered X-ray is different from that of the original X-ray. In this process, no X-ray photon energy is transferred to kinetic energy of electrons. The result of this scattering is usually a
broadened X-ray beam, therefore, it has limited interest to Computed X-ray tomography [80].

To sum up, the X-ray attenuation coefficient is related to x-ray photon energy of the beam $E$, atomic number $Z$ of the elements that compose the material and density of the investigated material $\rho$, as shown in Figure 2.31. The photoelectric absorption dominates when the incident X-ray energy is low and the atomic number of the investigated material is high, whereas the opposite is true for Compton scattering [81].

**Figure 2.31** Cause of attenuation: $\lambda$ is the wavelength, $Z$ is the atomic number and $\rho$ is the mass density. Adapted from Thorsten M Buzug [91].

### 2.6.2 Basic mathematics of reconstruction

Suppose an incident beam with intensity $I_0$ passes an object and emerges with an intensity of $I$ [82], as shown in Figure 2.32. According to Beer-Lambert Law or attenuation law, the beam intensity after traveling through a material could be described using equation:

$$I = I_0 \exp(- \int_L u(x) \, dx) \quad \text{(2-13)}$$

Where $u(x)$ is the X-ray attenuation coefficient at point $x$. 
In 2D, the X-ray projection $p(r,\theta)$ could be written as:

$$p(r,\theta) = \ln\left(\frac{l}{l_0}\right) = -\int u(x,y)\,ds$$  \hspace{1cm} (2-14)

In a polar coordinate system, the above equation could be written as:

$$p(r,\theta) = \int\int u(x,y) \cdot \delta(x\cos\theta + y\sin\theta - r)\,dx\,dy$$  \hspace{1cm} (2-15)

Radon in 1917 demonstrated a way to inversely transform the above equation [93]. Thus, the attenuation function $u(x,y)$ could be calculated through the Radon inverse transform, which is a mathematical basis for any X-ray tomography reconstruction. In practical applications, the filtered back-projection algorithm is typically used for parallel beam reconstruction, whereas a Feldkamp algorithm is applied for cone-beam reconstruction [78].

**Figure 2.32** Principle of transmission X-ray projection. Adapted from Miller et al. [92].

**Figure 2.33** Illustration of Radon transform for a 2D object in a polar coordinate system. Adapted from Wikipedia [94].
2.6.3 Synchrotron X-ray tomography

Synchrotron facilities were originally used to study collisions of subatomic particles in physics. Synchrotron radiation occurs when ultra-high energy electrons are forced to travel in a circular orbit. The X-ray beam produced is tangential to the curved electron storage ring [90]. Therefore, the beamlines are located around the storage ring. Figure 2.34 shows a schematic image of the Swiss Light Source, a third generation synchrotron light source.

![Schematic image of beamlines located tangent to electron storage ring at Swiss Light Source (SLS), Switzerland. Image courtesy of Paul Scherrer Institute (PSI) [95].](image)

Figure 2.34 Schematic image of beamlines located tangent to electron storage ring at Swiss Light Source (SLS), Switzerland. Image courtesy of Paul Scherrer Institute (PSI) [95].

With the wide use of synchrotron radiation or synchrotron light, many synchrotrons are solely used for the purpose of generating synchrotron light nowadays. The main advantages of X-ray beams generated by synchrotron over lab X-ray source include [96-97]:

1. **Monochromaticity**

   The use of a monochromatic beam will get rid of beam hardening artefacts and produce high signal to noise ratio.
II. High intensity

The X-ray beam intensity of a synchrotron light source is several orders of magnitude higher than that generated by a laboratory X-ray source. This high flux of photons at synchrotron significantly reduces the time required for image collection and opens new possibilities for in-situ time lapse experiment for dynamic process.

III. High coherence

The coherence nature of the synchrotron X-ray beam leads to easy setup of phase contrast imaging, through simply adjusting the sample to detector distance.
2.7 Reference


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CHAPTER 2
LITERATURE REVIEW


Chapter 3  Time resolved cyclic self-healing behaviour of Ti$_2$AlC studied by in-situ synchrotron X-ray tomography

The following sections in Chapter 3 have been prepared as a manuscript for submission to the Acta Materialia.

The author has designed, prepared and performed the in-situ synchrotron X-ray tomography experiment, analysed the collected data, interpreted the results and wrote the first draft and the final version of this manuscript.
CHAPTER 3 CYCLIC SELF-HEALING BEHAVIOUR OF Ti$_2$AlC

Time resolved cyclic self-healing behaviour of Ti$_2$AlC studied by in-situ synchrotron X-ray tomography

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Abstract

The self-healing behaviour of Ti$_2$AlC has the potential of largely improving its reliability as a high temperature structural material. Taking advantage of non-destructive synchrotron X-ray tomography, we performed a time lapse quantitative study of cyclic crack healing behaviour of Ti$_2$AlC at 1150 °C in air. Ti$_2$AlC exhibited remarkably self-healing capability of repeatedly repairing cracks for three healing cycles. Cracks with over 24 µm in width were successfully healed even in the third healing cycle in less than 66 minutes. The 2D tomographic images as well as 3D crack opening displacement maps implied that the dominant factor for crack healing rate was oxygen partial pressure in an early healing stage and changed to atom diffusion rate after significant oxide scale is formed. The crack healing kinetics in three healing cycles was quantified; it decreased dramatically in a previous healed zone.

Key words: Ti$_2$AlC; Self-healing; In-situ synchrotron X-ray tomography

3.1 Introduction

Layered ternary compounds: M$_{n+1}$AX$_n$ (n = 1, 2 or 3), known as MAX phase ceramics, where M is an early transitional metal, A is an element in IIIA or IVA group, and X is C or N, are arousing more and more attention because of their unusual combination of properties of metals and ceramics [1-6]. Among M$_{n+1}$AX$_n$ phase ceramic, Ti$_2$AlC is of special interest due to its low density (4.11 g/cm$^3$) [7], high strength and modulus at ambient temperature, good resistance to oxidation,
corrosion and thermal shock, and damage tolerance as well as easy machinability [4, 8-18]. Therefore, Ti$_2$AlC is considered to be suitable for high temperature applications, such as gas turbine engine components, thermal exchanger, etc.

As a ceramic, however, Ti$_2$AlC is sensitive to defects and cracks, which reduces its reliability. Recent research shows that this material exhibits self-healing capability under high temperatures, when it is exposed to oxygen containing environment [19-22]. This autonomous damage repair capability may significantly extend its service time and reduce the maintenance cost as high temperature structural components. Li and co-workers reported that Ti$_2$AlC was capable of repeatedly repairing damage for seven healing cycles at 1200 °C [23]. The healing of Ti$_2$AlC is an oxidation process where cracks or defects are filled by Al$_2$O$_3$ and/or TiO$_2$ through volume expansion [24]. Due to the strong bonding and well-matched thermal expansion coefficients between healing oxides and Ti$_2$AlC matrix, the mechanical strength was fully or partially recovered after healing.

The healing capability and kinetics of Ti$_2$AlC were usually evaluated based on previous oxidation experiments. The oxidation kinetics of Ti$_2$AlC has been extensively studied [12, 25-27]. Wang and co-workers reported parabolic oxidation kinetics for Ti$_2$AlC up to 1400 °C [28]. Basu and co-workers reported that Ti$_2$AlC exhibited cubic oxidation kinetics in air in the temperature range of 1000-1300 °C [25]. Despite the differences in these studies, the methodologies used were similar. Oxidation experiments were conducted using a polished Ti$_2$AlC sample and the oxidation kinetics studied through TGA and oxide scale measurements. However, for a complex crack healing process, models based on the polished surface oxidation experiment could be inaccurate or even problematic for three reasons. 1) The TGA measurement only monitors the weight gain during oxidation, while the weight loss of carbon through oxidation is not taken into account. Also, the actual healing and oxide scale growth process is a combination of the oxidation of Al and Ti. Without the mass ratio between Al$_2$O$_3$ and TiO$_2$, it is difficult to estimate the thickness of healing scale, which is of critical importance for successful healing and strength recovery. 2) Yang reported a microstructure difference between oxides formed on a flat surface and cavities [29]. He further pointed out that the microstructure of the Al$_2$O$_3$ layer was strongly affected by the radius of curvature of the surface. As a
CHAPTER 3  CYCLIC SELF-HEALING BEHAVIOUR OF Ti$_2$AlC

result, oxide scales measured on a flat surface may not represent the case for a crack surface which usually has large curvatures in various positions. 3) The shielding or closure effect of crack happened during healing is not considered in the oxidation process of a flat surface. Therefore it would be very beneficial if the crack healing behaviour could be directly observed and measured.

An ideal self-healing material should have the capability of repairing damage for many cycles with the healing efficiency not declining. It would be more interesting to study the healing kinetics and behaviour of Ti$_2$AlC in the later healing cycles. Due to the destructive characterization method used in previous studies, the re healing behaviour and kinetics of Ti$_2$AlC in previous healed zones is largely unexplored.

Thanks to the state of art synchrotron rapid X-ray tomography and the non-destructive nature of this technique, we for the first time were able to directly observe healing process of a crack and study the crack healing kinetics of Ti$_2$AlC at 1150 °C for three healing cycles.

3.2 Experiment

Powders of Ti (particle size < 48 µm, 99.5 wt% purity), Al (particle size < 75 µm, 99.5 wt% purity), and C (graphite, particle size < 45 µm, 99.5 wt% purity) were used as starting materials. The designed molar ratios of the Ti, Al and C powders was Ti : Al : C = 2 : 1.1 : 1 to make a Ti$_2$AlC ceramic. The mixed powders were put into a graphite mold coated with BN and then hot-pressed at 1400 °C for 8 hours with 30 MPa in an Ar atmosphere. Ti$_2$AlC samples for the synchrotron experiment were machined to a cylinder size with 10 mm in length and 2.5 mm in diameter. A chevron notch of 15 ° was introduced by wire electrical discharge machining into the cylinder sample to help to initiate the crack. Any cracks developed in this configuration are stable, aiding the imaging and healing process.

The self-healing experiment was performed by using a P2R mechanical testing rig, which is designed for insitu synchrotron X-ray tomography experiment. The rig has an air-bearing rotation system built in, allowing for simultaneous compression test during tomography scans [30]. A new laser-based heating system, providing near-
isothermal and linear temperature gradient up to 1700 °C, was mounted on the mechanical rig to heat the Ti$_2$AlC sample during the experiment [31]. In order to maintain the temperature at a certain fixed value, a pyrometer was used to read actual temperature and send feedback to the laser system. The whole thermal-mechanical test system was integrated into the TOMCAT beamline, at Swiss Light Source, Switzerland.

The thermal mechanical test set-up was shown in Figure 3.1a. A boron nitride holder with black-painted Al$_2$O$_3$ sleeve (3 mm in diameter and 0.5 mm in wall thickness) was mounted on the bottom ceramic ram. The black outer surface of the alumina sleeve was used to conduct the heat from laser to the sample, acting as a furnace. The Ti$_2$AlC sample was placed at the centre of the holder. A 15 ° wedge made of Ni-superalloy was mounted on the top ram to initiate the crack and keep the crack open at temperature.

![Figure 3.1](image)

Figure 3.1 (a) Illustrating the setup of the mechanical testing rig and laser-based heating system (left) and a CAD model of the sample is shown (right) with a wedge loading from top. (b) 3D segmented image of crack initiated after loading with crack width in tensile direction represented by colour.

The sample was firstly heated at a rate of 60 °C/min to 800 °C for crack initiation. 800 °C is chosen for crack initiation for the following two reasons: 1) Previous experiments showed that thermal expansion of the wedge during temperature
increase may result in further crack propagation or even catastrophic failure, if the crack initiation was conducted at room temperature; 2) The temperature is far below the healing temperature, therefore, no significant healing would happen at this temperature. The wedge was then driven at a compression rate of 1 µm/second until a load drop caused by crack growth was captured. After a desirable crack was observed by X-ray projections and further checked by reconstructed images, the sample was continuously heated to healing temperature of 1150 °C at 60 °C/min. Three “crack-healing” cycles were achieved in this experiment. For each healing cycle, the total healing time was about 66 minutes.

The synchrotron experiment was conducted using a monochromatic X-ray beam with photon energy of 80 keV. The exposure time for a single projection was 15 ms and 1001 projections were captured for each scan. For each healing cycle, 43 datasets were continuously captured with each taking about 1 minute in the initial 20 minutes’ healing and then changed to 2 minutes for the later healing process. The set-up of the beamline and fast x-ray tomography detector enable to measure with a voxel size of 0.65 µm and a field of view of 1.404 × 1.664 mm².

The datasets were reconstructed at TOMCAT by using a using a re-gridding Fourier transform-based reconstruction algorithm [32]. Each reconstructed 3D dataset contained 2560 × 2560 × 2160 voxels. Image processing and analysis was performed using Avizo 8.0 at Henry Moseley X-ray Imaging Facility in University of Manchester. The crack in each healing step was segmented by Avizo 8.0 and then characterised and features quantified using Matlab codes.

3.3 Results

3.3.1 2D crack cross sections and strength recovery

As mentioned before, three “crack-healing” cycles were achieved in the insitu thermal-mechanical synchrotron experiment. Figure 3.2 shows the 2D reconstructed X-ray tomographic micrographs in the crack growth direction (along x axis) before and after healing in these three healing cycles. The loads (along z axis) applied to generate these cracks were 55.2 N, 61.9 N and 45.0 N respectively.
After the first healing cycle, the original crack was healed to a final length of around 120 µm. The critical stress to drive this crack was estimated to be around 255 MPa ($\sigma = \frac{K_{IC}}{\sqrt{a}}$), which is lower than the flexural strength of Ti$_2$AlC (384 MPa). However, due to the sample geometry, the local stress at chevron notch tip would have already reached the strength of Ti$_2$AlC before the local stress at the unhealed crack reached its critical crack driving force. As a result, the crack propagated through a different crack route in the second loading cycle. For the third loading cycle, the load recorded for crack initiation was smaller than that for the first and second crack. This indicates that the mechanical strength had been partially recovered. The reduced mechanical strength recovery is likely to be the result of partially healed crack in the second healing cycle as shown in Figure 3.2b2, where a large unhealed area is seen at the crack root. Therefore, it is reasonable to assume that the healing percentage (especially at crack root) would have a strong influence on the mechanical strength recovery of this material.

**Figure 3.2** Two dimensional X-ray tomographic micrographs before and after healing at 1150 °C in air in three healing cycles: (a1) and (a2) are 1st healing cycle; (b1) and (b2) are 2nd healing cycle; (c1) and (c2) 3rd healing cycle.
3.3.2 2D time-resolved cross sections of cracks at different healing cycles

Two dimensional X-ray tomographic micrographs of the healing process in the first healing cycle are shown in Figure 3.3a. It is evident that the crack gradually disappeared as the heating time prolongs (from Figure 3.3a-1 to 3.3a-6). After 18 minutes’ heat treatment at 1150 °C, the opening part of the crack was almost fully healed, as indicated in Figure 3.3a-4. Although the crack area near the tip had a smaller crack width, it still remained partially healed. This indicates that the healing rate near crack root is significantly faster than that near crack tip. To quantify this difference, the crack was labelled and segmented from five 2D X-ray tomographic slices by using Avizo Software. Then the crack opening displacement along the crack growth direction was calculated as shown in Figure 3.3b. To better illustrate the difference in terms of healing rate, the crack opening displacement (COD) after 18 minutes’ healing was subtracted from the original COD, as shown in Figure 3.3c. The change in COD (ΔCOD) near the crack root is around 9 µm, while that near middle and tip is around 3 µm and 1 µm, respectively. There is a clear decreasing trend of ΔCOD from crack root to crack tip.

After 66 minutes’ heat treatment, there was still a crack area left unhealed in the middle of the crack, as indicated by the cycle in Figure 3.3a-6. In fact, this crack area remained unchanged after 33 minutes’ healing. A darker healing trace is clearly seen in the last step of healing, indicating a lower density or concentration of Ti and Al in the healed region.
Figure 3.3 (a) 2D X-ray tomographic micrographs in the first healing cycle at different healing stages. (b) COD measurements before healing and after 18 minutes’ heat treatment at 1150 °C in air. (c) ΔCOD measurements before healing and after 18 minutes’ heat treatment at 1150 °C in air.

Figures 3.4a and 3.4b show the two dimensional X-ray tomographic micrographs of the healing process in the second and third healing cycles. As the second crack had a different propagation route, the Ti₂AlC matrix near the second crack is more or less unaffected in the first healing cycle. Not surprisingly, most parts of the crack had been successfully healed after heat treatment for 66 minutes, as shown in Figure 3.4a-6. For the third crack, although it followed exactly the same path as the second one, the majority part of the crack area was still successfully healed, as shown in Figure 3.4b-6. The Ti₂AlC material showed remarkable healing capability for repeatedly repairing damage at the previous healed zone, which is crucial for an ideal healing material.

Similar to the first healing process, there is an unhealed area in the middle part of the crack after 66 minutes’ healing, as indicated by the white circles in Figure 3.4a-6 and
Figure 3.4b-6. However, unlike the first healing cycle where crack root shows a faster healing rate, the crack root part in the second and third healing cycle was left unhealed. Apart from that, the ΔCOD figures after 18 minutes’ healing in the second and third healing cycles still show a decreasing trend of the healing rate from crack root to crack tip (Figure 3.4c and 3.4d). The length of the low healing rate area in the crack root increased from 130 μm in the second healing cycle to around 250 μm in the third healing cycle, as indicated by the arrows in Figures 3.4c and 3.4d.

**Figure 3.4** (a) and (b) are 2D X-ray tomographic micrographs in the second and third healing cycles at different healing stages respectively. (c) and (d) are ΔCOD measurements before healing and after 18 minutes’ heat treatment at 1150 °C in the second and third healing cycles respectively.
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3.3.3 3D COD maps at different healing stages

The above 2D slice results implied a relationship between healing rate and crack position. Taking the advantage of 3D X-ray tomography, crack opening displacement in three dimensions was determined to better illustrate this relationship on a larger scale.

The 3D COD map in the first healing cycle is shown in Figure 3.5. The sample has a chevron-notch, therefore, the 3D COD map is a triangular shape. Consistent with the 2D results, the whole crack root part was almost fully healed after 18 minutes’ heat treatment as indicated by the red circle. Besides, the crack width near triangular edges changed dramatically during the initial healing process and was almost fully healed after 30 minutes’ heat treatment as indicated by the red lines. The relative dramatic change of crack opening displacement at crack root and edge indicates a higher healing rate in these areas than the rest of the crack. After 66 minutes’ healing, most part of the crack is healed with a small crack area in middle left partially unhealed.

Figure 3.6 shows the 3D COD map of the second healing cycle. Contrary to the first healing cycle, where the crack area near triangular top (crack root) and edges had a faster healing rate, these areas in the second healing cycle seemed to show a much slower healing rate than the rest of the crack. These areas remained almost unchanged during the initial 18 minutes’ heat treatment.

Another thing worth noting is that there are some crack areas remained unchanged after the initial 18 minutes’ heat treatment, as indicated by the red circles in Figure 3.6. In fact, the original crack width at these locations is comparable or even smaller than those that were fully healed after 66 minutes’ heat treatment. Therefore, the Ti$_2$AlC matrix materials needed to fill these areas should be more than sufficient. It can be seen that after 18 minutes’ healing, these areas were sealed by nearby healed zones. In this case, all paths for oxygen were blocked. The shortage of oxygen kept these isolated areas unchanged after they were effectively sealed.

Considering the crack in the third healing cycle propagated through the same path as the second crack, it would be more interesting to compare the healing rate in these
two healing cycles. Figure 3.7 shows the 3D COD map of the third healing cycle. It can be seen that the COD change in the initial 18 minutes’ healing is relatively smaller than that in the second healing cycle. This indicates a much slower healing rate in the third healing cycle. Similarly to the second healing cycle, the COD of crack root and edges in the third healing cycle remained almost unchanged in the initial healing stage, indicating a much slower healing rate in these areas than the rest of the crack. In addition, this unchanged area is further expanded from crack root to crack tip, which is consistent with the ΔCOD measurements in Figure 3.4.
**Figure 3.5** 3D COD maps in the first healing cycle at different healing stages, where crack opening displacement is represented by colour. The scale of the colourmap is tailored from 4 μm to 11 μm to show the COD change better in these different healing stages.
Figure 3.6 3D COD maps in the second healing cycle at different healing stages, where crack opening displacement is represented by colourmap.
Figure 3.7 3D COD maps in the third healing cycle at different healing stages, where crack opening displacement is represented by colourmap.
3.4 Discussion

3.4.1 Healing kinetics’ dependence on crack location

Before discussing the healing kinetics’ dependence on crack location, it is worth reviewing the homogeneous healing model proposed previously. The healing process of Ti$_2$AlC is essentially an oxidation process, where crack gaps are filled by Al$_2$O$_3$ and rutile TiO$_2$ [27]. The oxidation kinetics was revealed to be determined by atom diffusion rate through the Al$_2$O$_3$ layer. It was reported that the oxide scale formed after heat treatment in air is more or less uniform in thickness, regardless of grain orientation [11, 25]. Therefore, a homogeneous crack healing model was previously proposed. To compare this model with the actual healing process, the original crack in the first healing cycle was segmented and then the 3D crack volume was reduced layer by layer with a step size of 1.3 µm to simulate the homogeneous crack healing process, as shown in Figure 3.8. It can be seen that the colour in COD map changed uniformly over the whole crack area and a healed zone is developed from crack tip to crack root. In this model, the crack area at tip is always healed first, while that at crack root is healed last. Clearly, this homogeneous healing model deviates from the actual healing process.

Figure 3.8 Image based homogeneous crack healing model simulated by reducing 3D crack volume at a step size of 1.3 µm. Note that the colourmap is different from that used in the first healing cycle in Figure 3.5 to better illustrate the COD change.
As presented in Figure 3.5, the entire regions of crack root and edges have a much faster healing rate than the rest of the crack. Considering this macroscopic difference in healing rate, it is reasonable to infer that a macroscopic factor should account for the contradiction between the homogeneous model and the actual crack healing process. One explanation for this inhomogeneous healing process is by taking account of the influence of oxygen partial pressure [19]. Previous oxidation experiments on FIB cut notches had shown a faster oxidation rate at top of the notch than that at bottom, due to the variance of oxygen partial pressure. With an easy access to oxygen, the top part of the notch had a higher oxygen partial pressure, thus a faster oxidation rate. In the case of crack healing, it is reasonable to assume that the “zig-zag” shape of crack as well as crack closure effect during healing would result into a more significant difference in oxygen partial pressure over the whole crack. Consequently, due to a much shorter distance and an easy access to oxygen, the healing rate at triangular top and edges were faster than that in the middle part of the crack.

To further address the influence of oxygen partial pressure on healing rate, two positions (edge and middle) are chosen, as shown in Figure 3.9a. Normally, the edges will have an easier access to oxygen, thus a higher oxygen partial pressure. However, in the middle of the crack, the oxygen partial pressure should be much lower as there is a long distance for the oxygen to travel and the crack is closing during healing. The healing percentage as a function of time at crack middle is calculated by segmenting and measuring crack areas \( A(t) \) in five 2D X-ray tomographic slices along the crack growth direction (along x axis), hence:

\[
H = \frac{A(t = 0) - A(t)}{A(t = 0)} \times 100\
\]

The healing kinetics of the crack edge was determined by averaging the healing percentage at the two crack edges.
Figure 3.9 (a) Illustration of calculation positions. (b-d) are healing percentage as a function of time in the first, second and third healing cycles respectively.

Figure 3.9b shows the healing rates at both the middle and the edge in the first healing cycle. It is clear that the healing rate at the edge is higher than that at the middle. The biggest margin between the healing rate at mid and edge is seen at the beginning of the plot, indicating a more significant difference in the early healing stage.

In the second and third healing cycles, the healing rates between middle and edges are similar, even at an early healing stage, as shown in Figure 3.9c and 3.9d. Figure 3.10 shows the X-ray tomographic slices parallel to crack growth direction at the beginning of each healing cycle. It can be seen in Figure 3.10b and 3.10c that the triangular edges in these images have a darker contrast, indicating a lower density or concentration of Ti and Al in these areas than that in the rest part of the material. This decrease in Ti and Al concentration is due to the direct oxidation of the notch.
surface, which consumes large amount of Ti and Al. Significant oxides were formed before 2nd healing cycle (shown in Figure 3.10b) and the formed oxides further thickened before the 3rd healing cycle, as shown in Figure 3.10c. As a result, the atom diffusion rates at edges were largely decreased in the second and third healing cycles and became the deciding factor to further oxidation and crack healing. In extreme cases, the total depletion of the Al and Ti atoms would result into the loss of healing capability of Ti2AlC, as shown at the crack root areas in the second and third healing cycles.

![Figure 3.10](image-url) 2D X-ray tomographic slices parallel to crack growth direction at the original stage before healing in three healing cycles: (a) 1st healing cycle; (b) 2nd healing cycle; (c) 3rd healing cycle.
3.4.2 Healing kinetics comparison in different healing cycles

For an ideal healing material, damage should be repeatedly repaired with healing kinetics not declining. The overall healing kinetics is determined from the change in crack volume $V(t)$. This volume change is calculated from the 3D datasets by counting the number of voxels that represent the crack gap at a given time, $t$, therefore:

$$H_{\text{overall}} = \frac{V(t=0) - V(t)}{V(t=0)} \times 100\%$$

The overall healing rates in terms of percentage for different healing cycles are compared, as shown in Figure 3.11. As the second crack propagated along a different crack path, the healing material along the crack path is more or less virginal. Therefore, both the first and second healing cycles represent the crack healing process of virginal Ti$_2$AlC material. For the third crack, given that it grows through the healed zone of the second crack, the third healing cycle shows the re-healing process of a healed area.

Not surprisingly, the healing rate plot for the first and second healing cycle shows a similar trend and healing rate, as shown in Figure 3.11. After the initial 30 minutes’ heat treatment, the healing percentage reached over 90% and 75% for both the first and second healing. The healing process for the third healing cycle exhibits a slower healing rate, as shown in Figure 3.11. Healing percentage of less than 50% was achieved in the initial 30 minutes’ heat treatment. The slower healing rate in the third healing cycle could be attributed mainly to the existing oxide layer on the crack surface formed in previous healing cycles. Unlike the healing process in first and second healing cycles, the healing in the third healing cycle requires Al and Ti atoms to diffuse through existing Al$_2$O$_3$ and TiO$_2$ layers formed in the second healing cycle. As the Al$_2$O$_3$ layers formed on Ti$_2$AlC are known for their good oxidation protection to the Ti$_2$AlC matrix by slowing down the diffusion rate of reactants [25, 28], the healing rate in the third healing cycle will be significantly reduced.
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Figure 3.11 Crack healing percentage as a function of time in $1^{st}$, $2^{nd}$ and $3^{rd}$ healing cycles.

3.5 Conclusion

Our results demonstrated that rapid synchrotron X-ray tomography is a fascinating characterization method to study the crack healing behaviour of the MAX phase material Ti$_2$AlC. The crack opening displacement in two as well as three dimensions was measured with a high spatial resolution for three healing cycles. Based on our current results, some conclusion can be drawn.

I. Ti$_2$AlC exhibited remarkable healing ability of repeatedly repairing damage at 1150 °C in air for less than 66 minutes. The final healing percentage may have a significant influence on the mechanical strength recovery. A full strength recovery was observed in the experiment when the healing percentage is over 90 %, while a healing percentage of 85 % achieved only partial strength recovery.

II. For the crack healing process of Ti$_2$AlC, oxygen partial pressure and Ti & Al atom diffusion rate are proposed to be the two competing dominant factors. In the early stage of healing, oxygen partial pressure is the deciding factor.
As the oxide layers on the crack surfaces became thicker, the dominant factor changes to Ti & Al atom diffusion rate.

**III.** The healing kinetics would remain the more or less the same if the crack propagation path is different. However, the healing rate for a healed zone is significantly decreased due to reduced Ti & Al diffusion speed caused by existing oxide layers.

### 3.6 Acknowledgements

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3.7 Reference


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Supplementary information

**Figure 3.12** Secondary electron SEM image of etched Ti$_2$AlC sample. The average grain size is around 35 µm.

**Figure 3.13** XRD pattern of as received Ti$_2$AlC sample. Ti$_3$AlC impurity phase was detected.
Chapter 4 Crack healing behaviour of Cr$_2$AlC studied by X-ray tomography

The following sections in Chapter 4 have been prepared as manuscript for submission to the Journal of the American Ceramic Society. Some of the results have been given as an oral presentation at The American Ceramic Society on 39th International Conference and Expo on Advanced Ceramics and Composites, 25-30 January, 2015 in Florida, USA.

The author has designed, prepared and performed the X-ray tomography experiment, analysed the collected data, interpreted the results and wrote the first draft and the final version of this manuscript.
CHAPTER 4

CRACK HEALING BEHAVIOUR OF Cr$_2$AlC

Crack healing behaviour of Cr$_2$AlC studied by X-ray tomography

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Abstract

The autonomous crack healing capability of Cr$_2$AlC offers great potential to improve the reliability of the material and reduce maintenance costs of any component during service. In this work we performed a time lapse quantitative study of the crack healing behaviour of Cr$_2$AlC using computed X-ray tomography (CT). A precracked Cr$_2$AlC sample was under heat treatment at 1200 °C in air for 4 hours, 8 hours and 12 hours with CT scans taken between each step. The 2D tomographic images as well as 3D crack opening displacement maps show that the healing process of Cr$_2$AlC is more or less independent of crack location and has similar healing rate along the crack. The crack healing kinetics of Cr$_2$AlC followed a parabolic rate law with rate constant of $4.3 \times 10^{-3}$ $\mu$m$^2$·s$^{-1}$. The microstructure, composition and thickness of oxide scale in the healed crack area were characterized. The interactions between impurity Cr particles and crack healing were revealed through correlative study, combining X-ray tomographic slices with SEM images.

Key words: Cr$_2$AlC; Crack healing; X-ray tomography; Correlative study

4.1 Introduction

Recently, layered ternary compounds: M$_{n+1}$AX$_n$ (n=1, 2 or 3) phase ceramics, where M is an early transitional metal, A is an element in IIIA or IVA group and X is C or N (known collectively as MAX phase), are arousing more and more attention [1-3]. These materials exhibit an unusual combination of properties, such as high strength and modulus, excellent oxidation resistance, low density, thermal shock resistance,
damage tolerance as well as easy machinability [4-8]. Therefore, they are considered to be suitable for high temperature applications, such as gas turbine components, thermal exchanger, oxidation resistant coatings, etc. However, as a ceramic, they still bear the common drawbacks of low toughness and sensitivity to surface defects and cracks, which may reduce their reliability.

Recent research shows that these materials exhibit self-healing capability when they are exposed to an oxidizing environment at high temperatures [9-11]. Given their potential applications as high temperature structural materials, such autonomous healing capability would greatly improve their reliability and potentially reduce maintenance costs. Extensive studies have been done on Ti-Al-C ternary system. Song and co-workers reported that a crack with average width of 5 µm in Ti₃AlC₂ ceramic was healed by heat treatment at 1100 °C for 2 hours in air [12]. Yang and co-workers reported that FIB cut notches with 2 µm in width was healed by heat treatment at 1200 °C in air for 1 hour [9]. The self-healing of Ti-Al-C MAX phase ceramic is an oxidation process, where crack gaps or notches are filled by α-Al₂O₃ and rutile-TiO₂ through oxidation induced volume expansion [13]. Due to the intrinsic nature of this healing mechanism, healing is supposed to happen wherever it has Ti-Al-C matrix and oxygen. As a result, this system could achieve multiple healing capabilities, as reported by Li [11]. However, due to the formation of a weak and porous TiO₂ phase, the strength recovery after healing is greatly compromised. Therefore, it would be desirable if crack gap is filled by Al₂O₃ alone. A crack area healed by dense Al₂O₃ is expected to provide optimal strength recovery after healing.

Previous research on Cr₂AlC shows that the oxidation product of Cr₂AlC at high temperatures is primarily Al₂O₃ [14-17]. Without the porous TiO₂ phase, Cr₂AlC is believed to provide better strength recovery after healing than Ti-Al-C MAX phase ceramics. Li studied the strength recovery of Cr₂AlC after healing at 1100 °C in air for 4-100 hours and reported that the strength recovery of Cr₂AlC has a strong dependence on healing time [18]. Therefore, understanding the kinetics of healing is critical for predicting the healing strength recovery. Until now, the understandings for crack healing kinetics of Cr₂AlC are mainly based on thermalgravimetric analysis (TGA) experiments on plane surface and there are still some arguments on its isothermal oxidation behaviour [14,17]. The isothermal oxidation kinetics of Cr₂AlC
was first reported by Lin to obey a parabolic law at 1200 °C in air with a parabolic constant of 6.8×10^{-10} \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-1} [19]. Tian studied the isothermal behaviour of Cr$_2$AlC at 1100 and 1250 °C in air for 20 hours and confirmed the parabolic relation between the mass gain per unit surface area and oxidation time [14]. Lee studied the isothermal oxidation of Cr$_2$AlC at 900-1200 °C in air for 20 hours and reported that the oxidation curve deviated negatively from parabolic rate law at temperature above 1100 °C, which was explained by a mass loss through formation of gaseous CO and CrO$_3$ [17]. Recently, Li studied the isothermal oxidation of Cr$_2$AlC at 1100 and 1200 °C in air for 100 hours and reported that the oxidation kinetics of Cr$_2$AlC followed a cubic law instead of a parabolic one [18].

Besides these inconsistencies, oxidation kinetics of Cr$_2$AlC measured by TGA on a polished plane surface could be inaccurate or even problematic when it is applied to real crack healing process: 1) TGA measurements only monitor the weight gain during oxidation, while the weight loss of carbon and Cr is not taken into account. As a result, the weight gain measured by TGA is not linearly related to the oxide scale growth, which is crucial for a healing process. 2) Previous oxidation experiment on surface notch of Ti$_2$AlC indicates that the healing process of MAX phase materials may have a strong dependence on surface curvature [9]. However, this is not reflected in a plane surface oxidation. Therefore, it would be very beneficial if the crack healing behaviour could be directly observed and measured not only in two dimensions (2D) but also in three dimensions (3D) as well.

Thanks to the current capabilities of X-ray tomography and the non-destructive nature of this technique, we for the first time were able to directly observe crack healing of Cr$_2$AlC at different stages and obtain quantitative information on its healing kinetics.

### 4.2 Experiment

Bulk Cr$_2$AlC ceramic was prepared using a mixture of Cr (average particle size of 100 μm), Al (average particle size of 45 μm) and graphite (average particle size of 6 μm) powders with a molar ratio of Cr : Al : C = 2 : 1.15 : 1. A slight excess of Al was added to compensate for its loss during sintering. These powders were mixed for
3 hours using zirconia balls and then pressureless sintered (PLS) in a tube furnace under an argon flow in temperature range of 1100 °C to 1400 °C for 1 hour. After that, the PLS sintered samples were pulverized using Fritsch Pulverisette, type P-0150, Germany to obtain PLS Cr$_2$AlC powders. Then the PLS Cr$_2$AlC powders were sintered in a spark plasma sintering furnace at 1250 °C for 1 hour in flowing argon under a pressure of 50 MPa.

The Cr$_2$AlC specimen for the X-ray tomography experiment was machined to a cylinder of 7.5 mm in length and 2.5 mm in diameter. A chevron notch of 15° was introduced by wire electrical discharge into the sample to help to initiate a stable crack. The initial crack was made in a mechanical tester (MTS Alliance RT/100) by using a 15 degree wedge made of Ni superalloy at a displacement rate of 0.001 mm/min. A tomography scan was taken after a crack was observed in the X-ray projections. Then the cracked Cr$_2$AlC specimen was healed at 1200 °C for 4 hours, 8 hours, and 12 hours, respectively in a box furnace (Carbolite BWF) with tomography scans taken between each heat treatment step.

The high resolution X-ray tomography experiment was performed at Manchester X-ray Imaging Facility, by using X’radia Versa 500. The set-up of the X-ray tomography experiment is shown in Figure 4.1. The Cr$_2$AlC sample was mounted on a rotation stage, between the X-ray source and detector. The sample to X-ray source and sample to detector distance was set to 12 mm and 48 mm, respectively. By using this set-up, an X-ray tomography scan with a resolution of 0.677 µm$^3$/voxel was achieved in the experiment. The imaging voltage was set to 90 kV to maximize the contrast between Al$_2$O$_3$ and the Cr$_2$AlC matrix. For each scan, 45 seconds were taken for each projection and a total number of 1441 projections were collected. The X-ray tomography reconstructions were conducted using a Feldkamp-Davis-Kress (FDK) algorithm. Each reconstructed 3D dataset was 1988×1988×2030 in voxel with a field of view of 1.346×1.374 mm$^2$. Image processing and analysis was performed using FEI Avizo 8.0.

To study the microstructure of healing oxide, a Cr$_2$AlC sample with crack was healed at 1200 °C in air for 4 hours. The sample after heat treatment was ground with SiC paper and finished with colloidal silica. The cross section of the healed area...
CHAPTER 4  CRACK HEALING BEHAVIOUR OF Cr$_2$AlC

was characterized with scanning electron microscopes (SEM; Philips XL30 ESEM-FEG and FEI Quanta 650) equipped with energy-dispersive spectrometer system (EDS).

![X-ray tomography experiment setup](image)

**Figure 4.1** Set-up of X-ray tomography experiment.

**4.3 Results**

**4.3.1 2D X-ray tomographic cross sections of crack at different healing stages**

Two dimensional reconstructed X-ray tomographic micrographs perpendicular to the crack growth direction are shown in Figure 4.2. Some white particles with diameters from 10 µm to 30 µm are seen to be randomly distributed in the tomographic images. These particles were confirmed by EDS to be Cr particles and were probably formed through incomplete reaction during the sintering process.

The initial crack width before heat treatment is around 10 µm, shown in Figure 4.2a. It is evident that the crack width decreases gradually as the healing time prolongs (from Figure 4.2a to 4.2d). After 12 hours’ heat treatment at 1200 °C in air, some part of the crack was partially healed as indicated by black arrows in Figure 4.2d. As a crack with similar width in Ti$_2$AlC was healed at same temperature for less than one hour [13], it can be demonstrated that the healing rate of Cr$_2$AlC is much slower. The contrast within the crack area changed from dark black to grey, indicating that
crack area were filled by oxides which has an X-ray absorption coefficient higher than air but lower than Cr$_2$AlC matrix. The oxides were later confirmed by scanning electron microscopy and EDX to be composed of primarily Al$_2$O$_3$.

By comparing Figure 4.2a and 4.2b, it is clear that after 4 hours’ healing at 1200 °C, most of the crack area seems to have undergone a uniform shrinkage in crack width. Although the crack in the red rectangular has a similar width as the rest of the crack (shown in Figure 4.2a), it was nearly closed after 4 hours’ healing (shown in Figure 4.2b). This dramatic decrease in crack width suggests that the existence of Cr particles may significantly increase the healing kinetics in nearby crack areas. An enlarged image of the red rectangular area is shown in Figure 4.3. It is clear that an oxide layer of around 7 µm was formed after 4 hours’ healing on the crack surface adjacent to Cr particles, while the oxide layer formed in the remaining areas was around 2 µm on a single crack surface. During the healing process, the Cr particles that were directly exposed to air seemed to be “dissolved” in the matrix with secondary phase and some “micro voids” formed near the particles’ edge, as indicated by red arrows in Figure 4.3b. However, in the meantime, Cr particles not adjacent to crack surface remained stable. The contrast of the particles changed from white to grey, indicating a decreased concentration of Cr in this area.
Figure 4.2 2D X-ray tomographic cross sections at different healing stages: (a) original; (b) after 4 hours’ healing at 1200 °C in air; (c) after 8 hours’ healing at 1200 °C in air; (d) after 12 hours’ healing at 1200 °C in air.

Figure 4.3 2D X-ray tomographic cross sections of rectangular areas in Figure 4.2 at different healing stages: (a) original; (b) after 4 hours healing at 1200 °C in air; (c) after 8 hours healing at 1200 °C in air; (d) after 12 hours healing at 1200 °C in air.

4.3.2 3D COD maps at different healing stages

One of the many advantages of the X-ray tomography characterization technique is that three dimensional interior information of a bulk sample can be recorded. This is especially important when observing the healing process of a crack, as crack healing is inherently a three dimensional rather than two dimensional process. 2D information gained through surface observation could be less representative.

Here, we determined the three dimensional crack opening displacement map (COD) as shown in Figure 4.4. The 3D crack volume was segmented by using a threshold method in FEI Avizo software. Crack opening displacement was calculated from the segmented 3D crack volume by using Matlab codes. The 3D COD map was then generated by covering the 3D crack surface with colourmap representing crack opening displacement at corresponding positions. The trapezoid shape of the 3D COD map is because of the chevron-notch of the sample. Considering the crack opening displacement change between 8 hours and 12 hours is small, only the COD map of the final stage (after 12 hours healing) is shown here for brevity.
By comparing the 3D COD map of the original state (Figure 4.4a) with that after 4 hours’ heat treatment (Figure 4.4b), it can be seen that the crack width decreased more or less uniformly over the whole crack area during healing, which is consistent with the above 2D cross section results in Figure 4.2. After 12 hours’ heat treatment, the crack tip area was almost fully healed, as shown in Figure 4.4c. One thing worth noting is that as healing time progresses, some crack areas could be isolated from oxygen due to uneven local healing percentage. The result of this isolation is that some crack areas will be left unhealed, even as the healing time increases. However, in general the crack tip area is always healed first and the healed zone developed in an opposite direction of crack growth, from crack tip to crack root.
4.3.3 Microstructure of healed area

To study the microstructure of the healed area, a cracked Cr$_2$AlC sample was healed at 1200 °C in air for 4 hours and then sectioned along the crack growth direction. A typical secondary electron cross-sectional SEM image and the corresponding elemental maps of the healed area are shown in Figure 4.5a. The healed area was composed of three layers: one dark layer in the middle and two brighter layers on
both sides. The dark contrast layer was confirmed to be primarily Al$_2$O$_3$, while the bright layer was confirmed to be Cr$_7$C$_3$ through EDX map and point profiles in Figure 4.5a, 4.5b and 4.5c. It is worth noting that no Cr$_2$O$_3$ oxide was found in the healed area.

Figure 4.5 (a) Secondary electron cross-sectional SEM image and corresponding elemental maps of crack area after healing at 1200 °C in air for 4h. (b-c) EDX spectrum at positions 1 and 2 indicated by red and green cross in Figure 4.5a.

The microstructure of the healed area in four different positions (indicated by yellow rectangular) from crack root to crack tip is shown in Figure 4.6. It can be seen in Figure 4.6b1 and 4.6b2 that after 4 hours’ heat treatment at 1200 °C in air, the crack gap near the crack root was not fully healed. However, the crack gap in Figure 4.6b3 and 4.6b4 was almost fully healed. The average width of Al$_2$O$_3$ is comparable in positions b1, b2 and b3, indicating a similar healing rate along the crack as shown in
Table 4.1. The maximum crack width that could be healed by Al\textsubscript{2}O\textsubscript{3} at 1200 °C for 4 hours, therefore, is estimated to be around 4.8 µm.

It is worth noting that the crack in position b4 was healed purely by Al\textsubscript{2}O\textsubscript{3} and no Cr\textsubscript{7}C\textsubscript{3} layer is observed. The absence of Cr\textsubscript{7}C\textsubscript{3} is attributed to the high Al vacancy tolerance of Cr\textsubscript{2}AlC. \textit{Ab initio} calculation suggested that the Al vacancy tolerance could be as high as 0.5 for Ti\textsubscript{2}AlC [20]. As Cr\textsubscript{2}AlC has the same crystal structure as that of Ti\textsubscript{2}AlC, the Al vacancy tolerance could be similar. Therefore, a crack with a width of less than 2 µm could be healed by Al\textsubscript{2}O\textsubscript{3} without the formation of Cr\textsubscript{7}C\textsubscript{3} sublayers.

Higher magnification SEM images of the healed area are shown in Figure 4.7. It can be seen in Figure 4.7a that the oxide scale formed on the Cr\textsubscript{2}AlC substrate is composed of two sublayers: one inner dense columnar Al\textsubscript{2}O\textsubscript{3} layer and one outer porous layer. This similar structure was also observed by Yang in a re-sintering process of Cr\textsubscript{2}AlC samples at 1100 °C [10]. For the oxide scale formed near the crack tip in Figure 4.7b, only the dense columnar Al\textsubscript{2}O\textsubscript{3} layer is observed. These results suggest that the porous Al\textsubscript{2}O\textsubscript{3} layer was formed after the existence of the dense columnar layer Al\textsubscript{2}O\textsubscript{3}.
Figure 4.6 Cross sectional secondary electron SEM images of crack after healing at 1200 °C for 4 hours in air: (a) a cross section image parallel to the crack growth direction of the healed crack with lower magnification; (b) higher magnification images for the areas of “b1”, “b2”, “b3”, “b4” in Figure 4.6a.

Table 4.1 Average Al₂O₃ width calculated along crack

<table>
<thead>
<tr>
<th>Position</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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<tbody>
<tr>
<td>Average width of Al₂O₃ (µm)</td>
<td>2.45</td>
<td>2.37</td>
<td>2.43</td>
<td>1.08</td>
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</tbody>
</table>
4.4 Discussion

4.4.1 Crack healing kinetics’ dependence on crack location

Previous oxidation experiment on surface notch of Ti$_2$AlC had shown a faster oxidation kinetics on the top part of the notch than that on the bottom. With an easier access to oxygen, the top part of the notch usually has a higher oxygen partial pressure, therefore, a higher healing kinetics [9]. For the crack healing process, it is reasonable to assume that the “zig-zag” shape of crack as well as crack closure effect during healing would result into a more significant difference in oxygen partial pressure over the whole crack. To address the influence of oxygen partial pressure on overall healing rate, two positions on the crack are chosen. The edges are assumed to have an easier access to oxygen, thus a higher oxygen partial pressure. For areas in the middle of the crack, the oxygen partial pressure should be the lower as the oxygen transport distance is high. The overall healing percentage as a function of
time at these two positions were calculated by averaging five lines at each position as shown in Figure 4.8a.

The healing process at the edge and middle seems to have a similar trend as shown in Figure 4.8b. After the initial 4 hours’ heat treatment, the healing percentage between edge and middle is almost identical at about 45%. As heat treatment time prolongs, the healing rate in both the middle and edge decreased. After 12 hours’ healing, the healing percentage for the edge and middle reached about 80% and 87% respectively. This small difference of healing percentage between edge and middle during the entire healing process demonstrated that the overall healing rate of Cr₂AlC is more or less independent to the oxygen partial pressure variance caused by crack location.

**Figure 4.8** (a) Illustration of two calculation positions. (b) Crack healing percentage as a function of healing time calculated at middle and edge of the crack, respectively.
For the crack healing process, one common concern is that the healing near crack tip may not be as effective as that in other areas. The reason for this assumption can be explained from two perspectives: Firstly, with an easier access to oxygen, the crack root usually has a higher oxygen partial pressure, while the oxygen partial pressure in the tip is lower. Therefore, if the healing rate is sensitive to oxygen partial pressure, then the crack root will be closed before the crack tip. Secondly, considering the long distance of oxygen transportation from atmosphere to crack tip, the possibility of crack shielding and sealing is high. The shielding effect may further intensify the uneven healing situation between crack root and tip. In extreme cases, total blockage of a crack area will render it unhealed regardless of healing time. In Figure 4.9, crack opening displacement along the crack propagation direction at different healing stages is calculated. Each data point represents the average crack opening displacement of the nearby 200 pixels (135.4 µm). The initial crack is about 1000 µm in length and 13 µm in width at crack root. After 4 hours’ heat treatment, the COD reduced more or less equally along the crack at round 4 µm. However, an unusually large COD decrease could be seen as indicated by the dashed line. This result is consistent with previous observations where crack areas with Cr particles adjacent to crack surface have a faster healing kinetics. A similar “dissolution” phenomenon happened together with this “unusual” quick crack closure. The mechanism of this phenomenon will be discussed later. After 12 hours healing, crack area near tip is almost fully healed with COD of less than 1 µm.

This high healing percentage achieved near the crack tip as well as the independence of healing rate on crack location shown above is probably due to the fact that Cr$_2$AlC has a slower healing kinetics than many of its counterparts such as Ti$_2$AlC and Ti$_3$AlC [5, 14-15, 21-22]. The influence of this slower healing rate on crack healing could be addressed in two ways: 1) A slower oxidation kinetics under similar healing conditions (in air) suggests that the dominant factor for oxidation of Cr$_2$AlC is more likely to be atom diffusion rather than oxygen partial pressure. Therefore, the influence of crack location induced oxygen partial difference has small effect on crack healing kinetics. 2) This small difference in healing rate along the crack results in a homogeneous healing kinetics over the whole crack area. Therefore, the healed
zone will develop from crack tip towards crack root. In this way, the possibility of oxygen path blockage is largely reduced.

Figure 4.9 (a) Crack opening displacement (COD) calculated along crack growth direction at different healing steps. (b1~b4) 2D X-ray tomographic cross sections correlated to the COD plots at different healing stages.
4.4.2 Healing mechanism of Cr$_2$AlC

Based on the microstructure characterization of the healed area along the crack presented in Section 4.3 as well as previous oxidation experiments, the healing process of Cr$_2$AlC is proposed to generally have two stages: An early stage where Al and Cr are oxidized simultaneously as shown in reaction 4-1, below. In this stage a dense columnar Al$_2$O$_3$ layer is formed on the Cr$_2$AlC matrix. At high temperature, Cr$_2$O$_3$ is reported to be able to transform to CrO$_3$, which has a high volatile pressure above 1100 °C [23, 24]. Therefore, Cr$_2$O$_3$ is not detected in the healed region. After a continuous dense Al$_2$O$_3$ layer is formed, the diffusion rate of Cr and Al atoms will be largely reduced. However, due to a relative weak Cr-Al bond and a strong Cr-C bond, selective oxidation of Al will occur through grain boundaries of columnar Al$_2$O$_3$. In this case, a porous Al$_2$O$_3$ is formed on top of the columnar Al$_2$O$_3$ layer. As a result, the microstructure of the healed area varies along the crack. The crack tip with a relatively smaller crack width will be healed by solely dense Al$_2$O$_3$. For crack areas with larger crack width, the healed area will be composed of a middle layer of porous Al$_2$O$_3$ with dense Al$_2$O$_3$ layers on the two sides. The depletion of Al usually results in the formation of a Cr$_7$C$_3$ sublayer beneath the Al$_2$O$_3$ layer, as shown in reaction 4-2. Recent research by Li shows that the Cr$_7$C$_3$ will continue to react with oxygen and form Cr$_2$O$_3$, as shown in reaction 4-3 [25]. Therefore, for long time healing, Cr$_7$C$_3$ layer will become thinner over time.

\[
2Cr_2AlC + 6.5O_2 = 2Cr_2O_3 \uparrow + Al_2O_3 + 2CO_2 \uparrow \tag{4-1}
\]

\[
14Cr_2AlC + 12.5O_2 = 7Al_2O_3 + 4Cr_7C_3 + 2CO_2 \uparrow \tag{4-2}
\]

\[
2Cr_7C_3 + 16.5O_2 = 7Cr_2O_3 \uparrow + 6CO_2 \uparrow \tag{4-3}
\]

The complex reactions happened during the oxidation process of Cr$_2$AlC, as well as the weight loss due to the formation of CO$_2$ and Cr$_2$O$_3$, make it difficult to correlate the TGA data previously reported to the healing kinetics. Therefore, a direct COD measurement from the X-ray tomography data is shown in Figure 4.10a. The results show that the COD decreases as healing time increases, indicating the crack was
gradually healed over time. The curve fitting result shows that the kinetics of healed crack width follows a parabolic law with a parabolic constant of $4.3 \times 10^{-3} \, \mu m^2 \cdot s^{-1}$, indicating crack healing rate decreases over time.

![Graph](image)

**Figure 4.10** (a) Crack opening displacement as a function of time. (b) Square of healed crack width as a function of oxidation time.

### 4.4.3 Correlative study

Previous results indicate that the existence of Cr particles may accelerate the healing process of nearby crack surface. This phenomenon is very interesting, because the existence of impurity Cr phase could be turned into a positive factor for the healing ability of this material. To further investigate this phenomenon, correlative analysis was conducted on the Cr$_2$AlC sample, which had been scanned by X-ray tomography in several healing steps. The cylindrical Cr$_2$AlC sample was ground layer by layer along the crack growth direction until it reaches the tomographic slice as shown in Figure 4.11. It can be seen that the secondary electron SEM image (Figure 4.11e) matches well with the X-ray tomographic slices (Figure 4.11d).

It can be seen in the tomographic micrographs from Figure 4.11a to Figure 4.11d that there were two particles interacting with the crack healing process, as indicated by arrows in Figure 4.11a. The original crack passes through particle 1, breaking it into two smaller parts. Although it seems that the particle 2 is not in direct contact with the crack, in subsequent tomographic slices the crack propagated along the interface of Cr particle 2 and the Cr$_2$AlC matrix (not shown here for brevity). After 4 hours’ heat treatment at 1200 °C, the right part of particle 1 disappeared, leaving a white
layer around the original shape of the Cr particle, as shown in Figure 4.11b. In the meantime, the relatively large left part of particle 1 became smaller and then finally disappeared after 12 hours’ heat treatment at 1200 °C, as shown in Figure 4.11d. A similar white layer is observed around the original position of the left part of particle 1. A higher magnification image of the healed area near the Cr particle and the corresponding elemental mappings are shown in Figure 4.10f and 4.10h. Consistent with the tomographic slices, a grey area (composed of Cr and Al) was surrounded by the white layers (composed of Cr and C). Post element ratio calculation suggests that the grey area is CrAl, while the white layer is Cr$_7$C$_3$.

A similar process was observed on the interaction of crack healing and particle 2. However, the Cr$_7$C$_3$ layer gradually disappeared as healing time prolongs. After 12 hours’ heat treatment, the Cr$_7$C$_3$ was totally gone, with the formation of a pore, as shown in Figure 4.11g.
Figure 4.11 (a-d) 2D X-ray tomographic slices parallel to crack growth direction of Cr$_2$AlC after healing at 1200 °C in air at different healing time. (e) Secondary electron SEM image correlate to Figure 4.11d. (f-g) Higher magnification SEM images of healed area indicated by red rectangle in Figure 4.11e. (h) EDX elemental maps of Figure 4.11f.
CHAPTER 4  CRACK HEALING BEHAVIOUR OF Cr$_2$AlC

Based on the above analysis, an overall reaction for the crack area with a Cr particle nearby is proposed:

$$3Cr_2AlC + 4Cr + 3O_2 \rightarrow CrAl + Cr_2O_3 + Al_2O_3 + Cr_7C_3$$  \hspace{1cm} (4-4)

In the initial process, the Cr particle is oxidized to form Cr$_2$O$_3$. The existence of Cr$_2$O$_3$ provides a nucleation site for Al$_2$O$_3$, thus increasing the formation speed of Al$_2$O$_3$ and accelerating the diffusion of Al from nearby Cr$_2$AlC matrix. The depletion of Al at the Cr-Cr$_2$AlC interface result in the formation of a Cr$_7$C$_3$ layer. As the healing time prolongs, Cr$_7$C$_3$ continues to react with oxygen to form Cr$_2$O$_3$ and the Cr$_2$O$_3$ is subsequently transformed to the CrO$_3$ phase, which has a high volatile pressure at high temperature. The vaporization of CrO$_3$ left some large pores in the healed area, which may have a negative effect on strength recovery after healing.

4.5 Conclusion

Our results demonstrated that non-destructive x-ray tomography together with post correlative study can be used to study dynamic crack healing process of Cr$_2$AlC. The healing process of Cr$_2$AlC at 1200 °C in air is recorded by X-ray tomography with a resolution of 0.677 µm$^3$/voxel. Based on our current results, a few conclusions could be made as the followings.

I. The crack healing of Cr$_2$AlC is an oxidation process, where crack gap is filled by purely Al$_2$O$_3$. A sublayer of Cr$_7$C$_3$ is observed when the crack width exceeds 2 µm. The Al$_2$O$_3$ scale is composed of a dense columnar layer and a porous layer.

II. The crack healing kinetics of Cr$_2$AlC at 1200 °C in air followed a parabolic rate law with constant of $4.3\times10^{-3}$ µm$^2$·s$^{-1}$. The maximum crack width that could be fully healed at 1200 °C in air for 4 and 12 hours is around 4.8 µm and 10 µm respectively.

III. The existence of impurity Cr particles facilitated the healing process by providing Cr$_2$O$_3$ nucleation site and the post evaporation of Cr$_2$O$_3$ may leave large pores near the healed area, which may reduce strength recovery.
4.6 Acknowledgements

The authors would like to thank China Scholarship Council for providing the financial support on this research.
4.7 Reference


Supplementary information

Figure 4.12 Band contrast EBSD image of as received Cr$_2$AlC sample. The average grain size is around 23 µm.

Figure 4.13 XRD pattern of as received Cr$_2$AlC sample. A small amount of impurity Cr phase was detected.
Chapter 5 Conclusion and future work

5.1 Conclusion

In the present study, the autonomous crack healing behaviour of Ti$_2$AlC and Cr$_2$AlC were investigated using both synchrotron and laboratory Computed X-ray tomography at temperatures of 1150 °C and 1200 °C, respectively. Computed X-ray tomography, especially rapid speed high resolution synchrotron X-ray tomography, proved its unique advantage to study the crack healing process dynamically. Three-dimensional internal information was obtained at different healing stages, which helped to deepen the understanding of crack healing in MAX phase ceramics. Based on results presented in previous chapters, some main conclusion can be made:

I. Ti$_2$AlC shows a remarkable capability of repeatedly repairing cracks at 1150 °C in air. Crack locations with over 24 μm in width were successfully healed in less than 66 minutes’ heat treatment, even in the third healing cycle. In comparison, the crack healing kinetics of Cr$_2$AlC is significantly slower. The crack root with around 13 μm in width was partially healed at 1200 °C in air after 12 hours. This result is consistent with previous surface oxidation experiments reported on Ti$_2$AlC and Cr$_2$AlC, where the oxidation kinetics of Cr$_2$AlC is several orders of magnitude slower than that of Ti$_2$AlC. The excellent oxidation resistance, which is usually an advantage of Cr$_2$AlC, is a downside in terms of healing speed.

II. The rehealing process of Ti$_2$AlC will maintain its original healing rate if the crack grows following a new propagation path after healing, which is seen in the second healing cycle. However, the rehealing rate of the crack propagated through the same path (previous healed area) will result in a retardation of the healing speed due to the oxidation protection provided by existing oxides, which was observed in the third healing cycle in this study. Ideally, the crack will propagate through a new path after every healing cycle. In this way, the healing ability is maximized.
III. The crack healing behaviour of Ti$_2$AlC shows a strong dependence on crack locations, where the crack root in the first healing cycle exhibited much faster healing rate than that of the crack tip. While the crack healing of Cr$_2$AlC is more or less independent of crack locations, where crack area near tip is always healed first and the healed area is expected to develop from crack tip to crack root. The reason of a stronger dependence on crack location for Ti$_2$AlC could be attributed to its higher oxidation rate, thus being more sensitive to oxygen partial pressure. With easier access to oxygen, the oxygen partial pressure at crack root is higher than that at crack tip. Therefore, if a crack healing process is sensitive to oxygen partial pressure, a faster healing rate at the crack root is expected, which is the case for Ti$_2$AlC.

IV. The strength recovery after healing is closely related to healing percentage. A full strength recovery was achieved when the healing percentage is over 90% after the first healing cycle. However, a partial strength recovery is observed after the second healing cycle, when the healing percentage is around 85%. For the loading geometry tested, the unhealed crack root is more detrimental to strength recovery than internal unhealed crack area.

V. The impurity Cr particles in Cr$_2$AlC were revealed to have a positive effect in terms of crack healing speed. However, the structural integrity of the healed areas may be compromised due to the large pores left. These are probably formed by evaporation of Cr$_2$O$_3$ at high temperature.

VI. The microstructure of the healed region in Cr$_2$AlC is dependent on its crack width. Therefore, along the crack, the microstructure could be different. The crack area near crack tip is healed mainly by dense Al$_2$O$_3$ without the formation of Cr$_7$C$_3$. While the crack area healed at crack root is composed of a dense Al$_2$O$_3$ layer adjacent to matrix and a porous Al$_2$O$_3$ layer next to the dense Al$_2$O$_3$ layer. In addition, the formation of Cr$_7$C$_3$ underneath the Al$_2$O$_3$ layer is usually observed for crack locations with a larger width.
5.2 Future work

Based on results and discussions presented in this thesis, a number of interesting fields concerning the healing behaviour of MAX phase ceramics is proposed.

5.2.1 Microstructure characterization of healing oxide of Ti$_2$AlC in different healing cycles

I. Previous oxidation experimental work on the surface notch of Ti$_2$AlC showed a microstructure difference between oxides formed at the bottom and the top part of the notch, due to a difference in surface curvature. Given that the crack propagation in MAX phase ceramics usually exhibits a “zig-zag” crack path, the surface curvature varies along the crack. Therefore, it would be interesting to investigate the influence of crack surface curvature on microstructure of oxide formed after healing.

II. In Chapter 3, the Ti$_2$AlC shows a remarkable cyclic healing capability. For an ideal healing material, strength should be recovered after each healing cycle. As the post-strength recovery is closely related to the microstructure of the healed area, it would be beneficial to compare the microstructures of oxides formed after each healing cycle and relate that to the strength recovery after healing.

III. In addition, the healed area of Cr$_2$AlC characterized in Chapter 4 showed an influence of crack width on the composition and microstructure of the healing oxides. The healing oxide formed at the crack tip is different from that formed at the crack root. Thus, it is worth analysing the influence of crack width on composition and microstructures of oxides formed in Ti$_2$AlC.

5.2.2 Post-healing crack propagation in healed area

In Chapter 4, the oxide microstructure of Cr$_2$AlC is revealed to be related to the crack width due to a preferential oxidation reaction. As a result, the microstructure of healed area varies along the crack. As the crack propagated through a healed area, different phases and structures of oxides are expected to be formed ahead of the
crack tip. Therefore, it is interesting to observe how crack propagates through these healed areas.

5.2.3 Image based modelling work on crack healing kinetics and post-crack growth of MAX phase ceramics

I. In Chapter 3, the comparison between the uniform healing model and actual healing data implied that the healing rate varies according to crack location, which is probably due to the influence of oxygen partial pressure. Simulation studies taking account of the oxygen flow within the crack would be a better approximation to the actual situation and thus deepening our understandings for the crack healing kinetics of MAX phase ceramics.

II. The ultimate purpose of the self-healing mechanism is to regain a material’s structural integrity. The post-healing crack growth is shown in Chapter 3 to be related to healing percentage and unhealed crack area. Therefore, it would be interesting to simulate the influence of these factors on strength recovery and crack propagation.