

Effect of Si Alloying on the Self-healing Kinetics of Cr₂AlC
and
Phase Formation of Nb₂AlC Thin Films

Von der Fakultät für Georessourcen und Materialtechnik der
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 Cr_2AlC and Phase Formation of Nb_2AlC Thin Films**

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Abstract

In the first part of this thesis, the phase stability of $(\text{Cr}_{1-x}\text{M}_x)_2(\text{Al}_{1-y}\text{A}_y)(\text{C}_{1-z}\text{X}_z)$ ($M = \text{Ti}, \text{Hf}, \text{Zr}; A = \text{Si}, X = \text{B}$, space group $\text{P6}_3 / \text{mmc}$, prototype Cr_2AlC) was studied using *ab initio* calculations. Based on the energy of mixing data as well as the density of states (DOS) analysis, $(\text{Cr}_{1-x}\text{Zr}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}\text{Hf}_x)_2\text{AlC}$ are predicted to be unstable, whereas $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$, $\text{Cr}_2(\text{Al}_{1-y}\text{Si}_y)\text{C}$ and $\text{Cr}_2\text{Al}(\text{C}_{1-z}\text{B}_z)$ are predicted to be stable or metastable. The density of states analysis reveals that small differences in the position of the Fermi level alters the phase stability: $(\text{Cr}_{1-x}\text{Zr}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}\text{Hf}_x)_2\text{AlC}$ are predicted to be unstable or metastable as the Fermi level lies at a peak position. While the Cr dominated DOS for $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ plateaus at the Fermi level indicating stability. Implications of these results for the vapour phase condensation of self-healing Cr_2AlC based materials are discussed.

The second part of the thesis deals with the effect of Si alloying on the self-healing kinetics of Cr_2AlC films. Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films were synthesized by DC magnetron sputtering at 600°C in an industrial chamber. Oxidation experiments were performed at 1120°C in air for 4 hours for the Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) films. The crystal structure, microstructure and chemical composition of the as-deposited as well as oxidized films have been investigated. It was found that alloying Cr_2AlC with up to 0.7 at% Si causes an increase in self-healing rate of up to $40 \pm 17\%$. Electron microscopy and atom probe tomography data support the notion that the here reported Si concentration induced 40% increase in self-healing rate is enabled by the Si concentration induced, and hence concomitant, increase in nucleation density of the healing agent.

In the last part of the thesis, the relationship between chemical composition and phase formation of Nb-Al-C thin films was studied by combinatorial thin film synthesis and *ab initio* calculations. Thin films with lateral chemical composition gradients were synthesized by DC magnetron sputtering using elemental targets at substrate temperatures of 710-870 °C. The lowest formation temperature for Nb₂AlC is between 710 and 750 °C. A predominantly single phase Nb₂AlC region where 99% of the X-ray diffraction intensity originates from Nb₂AlC was identified. Furthermore, selected area electron diffraction analysis reveals the local formation of single phase Nb₂AlC. The limited Al solubility in Nb₂AlC compared with Cr₂AlC can be readily understood by comparing the defect formation energy of Al substituting Nb and Cr in Nb₂AlC and Cr₂AlC, respectively. This methodology may serve as indicator for the magnitude of the A-element homogeneity range in $M_{n+1}AX_n$ phases. The structural and elastic properties of Nb₂AlC determined experimentally are in very good agreement with the *ab initio* calculated data.

Zusammenfassung

Im ersten Teil der Arbeit wird die Phasenstabilität von $(\text{Cr}_{1-x}\text{M}_x)_2(\text{Al}_{1-y}\text{A}_y)(\text{C}_{1-z}\text{X}_z)$ ($M = \text{Ti, Hf, Zr; A = Si, X = B, Raumgruppe } P6_3 / mmc, \text{ Prototyp } \text{Cr}_2\text{AlC}$) mittels *ab initio*-Berechnungen untersucht. Auf der Grundlage von Daten zur Mischungsenergie sowie Zustandsdichteanalysen (density of states analyses, DOS) werden $(\text{Cr}_{1-x}\text{Zr}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}\text{Hf}_x)_2\text{AlC}$ als instabile Phasen vorhergesagt, während $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$, $\text{Cr}_2(\text{Al}_{1-y}\text{Si}_y)\text{C}$ und $\text{Cr}_2\text{Al}(\text{C}_{1-z}\text{B}_z)$ als stabile bzw. metastabile Phasen errechnet werden. Die Zustandsdichteanalysen zeigen, dass geringe Unterschiede in der Position der Fermi-Level die Phasenstabilität beeinflussen: $(\text{Cr}_{1-x}\text{Zr}_x)_2\text{AlC}$ und $(\text{Cr}_{1-x}\text{Hf}_x)_2\text{AlC}$ werden als instabil bzw. metastabil vorhergesagt, da das Fermi-Niveau in einem Hochpunkt liegt, während für die Cr-dominierten Zustandsdichten im $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ das Fermi-Niveau in einem Plateau liegt und somit auf Phasenstabilität hindeuten. Die Auswirkung dieser Ergebnisse auf die Schichtsynthese mittels Gasphasenkondensation von selbstheilenden Cr_2AlC -Basiswerkstoffen wird diskutiert.

Im zweiten Teil der Arbeit wird der Einfluss der Legierung mit Si auf die Selbstheilungskinetik von Cr_2AlC -Dünnschichten untersucht. Cr_2AlC - und $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$)-Dünnschichten wurden mittels DC-Magnetronsputters bei 600°C in einer Industrieanlage synthetisiert und anschließend bei $1120^\circ\text{C}/4\text{h}$ an Luft oxidiert. Die chemische Zusammensetzung, Kristallstruktur und die Mikrostruktur der abgeschiedenen Schichten sowie der oxidierten Schichten wurde untersucht. Die Ergebnisse zeigen, dass die Legierung mit bis zum 0,7% Si führt zu einem Anstieg der Selbstheilungsrate um bis zu $40 \pm 17\%$. Die Daten der Elektronenmikroskopie und Atomsondentomographie unterstützen das Konzept, dass die hier berichtete Si-Konzentration induzierte 40%ige Erhöhung der Selbstheilungsrate durch die Si-

Konzentration induzierte, und somit die begleitende, Erhöhung der Nukleationsdichte des Heilungsmittel ermöglicht wird.

Im letzten Teil der Arbeit wird der Zusammenhang zwischen der chemischen Zusammensetzung und der Phasenbildung in Nb-Al-C-Schichten mittels kombinatorischer Dünnschichtsynthese und *ab initio*-Berechnungen untersucht. Dünnschichten mit lateralem Zusammensetzungsgradienten wurden mittels DC-Magnetronspüterns mit elementaren Targets bei Substrattemperaturen von 710-870°C abgeschieden. In Bezug auf die Phasenbildung in Nb₂AlC wurde die niedrigste Bildungstemperatur zwischen 710 und 750 °C gemessen. Diese Methode kann als Indikator für die Größe des A-Element Homogenitätsbereich in $M_{n+1}AX_n$ Phasen dienen. Die strukturellen und elastischen Eigenschaften von Nb₂AlC bestimmt sind experimentell in sehr guter Übereinstimmung mit der *ab initio* berechneten Daten.

Preface

The following papers contributed to this thesis:

Paper I

**Phase stability predictions of $(\text{Cr}_{1-x}\text{M}_x)_2(\text{Al}_{1-y}\text{A}_y)(\text{C}_{1-z}\text{X}_z)$
($M = \text{Ti, Hf, Zr}$; $A = \text{Si}$, $X = \text{B}$)**

L. Shang, D. Music, M. to Baben, J.M. Schneider
Journal of Physics D: Applied Physics 47 (2014) 065308

Paper II

40% increase in Cr_2AlC self-healing rate by minute Si additions

L. Shang, K.G. Pradeep, S. Sandlöbes, M. to Baben, J.M. Schneider
Submitted

Paper III

**Phase formation of Nb_2AlC investigated by combinatorial thin film synthesis
and *ab initio* calculations**

L. Shang, M. to Baben, K.G. Pradeep, S. Sandlöbes, M. Amalraj, M. Hans, K. Chang,
D. Music, D. Primetzhof, J.M. Schneider
In Press, Journal of the European Ceramic Society

Publications related to the topics of this thesis:

Solid particle erosion behaviour of thin film Cr_2AlC MAX phase nanolaminates

D. Eichner, A. Schlieter, C. Leyens, L. Shang, M. to Baben, J.M. Schneider
In Manuscript

**Reducing the erosive wear rate of Cr_2AlC MAX phase ceramic by oxidative
healing of local impact damage**

L. Shen, D. Eichner, S. van der Zwaag, C. Leyens, W.G. Sloof
Wear 358-359 (2016) 1-6

Other publications:

Oxygen incorporation in $M_2\text{AlC}$ ($M = \text{Ti, V, Cr}$)

M. to Baben, L. Shang, J. Emmerlich, J.M. Schneider
Acta Materialia 60 (2012) 4810-4818

Nanometer-scale voids in MAX phase Cr_2AlC

Y.T. Chen, D. Music, L. Shang, J. Mayer, J.M. Schneider
In Manuscript

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Table of Contents

1	Introduction.....	1
2	Theoretical methods.....	6
2.1	<i>Ab initio</i> calculations.....	6
3	Experimental methods.....	11
3.1	Magnetron sputtering.....	11
3.1.1	Magnetron sputtering of Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films	11
3.1.2	Magnetron sputtering of Nb-Al-C thin films	13
3.2	Characterization.....	13
3.2.1	Characterization of Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films	13
3.2.2	Characterization of Nb-Al-C thin films	15
4	Results and discussion.....	19
4.1	Phase stability predictions of $(\text{Cr}_{1-x},\text{M}_x)_2(\text{Al}_{1-y},\text{A}_y)(\text{C}_{1-z},\text{X}_z)$ ($\text{M} = \text{Ti, Hf, Zr}$; $\text{A} = \text{Si, X} = \text{B}$).....	19
4.1.1	Introduction	19
4.1.2	<i>Ab initio</i> calculations.....	20
4.1.3	Summary.....	30
4.2	Effect of Si alloying on the self-healing kinetics of Cr_2AlC : enhanced self-healing rate of $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) films at 1120°C in air.....	30
4.2.1	Introduction	30
4.2.2	Experiments	32
4.2.3	Summary.....	48
4.3	Phase formation of Nb_2AlC investigated by combinatorial thin film synthesis and <i>ab initio</i> calculations	50
4.3.1	Introduction	50
4.3.2	Experiments and <i>ab initio</i> calculations	52
4.3.3	Summary.....	62
	Conclusions	63
5	Future work	66
6	References	68

1 Introduction

Nowadays, component properties are commonly designed to meet the operational demands in various environments for a certain period of time before efforts have to be made to repair or replace the component parts “externally”. Unlike conventional materials, self-healing materials are designed in such a way that the damage which has been inflicted during service of a component part made of or protected by a self-healing material can be healed autonomously (Figure 1). The high reliability and durability of the self-healing materials make them especially attractive for applications where a component part is difficult and expensive to repair, for example, for using as asphalt concrete, underground piping material and protective coating for the turbine blade. An ideal crack healing material should exhibit the following properties [1]:

- It can heal crack damage completely, i.e. the material has identical or enhanced properties after healing than before the crack formed.
- It can heal crack damage autonomously, i.e. without addition of a healing agent and while the component is in service.
- It can heal crack damage multiple times.

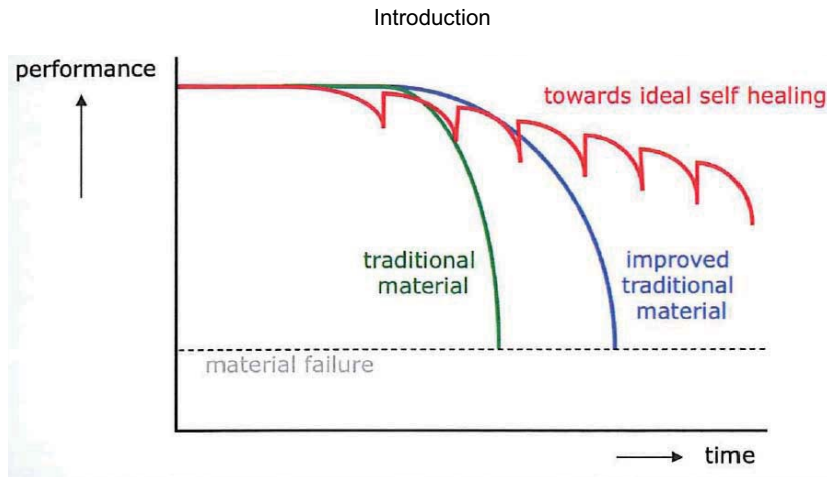


Figure 1: Materials performance as a function of time [2].

Similar to crack damage, erosion damage due to the impact of solid particles involves crack formation and abrasion of the protective material. Hence, extended from the crack damage management concept, an ideal erosion damage healing material should exhibit the following properties:

- It can heal surface crack networks and interlayer cracks completely and autonomously.
- It can heal surface scratches completely and autonomously.
- It can heal erosion damage repeatedly.

Although no ideal crack healing material has been discovered yet, the ability for crack healing was demonstrated already for some polymers, metals and ceramics [1, 3]. The candidate self-healing materials focused in this thesis are the so called $M_{n+1}AX_n$ phases (M : early transition metal, A : A group element, mostly IIIA or IVA, X : C or N, $n = 1-3$). The $M_{n+1}AX_n$ phases are nanolaminates consisting of periodically sequenced

Introduction

layers with metallic ($M-A$) and covalent/ionic bonding ($M-X$) [4-6]. Hence, they exhibit a singular combination of ceramic and metallic properties such as high stiffness [7, 8] and thermal stability [4, 9], good thermal and electrical conductivity [4], good machinability [4], good oxidation [10-16] and corrosion resistance [4], which makes them attractive for many advanced applications involving very high temperatures and harsh environments. Recently it has been shown that the $M_{n+1}AX_n$ phases Ti_3AlC_2 [17], Ti_2AlC [18, 19] and Cr_2AlC [20] exhibit autonomous self-healing behavior. Cracks are filled and hence healed by oxidation products of the M and A elements in the $M_{n+1}AX_n$ phase at high operating temperatures. After crack healing the fracture strength of Ti_2AlC [19] is recovered to the level of the virgin material. However, it was shown that the oxide scale covering $Ti_{n+1}AlC_n$ phases consists of Al_2O_3 as well as TiO_2 [16-19], where the latter may act as crack initiation sites. Therefore, it is anticipated that Cr_2AlC based materials are advantageous self-healing materials since $\alpha-Al_2O_3$ formation has been reported for oxidation at 1000 °C and above [10-15, 21]. Moreover, a proof-of-concept of multiple erosion damage healing of Cr_2AlC has been demonstrated experimentally [22]. However, the Al_2O_3 scale formed on Cr_2AlC is slow-growing, which results in long healing time even at high temperature. As it is well known that the oxidation rate of Cr_2AlC can be affected by alloying, for example, with Ti [23], it is anticipated that alloying candidates which increase the healing rate of Cr_2AlC can be identified.

Therefore, the goal of this thesis is three-fold: firstly, to select the potential alloying candidates for enhancing Cr_2AlC self-healing rate based on theoretical phase stability predictions; secondly, to provide an experimental evaluation of the effect of the alloying element concentration on the self-healing rate of Cr_2AlC ; Lastly, to investigate the phase formation of Nb_2AlC by combinatorial thin film synthesis and *ab*

Introduction

initio calculations since Nb₂AlC may be another potential self-healing $M_{n+1}AX_n$ phase material.

With the advancement in computational power and theory of electronic structure calculation, knowledge-based materials design guided by quantum mechanics could be realized. In chapter 4.1, the phase stability of $(Cr_{1-x}M_x)_2(Al_{1-y}A_y)(C_{1-z}X_z)$ ($M = Ti, Hf, Zr$; $A = Si$, $X = B$) was studied using *ab initio* calculations. Based on the energy of mixing data as well as the density of states (DOS) analysis, $(Cr_{1-x}Zr_x)_2AlC$ and $(Cr_{1-x}Hf_x)_2AlC$ are predicted to be unstable, whereas $(Cr_{1-x}Ti_x)_2AlC$, $Cr_2(Al_{1-y}Si_y)C$ and $Cr_2Al(C_{1-z}B_z)$ are predicted to be stable or metastable. Therefore, it is suggested that Ti, Si and B are promising alloying candidates. Since experimentally, Yu *et al.* [24] reported synthesis of bulk $Cr_2AlSi_{0.2}C$, Si was selected as the alloying element for synthesizing $Cr_2(Al_{1-x}Si_x)C$ ($0 < x < 1$) thin films by combinatorial DC magnetron sputtering. In chapter 4.2, the oxidation of the Cr_2AlC and $Cr_2Al_{1-x}Si_xC$ ($0 < x \leq 0.06$) films synthesized by DC magnetron sputtering at 600 °C was studied. The crystal structure, microstructure and chemical composition of the as-deposited as well as oxidized films were investigated. 40% increase in Cr_2AlC self-healing rate has been achieved by alloying with 0.7 at% Si. Electron microscopy and atom probe tomography data support the notion that the here reported Si concentration induced 40% increase in self-healing rate is enabled by the Si concentration induced, and hence concomitant, increase in nucleation density of the healing agent.

Chapter 4.3 focuses on another potential self-healing $M_{n+1}AX_n$ phase material Nb₂AlC. The relationship between chemical composition and phase formation of Nb-Al-C thin films was studied by combinatorial thin film synthesis and *ab initio* calculations. Thin films with lateral chemical composition gradients were synthesized by DC magnetron sputtering using elemental targets at substrate temperatures of 710-870 °C. The

Introduction

lowest formation temperature for Nb_2AlC is between 710 and 750 °C. A predominantly single phase Nb_2AlC region where 99% of the X-ray diffraction intensity originates from Nb_2AlC was identified. The lattice parameters and mechanical properties of Nb_2AlC were reported.

2 Theoretical methods

2.1 *Ab initio* calculations

Density Functional Theory (DFT) is a quantum mechanical computational approach used to describe the electronic structure of many-electron systems. It was conceived in 1927, shortly after the foundation of quantum mechanics, by Thomas and Fermi [25, 26]. However, the Thomas and Fermi model is semi-classical and it did not solve the many-body interaction issues. Then in the middle of the 1960s, Hohenberg and Kohn [27] laid a firm theoretical foundation demonstrating that the ground state properties of a many-electron system are a functional of the electron density and that the ground state energy minimizes this electron energy functional.

In this thesis, *ab initio* calculations based on density functional theory [28] were performed using the Vienna *ab initio* simulation package (VASP) [29]. Generalized-gradient approximation (GGA) based projector augmented wave potentials [30] were used, as well as a Monkhorst-Pack scheme [31] for reciprocal-space integration and the tetrahedron method with Blöchl-corrections for the total energy [32]. The convergence criterion for the total energy (E) was 0.01 meV within a 500 eV cutoff. $2 \times 2 \times 2 M_{n+1}AX_n$ phase supercells containing 64 atoms were used on a $5 \times 5 \times 3$ k -points grid.

The structural optimization was performed by a least square fitting of the total energy obtained from at least nine calculations using three different sets of a and c/a values with the following polynomial function:

$$E(a, c) = x_1 \cdot a^2 + x_2 \cdot c^2 + x_3 \cdot a \cdot c + x_4 \cdot a + x_5 \cdot c + x_6. \quad (1)$$

Theoretical methods

For these calculations, ions were allowed to relax, so that the energetic minimum with respect to the lattice parameters a and c as well as the internal free parameters could be obtained. The energy of formation ΔE_f was calculated by the following formula:

$$\Delta E_f = \frac{1}{\sum n_i} (E_{\text{tot}} - \sum n_i \cdot E_i), \quad (2)$$

where E_{tot} is the total energy of the compound, n_i is the number of atoms of species i in the compound and E_i is the energy of species i in its reference state.

The calculated total energy and lattice parameters of the pure reference elements are listed in Table 1.

Table 1: Calculated total energy and lattice parameters of the pure reference elements.

Element	Structure	a (Å)	c/a	E_{tot} (eV/atom)
Cr	bcc	2.851	---	-9.451
Al	fcc	4.039	---	-3.713
C	diamond	3.575	---	-9.096
Ti	hcp	2.936	1.589	-7.793
Hf	hcp	3.194	1.592	-9.824
Zr	hcp	3.244	1.600	-8.421
Si	diamond	5.470	---	-5.424
B	rhombohedral	2.831	---	-6.686

Theoretical methods

Nb	bcc	3.297	---	-10.251
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To evaluate the phase stability of $(\text{Cr}_{1-x}\text{M}_x)_2(\text{Al}_{1-y}\text{A}_y)(\text{C}_{1-z}\text{X}_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si, X} = \text{B}$), the compositions of the alloying elements were designed as the following:

- The Ti, Hf and Zr contents in the M sublattice were 0/32, 1/32, 2/32, 4/32, 8/32, 16/32, 24/32 and 32/32 so that $x = 0.000, 0.031, 0.063, 0.125, 0.250, 0.500, 0.750$ and 1.000 , respectively.
- The Si and B contents in the A and X sublattices were 0/16, 1/16, 2/16, 4/16, 8/16, 12/16 and 16/16 so that $y, z = 0.000, 0.063, 0.125, 0.250, 0.500, 0.750$ and 1.000 , respectively.

Five $2 \times 2 \times 2$ supercell configurations containing 64 atoms were probed (see Figure 2 for an M sublattice example). Configuration (a) was based on special quasirandom structures (SQS) [33]. The (111) planes from NaCl SQS were used to build the M -C planes in the Cr_2AlC based supercells. The SQS implementation via short-range order (SRO) parameter is available within the locally self-consistent Green's function (LSGF) software package [34, 35]. Here, the LSGF code was only used to generate SQS supercells required for the calculations within the VASP code. The Warren-Cowley SRO parameter [36] was applied to account for randomness and the values of < 0.02 were obtained within 5 coordination shells. Other configurations were ordered and, in particular, the configuration (b) is clustered (*c.f.* Figure 2). This configuration sampling approach was used for metastable $\text{Ti}_{1-x}\text{Al}_x\text{N}$ [37] and clustering has been observed via atom probe tomography [38-40]. As configuration (b) in these $M_{n+1}\text{AX}_n$ phase solutions on the M sublattice were the most stable, *i.e.* clustering occurred, A and X sublattices were probed with less configurations

Theoretical methods

excluding SQS due to very demanding supercell construction. In the discussion in chapter 4.1, only clustered configurations are discussed as they appear to be the ground state.

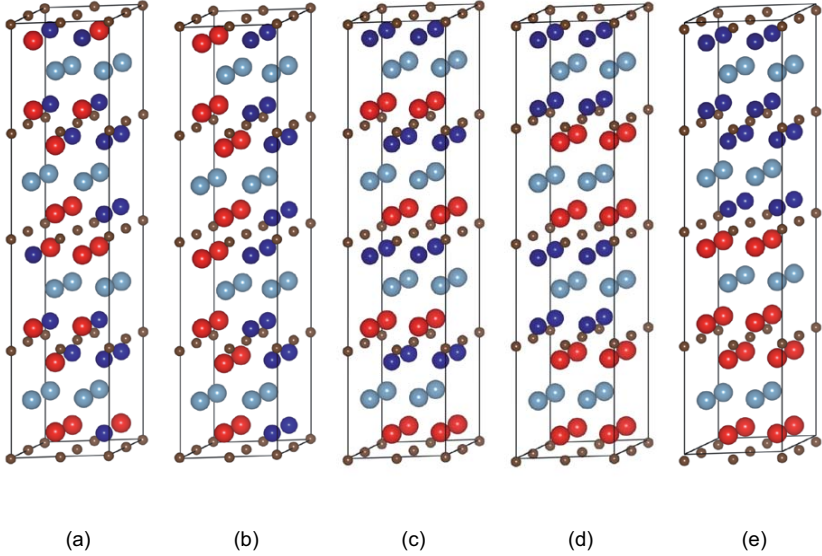


Figure 2: Supercell configurations considered for $(\text{Cr}_{0.5}, \text{M}_{0.5})_2\text{AlC}$ ($M = \text{Ti}, \text{Hf}, \text{Zr}$). The dark blue spheres correspond to Cr atoms, red to M atoms, light blue to Al atoms and brown to C atoms.

The energy of mixing ΔE_{mix} at 0 K for each composition with alloying elements on M, A and X sites was calculated by evaluating the energy difference between the solid solution $(\text{Cr}_{1-x}, \text{M}_x)_2(\text{Al}_{1-y}, \text{A}_y)(\text{C}_{1-z}, \text{X}_z)$ and the unmixed components Cr_2AlC , M_2AlC , Cr_2AC and Cr_2AlX ($M = \text{Ti}, \text{Hf}, \text{Zr}$; $A = \text{Si}$, $X = \text{B}$):

for alloying on M site:

$$\Delta E_{\text{mix}} = \Delta E_{\text{f}}((\text{Cr}_{1-x}, \text{M}_x)_2\text{AlC}) - (1-x)\Delta E_{\text{f}}(\text{Cr}_2\text{AlC}) - x\Delta E_{\text{f}}(\text{M}_2\text{AlC}), \quad (3)$$

Theoretical methods

for alloying on A site:

$$\Delta E_{\text{mix}} = \Delta E_f(\text{Cr}_2(\text{Al}_{1-y}, \text{A}_y)\text{C}) - (1-y)\Delta E_f(\text{Cr}_2\text{AlC}) - y\Delta E_f(\text{Cr}_2\text{AC}), \quad (4)$$

for alloying on X site:

$$\Delta E_{\text{mix}} = \Delta E_f(\text{Cr}_2\text{Al}(\text{C}_{1-z}, \text{X}_z)) - (1-z)\Delta E_f(\text{Cr}_2\text{AlC}) - z\Delta E_f(\text{Cr}_2\text{AX}). \quad (5)$$

To study the solubility of Al in Nb_2AlC and Cr_2AlC , the energy of formation for Al substituting M ($M = \text{Nb}, \text{Cr}$) was calculated using the following equation:

$$\Delta E_{f, \text{Al} \rightarrow M} = 1/x(E_{M_{2-x}\text{Al}_{1+x}\text{C}} - E_{M_2\text{AlC}} + xE_M - xE_{\text{Al}}). \quad (6)$$

One M ($M = \text{Nb}, \text{Cr}$) atom was substituted by one Al atom in the supercell, resulting in 31 M , 17 Al and 16 atoms and an M/Al ratio of 1.82.

The bulk modulus of Nb_2AlC was determined by fitting energy-volume curves using the Birch-Murnaghan equation of states [41]. The corresponding elastic modulus was calculated using a Poisson's ratio of $\nu = 0.257$ [42].

3 Experimental methods

In this work, $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) and Nb-Al-C films were synthesized by combinatorial DC magnetron sputtering [43]. This deposition technique allows the formation of concentration gradients. Hence the relationship between chemical composition, structure and mechanical properties can be investigated efficiently if spatially resolved characterization techniques are employed [43]. The oxidation experiments were performed at 1120 °C in air for 4 hours for Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) films. The heating and cooling rates were 50 °C/min and 10 °C/min respectively. To characterize the samples, various characterization techniques were employed and the details can be found in section 3.2.

3.1 Magnetron sputtering

3.1.1 Magnetron sputtering of Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films

Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films were synthesized by DC magnetron sputtering in an industrial chamber (CC800/9, CemeCon AG, Wuersele, Germany). A compound target with a size of 50 cm x 8.8 cm x 1 cm produced by a powder metallurgical process consisting of a Cr:Al:C stoichiometry of 2:1:1 (provided by PLANSEE Composite Materials GmbH, Lechbruck am See, Germany) was used to deposit Cr_2AlC films. A split compound target displayed in Fig. 3(a) was used to deposit the $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films shown in Fig. 3(b). The split target with a size of 50 cm x 8.8 cm x 1 cm (provided by PLANSEE Composite Materials GmbH, Lechbruck am See, Germany) was also produced via a powder metallurgical route consisting of a Cr:Al:C stoichiometry of 2:1:1 in the upper part, and in the lower part a Cr:Si:C stoichiometry of 2:1:1. In Fig. 3(b) the 23 polycrystalline $\alpha\text{-Al}_2\text{O}_3$ substrates

Experimental methods

(KERAFOIL Keral 99, 1.5 cm x 1.5 cm x 0.038 cm, as-fired, roughness $R_a = 0.2 \mu\text{m}$) as displayed were located along the vertical target axis at a distance of 5 cm to the magnetron and heated to 600 °C prior to deposition. The base pressure was below 1 mPa and the Ar pressure during deposition was 190 mPa. The combinatorial deposition was performed at 600 °C for 3 hours with a target power density of 2.2 W/cm². The geometric arrangements of the Si and Al rich target segments displayed in Fig. 3(a) results in a Si concentration gradient in the as-deposited films which was measured along the vertical target axis by energy dispersive X-ray spectroscopy (EDS) as depicted in Fig. 3(c).

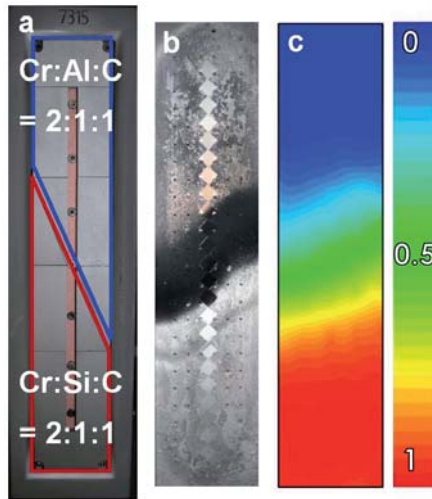


Figure 3: (a) Photograph of the split Cr-Al-C / Cr-Si-C target. (b) Photograph of the 23 coated substrates on the sample holder located along the vertical axis of the target. (c) Si concentration gradient x ($0 < x < 1$) in the as-deposited films measured along the vertical axis of the target.

3.1.2 Magnetron sputtering of Nb-Al-C thin films

Nb-Al-C thin films with lateral chemical composition gradients were synthesized by combinatorial DC magnetron sputtering [43] in a high vacuum chamber using Nb (99.95% purity), Al (99.99% purity) and C (99.99% purity) targets with 50.8 mm in diameter. Sapphire (001) wafers with 50.8 mm in diameter were used as substrates and heated to the deposition temperatures prior to deposition. The sample to target distance was 100 mm. The base pressure after heating was below $2 \cdot 10^{-4}$ Pa and the Ar pressure during deposition was 0.4 Pa. The depositions were performed at 710, 750, 800 and 870 °C for 60 min. The power densities at the Nb, Al and C targets were 5.4, 2.5 and 9.9 W/cm², respectively. In the predominantly single phase Nb₂AlC region, the film exhibited a thickness of about 1.2 µm, corresponding to a deposition rate of 20 nm/min.

3.2 Characterization

3.2.1 Characterization of Cr₂AlC and Cr₂Al_{1-x}Si_xC (0 < x < 1) films

Characterization of Cr₂Al_{1-x}Si_xC (0 < x < 1) films was performed using measurement grid points along the Si gradient with 7 mm in spacing resulting in 3 points measured per deposited film.

Structural analysis was carried out using X-ray diffraction (XRD) in a Bruker AXS D8 Discover General Area Detector Diffraction System (GADDS) with Cu Kα radiation at room temperature for Cr₂AlC and Cr₂Al_{1-x}Si_xC (0 < x < 1) films. The voltage and current settings were 40 kV and 40 mA respectively. An incidence angle of 10° and a pinhole collimator with 0.5 mm in diameter was used.

Energy dispersive X-ray spectroscopy and scanning electron microscopy (SEM) (JEOL JSM-6480 with attached EDAX Genesis 2000) was used for compositional

Experimental methods

and microstructural investigations, respectively. For chemical composition analysis, a Cr-Al-Si-C film sample quantified by wavelength dispersive X-ray spectroscopy (WDS) served as standard and an acceleration voltage of 12 kV was used. For $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films, 3 compositions were measured on each coated substrate, resulting in 69 compositions in total. Henceforth, we will refer to each composition as individual sample for simplicity. For microstructural imaging, an acceleration voltage of 10 kV was used.

For cross-sectional sample preparation, a copper layer was deposited onto the sample surface to enhance electrical conductivity as well as to protect the film. The samples were then embedded in resin and afterwards grinded and polished with diamond paper and diamond suspensions, respectively.

The surface oxide layer thicknesses of the oxidized samples were measured by the so called “cut-and-weigh” method. SEM images of the film cross sections were printed out on DIN A4 paper (80 g/m² paper white) and weighed using an analytical balance (AZ64, Sartorius, Germany) with an accuracy of 0.1 mg. Afterwards the oxide layer fraction of the image were carefully cut along the contour and then weighed. Knowing the length l , height t_0 and weight w_0 of the SEM image, and the weight of the oxide layer w , the average thickness t of the oxide layer distributed over a length of l can be calculated using the following equation:

$$t = \frac{w}{w_0} t_0 \quad (7)$$

The thickness data for each composition was calculated by averaging 6 thickness values obtained from SEM images measured at 6 positions evenly distributed over the sample cross section. Since each SEM image covers a length of 25-50 μm , sufficient statistics have been obtained over a length of 150-300 μm by averaging 6

Experimental methods

thickness values. The standard deviation calculated from the 6 individual thickness measurements serves as measure for the thickness distribution.

Transmission electron microscopy (TEM) imaging was performed to reveal the cross sections of the as-deposited samples using a Philips CM20 TEM operated at 200 kV. The cross-sectional TEM samples were prepared using a dual-beam focused ion beam (FIB) workstation FEI Helios NanoLab 660 equipped with a concentric transmission detector. The scanning transmission electron microscopy (STEM) imaging was performed in the dual-beam FIB operated at 30 kV. For quantitative analysis of the grain size of the cross-sectional TEM samples, image analysis software ImageJ [44] was used.

To measure the local chemical composition, particularly the Si distribution in the oxidized *MAX* phase sample containing 0.7 at% Si after oxidation, tips for 3D atom probe tomography (3D APT) analysis were prepared by site-specific lift out from three different sample regions in a FIB workstation FEI Helios NanoLab 660. Specifically, the tips were aligned along the growth direction and were extracted from the oxide region, the Al depleted chromium carbide region immediately below the oxide region and the *MAX* phase region underneath the chromium carbide region. The 3D APT measurements were performed at a temperature of 60 K in a Cameca LEAP 4000X HR in the laser pulse mode with a laser pulse energy of 40 pJ. Data reconstruction and analysis were done using the Cameca IVAS 3.6.8 software.

3.2.2 Characterization of Nb-Al-C thin films

To characterize the Nb-Al-C thin films, measurements were performed along a 7 mm x 7 mm mesh over the whole wafer. A measurement grid with 7 mm spacing between each grid point was applied as shown in Figure 4. To precisely identify the

Experimental methods

predominantly single phase Nb_2AlC region, a finer measurement grid with 1.75 mm spacing between each grid point was applied as shown in Figure 4. In total 99 grid points were used and hence 99 different compositions were measured per wafer. Henceforth, we will refer to the grid points as individual samples for simplicity. The chemical composition was measured by energy dispersive X-ray spectroscopy in a JEOL JSM-6480 scanning electron microscope equipped with an EDAX Genesis 2000 system using an acceleration voltage of 10 kV. Each measurement covered an area of $42\text{ }\mu\text{m} \times 32\text{ }\mu\text{m}$. A Nb-Al-C thin film sample quantified by Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) served as standard.

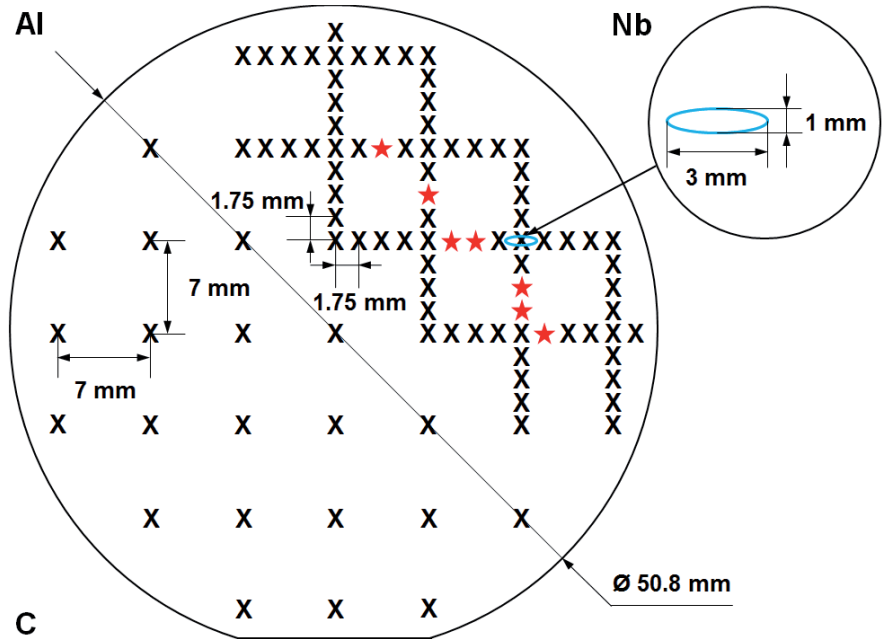


Figure 4: Schematic drawing of the probed grid points by means of XRD and EDS. The asterisks indicate the positions of the 7 predominantly single phase Nb_2AlC

Experimental methods

samples. The XRD irradiated surface ellipse is schematically drawn. The dimensions of the ellipse are shown in the enlarged inset.

The ToF-ERDA measurement was carried out at the tandem accelerator laboratory at Uppsala University, Sweden. $^{127}\text{I}^{8+}$ primary ions with 36 MeV energy were used as projectiles and the recoils were monitored in a time-of-flight setup with a detection angle of 45° . Further details regarding the setup can be found in a detector efficiency study by Zhang *et al.* [45]. Systematic uncertainties in the order of 5% of the deduced values for the concentrations may be expected due to possible inaccuracies in the employed detection efficiencies and the stopping power for primary and recoiling particles. The obtained depth profile (ca. 300 nm penetration depth) of Nb, Al and C was homogenous and average values were used for EDS calibration.

Structural analysis was carried out using XRD in a Bruker AXS D8 Discover General Area Detector Diffraction System (GADDS) with Cu K α radiation on the same grid points as applied for the EDS measurements (Figure 4). The set voltage and current were 40 kV and 40 mA, respectively. The primary beam was collimated using a pinhole with 0.5 mm in diameter. An incidence angle of $\theta = 10^\circ$ was used for detector scans and an incidence angle of $\theta = 6.4^\circ$ together with a detector position of $2\theta = 12.8^\circ$ were used for resolving the (002) peak of Nb₂AlC. The irradiated surface ellipse dimensions measured using a fluorescence sample were 1 mm in width and 3 mm in length (Figure 4) for $\theta = 10^\circ$. The corresponding irradiated area is 2.4 mm².

TEM imaging was performed using a Philips CM20 TEM operated at 200 kV. The cross-sectional samples were prepared using a dual-beam FIB workstation FEI Helios NanoLab 660.

Experimental methods

The elastic properties were measured by nanoindentation in a Hysitron TI-900 TriboIndenter employing the method of Oliver and Pharr [46]. The thin film had an arithmetic mean roughness (R_a) of 40 nm. 25 indentations were performed per grid point or sample with a Berkovich tip at a maximum load of 4 mN. The contact area was determined by a calibration measurement on fused silica. A Poisson's ratio of $\nu = 0.257$ [42] was used to calculate the elastic moduli of the Nb_2AlC samples. The elastic modulus was obtained by averaging over 175 values.

4 Results and discussion

4.1 Phase stability predictions of $(\text{Cr}_{1-x}\text{M}_x)_2(\text{Al}_{1-y}\text{A}_y)(\text{C}_{1-z}\text{X}_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si, X = B}$)

4.1.1 Introduction

The $M_{n+1}AX_n$ phases (M : early transition metal, A : A group element, mostly IIIA or IVA, X : C or N, $n = 1-3$) are nanolaminates consisting of periodically sequenced layers with metallic ($M-A$) and covalent/ionic bonding ($M-X$) [4-6]. Hence, they exhibit a singular combination of ceramic and metallic properties such as high stiffness [7, 8] and thermal stability [4, 9], good thermal and electrical conductivity [4], good machinability [4], good oxidation [10-16] and corrosion resistance [4], which makes them attractive for many advanced applications involving very high temperatures and harsh environments. Recently it has been shown that the $M_{n+1}AX_n$ phases Ti_3AlC_2 [17], Ti_2AlC [18, 19] and Cr_2AlC [20] exhibit autonomous self-healing behavior. Cracks are filled and hence healed by oxidation products of the M and A elements in the $M_{n+1}AX_n$ phase at high operating temperatures. After crack healing the fracture strength of Ti_2AlC [19] is recovered to the level of the virgin material. However, it was shown that the oxide scale covering $\text{Ti}_{n+1}\text{AlC}_n$ phases consists of Al_2O_3 as well as TiO_2 [16-19], where the latter may act as crack initiation sites. Therefore, it is anticipated that Cr_2AlC based materials are advantageous self-healing materials since $\alpha\text{-Al}_2\text{O}_3$ formation has been reported for oxidation at 1000 °C and above [10-15, 21]. Moreover, a proof-of-concept of multiple erosion damage healing of Cr_2AlC has been demonstrated experimentally [22]. However, the Al_2O_3 scale is slow-growing, which results in long healing times even at high temperature. As it is well known that

Results and discussion

the oxidation rate of Cr_2AlC can be affected by alloying, for example, with Ti [23], it is aimed to identify alloying candidates that may increase the healing rate. Si and B are investigated here as potential alloying elements as they act as grain refiners in titanium alloys [47, 48]. In addition to Ti, also the other two naturally occurring group IVB elements, Hf and Zr, are studied as potential alloying agents. While alloying candidates are expected to affect the self-healing behavior of Cr_2AlC , no systematic study of the phase stability of $(\text{Cr}_{1-x}, \text{M}_x)_2(\text{Al}_{1-y}, \text{A}_y)(\text{C}_{1-z}, \text{X}_z)$ solid solutions has been reported to date. Therefore, this work aims to provide a theoretical evaluation on the phase stability of Cr_2AlC based solid solutions with the above described alloying agents to select alloying elements for future design of Cr_2AlC based materials with increased self-healing kinetics compared to Cr_2AlC .

The influence of the alloying elements on the M , A and X sites on the phase stability of $(\text{Cr}_{1-x}, \text{M}_x)_2(\text{Al}_{1-y}, \text{A}_y)(\text{C}_{1-z}, \text{X}_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si}$, $X = \text{B}$, space group $\text{P6}_3 / \text{mmc}$, prototype Cr_2AlC) was studied using *ab initio* calculations. The results are discussed based on the energy of mixing data as well as the density of states (DOS) analysis. $(\text{Cr}_{1-x}, \text{Zr}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}, \text{Hf}_x)_2\text{AlC}$ are predicted to be unstable, whereas $(\text{Cr}_{1-x}, \text{Ti}_x)_2\text{AlC}$, $\text{Cr}_2(\text{Al}_{1-y}, \text{Si}_y)\text{C}$ and $\text{Cr}_2\text{Al}(\text{C}_{1-z}, \text{B}_z)$ are predicted to be stable or metastable.

4.1.2 *Ab initio* calculations

4.1.2.1 Energy of mixing of $(\text{Cr}_{1-x}, \text{M}_x)_2(\text{Al}_{1-y}, \text{A}_y)(\text{C}_{1-z}, \text{X}_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si}$, $X = \text{B}$)

Figure 5 shows the calculated energy of mixing ΔE_{mix} for $(\text{Cr}_{1-x}, \text{M}_x)_2(\text{Al}_{1-y}, \text{A}_y)(\text{C}_{1-z}, \text{X}_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si}$, $X = \text{B}$) as a function of alloying element content (x , y and z), the values of which are listed in Table 2. It can be seen that the energy of mixing for $(\text{Cr}_{1-x}, \text{Hf}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}, \text{Zr}_x)_2\text{AlC}$ increases from 0 to 0.073 and 0.087 eV/atom,

Results and discussion

respectively, as x increases from 0 to 0.25 and is positive over the whole x range. The energy of mixing for $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ is slightly positive as x increases from 0 to 0.063 and then becomes negative as x increases further. Moreover, the most negative value -0.045 eV/atom is achieved at $x = 0.5$. The energy of mixing for $\text{Cr}_2(\text{Al}_{1-y}\text{Si}_y)\text{C}$ and $\text{Cr}_2\text{Al}(\text{C}_{1-z}\text{B}_z)$ is slightly negative as x increases from 0 to 1. This indicates that $(\text{Cr}_{1-x}\text{Hf}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}\text{Zr}_x)_2\text{AlC}$ are unstable with respect to Cr_2AlC and the hypothetical Hf_2AlC and Zr_2AlC . $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ could be stable or metastable with respect to Cr_2AlC and Ti_2AlC , which is consistent with the prediction from Sun *et al* [49]. However, the calculated energy of mixing at $x = 0.5$ and $x = 0.75$ in this work is more negative than that calculated by Sun *et al*. This could be due to the different supercell sizes used in the calculations. $\text{Cr}_2(\text{Al}_{1-y}\text{Si}_y)\text{C}$ and $\text{Cr}_2\text{Al}(\text{C}_{1-z}\text{B}_z)$ with mixing energies varying from -0.0004 to -0.0054 eV/atom are expected to be stable or metastable with respect to Cr_2AlC and the hypothetical Cr_2SiC and Cr_2AlB . However, it is well known that when kinetically limited synthesis techniques are employed, metastable phases form, as it has been reported for $\text{Ti}_{1-x}\text{Al}_x\text{N}$ [37] and $\text{Cr}_{1-x}\text{Al}_x\text{N}$ [50]. Hence, it is reasonable to assume that under non-equilibrium conditions, for example, during plasma assisted vapour deposition, $(\text{Cr}_{1-x}\text{Hf}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}\text{Zr}_x)_2\text{AlC}$ may form as metastable phases. The calculated energy of mixing for $\text{Ti}_{1-x}\text{Al}_x\text{N}$ [37] and $\text{Cr}_{1-x}\text{Al}_x\text{N}$ [50] are reported to be in the range of 0.05 to 0.15 eV/atom and hence comparable to the data obtained here for all solid solutions investigated.

Results and discussion

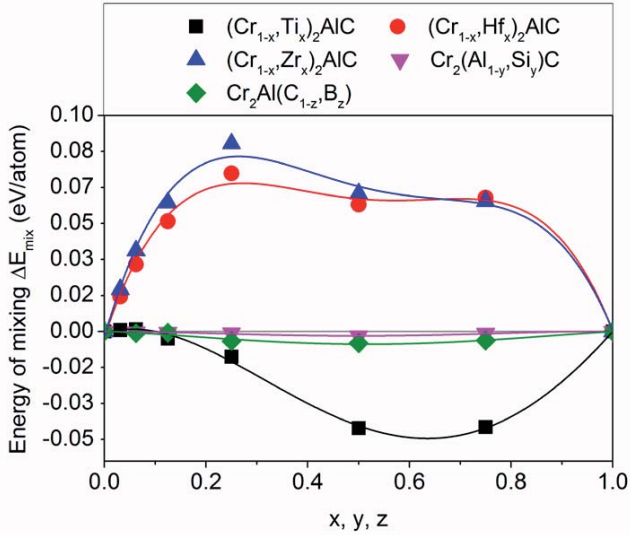


Figure 5: Energy of mixing ΔE_{mix} for $(\text{Cr}_{1-x}, M_x)_2(\text{Al}_{1-y}, A_y)(\text{C}_{1-z}, X_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si}$, $X = \text{B}$) as a function of alloying element content (x , y and z). The curves are polynomial fits of the data.

Table 2 lists the fraction percentage of alloying element r , calculated lattice parameters a and c , equilibrium volume V , energy of formation ΔE_f and energy of mixing ΔE_{mix} for $(\text{Cr}_{1-x}, M_x)_2(\text{Al}_{1-y}, A_y)(\text{C}_{1-z}, X_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si}$, $X = \text{B}$). The change in lattice parameters with alloying element substitutions could be due to the size effect of the alloying atoms, the difference in bonding characters (i.e. metallic or covalent bonds), the geometric alteration of the bonding configuration [51] *etc.*.

Table 2: Fraction percentage of alloying element r , calculated lattice parameters a and c ($\text{\AA}$), equilibrium volume V ($\text{\AA}^3$), energy of formation ΔE_f (eV/atom) and energy

Results and discussion

of mixing ΔE_{mix} (eV/atom) for $(\text{Cr}_{1-x}\text{M}_x)_2(\text{Al}_{1-y}\text{A}_y)(\text{C}_{1-z}\text{X}_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si}$, $X =$

B).

Phases	r	a	c	V	ΔE_f	ΔE_{mix}
Cr_2AlC	0.0000	2.845	12.710	89.12	-0.230	--
$\text{Cr}_{1.9375}\text{Ti}_{0.0625}\text{AlC}$	0.0156	2.852	12.738	89.73	-0.244	0.0006
$\text{Cr}_{1.875}\text{Ti}_{0.125}\text{AlC}$	0.0313	2.859	12.759	90.34	-0.258	0.0010
$\text{Cr}_{1.75}\text{Ti}_{0.25}\text{AlC}$	0.0625	2.873	12.825	91.65	-0.292	-0.0033
$\text{Cr}_{1.5}\text{Ti}_{0.5}\text{AlC}$	0.1250	2.900	12.936	94.21	-0.358	-0.0117
CrTiAlC	0.2500	2.949	13.186	99.34	-0.506	-0.0448
$\text{Cr}_{0.5}\text{Ti}_{1.5}\text{AlC}$	0.3750	2.999	13.486	105.01	-0.621	-0.0442
Ti_2AlC	0.5000	3.071	13.722	112.10	-0.693	--
$\text{Cr}_{1.9375}\text{Hf}_{0.0625}\text{AlC}$	0.0156	2.859	12.760	90.30	-0.231	0.0162
$\text{Cr}_{1.875}\text{Hf}_{0.125}\text{AlC}$	0.0313	2.875	12.831	91.86	-0.232	0.0310
$\text{Cr}_{1.75}\text{Hf}_{0.25}\text{AlC}$	0.0625	2.906	12.914	94.45	-0.244	0.0511
$\text{Cr}_{1.5}\text{Hf}_{0.5}\text{AlC}$	0.1250	2.963	13.175	100.18	-0.287	0.0732
CrHfAlC	0.2500	3.073	13.483	110.26	-0.432	0.0587
$\text{Cr}_{0.5}\text{Hf}_{1.5}\text{AlC}$	0.3750	3.174	13.884	121.13	-0.559	0.0619
Hf_2AlC	0.5000	3.270	14.388	133.24	-0.751	--
$\text{Cr}_{1.9375}\text{Zr}_{0.0625}\text{AlC}$	0.0156	2.862	12.782	90.67	-0.226	0.0195
$\text{Cr}_{1.875}\text{Zr}_{0.125}\text{AlC}$	0.0313	2.880	12.838	92.21	-0.222	0.0374
$\text{Cr}_{1.75}\text{Zr}_{0.25}\text{AlC}$	0.0625	2.907	12.946	94.71	-0.230	0.0597
$\text{Cr}_{1.5}\text{Zr}_{0.5}\text{AlC}$	0.1250	2.993	13.143	101.93	-0.261	0.0870
CrZrAlC	0.2500	3.115	13.455	113.03	-0.401	0.0639
$\text{Cr}_{0.5}\text{Zr}_{1.5}\text{AlC}$	0.3750	3.237	13.861	125.76	-0.522	0.0603

Results and discussion

Zr ₂ AlC	0.5000	3.334	14.600	140.51	-0.700	--
Cr ₂ Al _{0.9375} Si _{0.0625} C	0.0156	2.850	12.654	89.01	-0.228	-0.0004
Cr ₂ Al _{0.875} Si _{0.125} C	0.0313	2.844	12.621	88.43	-0.226	-0.0005
Cr ₂ Al _{0.75} Si _{0.25} C	0.0625	2.853	12.502	88.13	-0.221	-0.0008
Cr ₂ Al _{0.5} Si _{0.5} C	0.1250	2.865	12.279	87.30	-0.213	-0.0022
Cr ₂ Al _{0.25} Si _{0.75} C	0.1875	2.872	12.088	86.36	-0.202	-0.0009
Cr ₂ SiC	0.2500	2.879	11.898	85.42	-0.191	--
Cr ₂ AlC _{0.9375} B _{0.0625}	0.0156	2.849	12.704	89.30	-0.225	-0.0008
Cr ₂ AlC _{0.875} B _{0.125}	0.0313	2.852	12.705	89.49	-0.220	-0.0006
Cr ₂ AlC _{0.75} B _{0.25}	0.0625	2.860	12.705	90.02	-0.212	-0.0045
Cr ₂ AlC _{0.5} B _{0.5}	0.1250	2.869	12.640	90.07	-0.190	-0.0054
Cr ₂ AlC _{0.25} B _{0.75}	0.1875	2.887	12.661	91.41	-0.165	-0.0042
Cr ₂ AlB	0.2500	2.892	12.707	92.02	-0.138	--

4.1.2.2 Electronic origin of the phase stability of (Cr_{1-x},M_x)₂(Al_{1-y},A_y)(C_{1-z},X_z) (*M* = Ti, Hf, Zr; *A* = Si, *X* = B)

To identify the electronic origin of the phase stability of (Cr_{1-x},M_x)₂(Al_{1-y},A_y)(C_{1-z},X_z) (*M* = Ti, Hf, Zr; *A* = Si, *X* = B), the total DOS as well as partial density of states (PDOS) for (Cr_{0.5},Ti_{0.5})₂AlC, (Cr_{0.5},Hf_{0.5})₂AlC, (Cr_{0.5},Zr_{0.5})₂AlC, Cr₂(Al_{0.5},Si_{0.5})C and Cr₂Al(C_{0.5},B_{0.5}) are illustrated in Figures 6-10. In all solid solutions, the largest contribution to states near Fermi level comes from metal-to-metal *d-d* interactions. There is no band gap and the DOS distributions have finite values at the Fermi level. Strong hybridization has been found for *M d*, *A p*, and *C p* states leading to the formation of covalent *M-A* and *M-C* bonds, which is consistent with earlier work [5, 6].

Results and discussion

For $(\text{Cr}_{0.5}, \text{Ti}_{0.5})_2\text{AlC}$, $(\text{Cr}_{0.5}, \text{Hf}_{0.5})_2\text{AlC}$ and $(\text{Cr}_{0.5}, \text{Zr}_{0.5})_2\text{AlC}$, interestingly, the PDOS of the transition metals Ti, Hf and Zr exhibit no shift in the energy level compared to Cr (*c.f.* Figures 6-8). The states which are located from approximately -7 to -2.8 eV below the Fermi level, originate from the hybridization of transition metal *d*-C *p* orbitals. The states located at adjacent higher energy levels, extending from approximately -2.8 to -1 eV, are dominated by the hybridized transition metal *d*-A *p* orbitals. The Fermi level of $(\text{Cr}_{0.5}, \text{Ti}_{0.5})_2\text{AlC}$ lies at an even region, and that of $(\text{Cr}_{0.5}, \text{Hf}_{0.5})_2\text{AlC}$ is located near a peak, while $(\text{Cr}_{0.5}, \text{Zr}_{0.5})_2\text{AlC}$ has the Fermi level located at a peak position. Moreover, the DOS at the Fermi level is dominated by the PDOS of Cr. The shape of the DOS at the Fermi level and its implications for the stability has been studied for Ti and Ni-based intermetallic compounds [52, 53] as well as for $M_2\text{AlC}$ (0001) ($M = \text{Ti}, \text{Cr}, \text{V}$; $A = \text{Al}, \text{Ga}, \text{Ge}$) surface energy [54]. Ravindran and Asokamani [52] have analyzed the phase stability of several intermetallics, such as Ti-Al, Ti-Fe, Zr-Al and Sc-Al, and correlated this to the DOS data. They pointed out that a peak in the vicinity of the Fermi level implies that a small perturbation in the Fermi level is associated with large changes in the number of states at the Fermi level, leading to reduced stability. The authors suggest that a compound is stable if its Fermi level falls on a pseudogap which separates the bonding region from antibonding/nonbonding region, while it is unstable or metastable if its Fermi level is located at a peak position. Therefore, the DOS based appraisal of the stability of the transition metal alloyed solid solutions is consistent with the previously discussed energy of mixing data (*c.f.* Figure 5 and Table 2).

For $\text{Cr}_2(\text{Al}_{0.5}, \text{Si}_{0.5})\text{C}$ and $\text{Cr}_2\text{Al}(\text{C}_{0.5}, \text{B}_{0.5})$, the basic DOS features are similar to that of $(\text{Cr}_{0.5}, M_{0.5})_2\text{AlC}$ ($M = \text{Ti}, \text{Hf}, \text{Zr}$) (*c.f.* Figures 9 and 10). The Fermi levels of $\text{Cr}_2(\text{Al}_{0.5}, \text{Si}_{0.5})\text{C}$ and $\text{Cr}_2\text{Al}(\text{C}_{0.5}, \text{B}_{0.5})$ are located at an even region. Therefore, the

Results and discussion

solutions are expected to be either stable or metastable. This is in agreement with the previous conclusions drawn from the energy of mixing data (*c.f.* Figure 5 and Table 2). In Figure 9 it can be seen that the Cr *d*-Si *p* bonding states are located at lower energy level compared to the Cr *d*-Al *p* bonding states, indicating increased stiffness of the Cr-Si bonds compared to Cr-Al bonds. This is consistent with the valence electron concentration induced stiffness enhancement predicted for $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ ($0 \leq x \leq 1$) as Al is substituted by Si [55]. Based on this prediction, a reduction in valence electron concentration as facilitated by the substitution of C by B should cause the Cr *d*-B *p* bonding states to be located at higher energy level relative to Cr *d*-C *p* bonding states, indicating decreased stiffness of the Cr-B bonds compared to Cr-C bonds. While attempts were made to substitute C in $M_{n+1}\text{AX}_n$ phases by B, Kephart *et al* [56] have reported the unsuccessful bulk synthesis of Ti_2GeB and Ti_3GeB_2 . Based on the calculation results, B and Si incorporation into Cr_2AlC appear to be possible. The here presented lattice parameter data (*c.f.* Table 2) will enable experimental validation of the here presented predictions.

Results and discussion

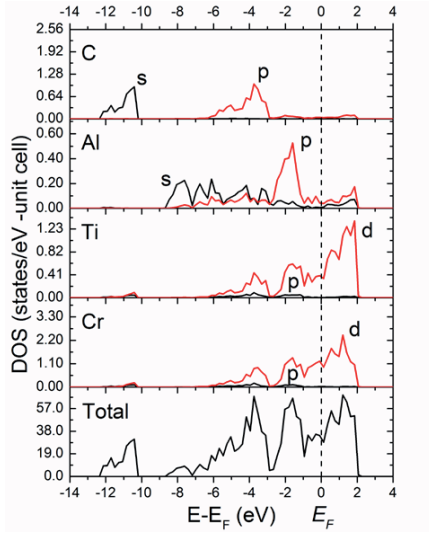


Figure 6: Total and partial density of states (DOS) for $(\text{Cr}_{0.5}\text{Ti}_{0.5})_2\text{AlC}$. The Fermi level is set to zero.

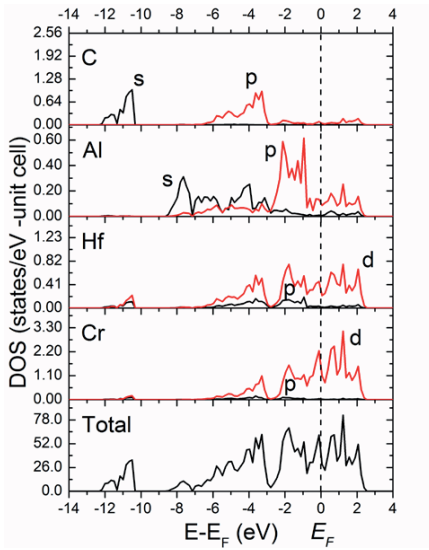


Figure 7: Total and partial density of states (DOS) for $(\text{Cr}_{0.5}\text{Hf}_{0.5})_2\text{AlC}$. The Fermi level is set to zero.

Results and discussion

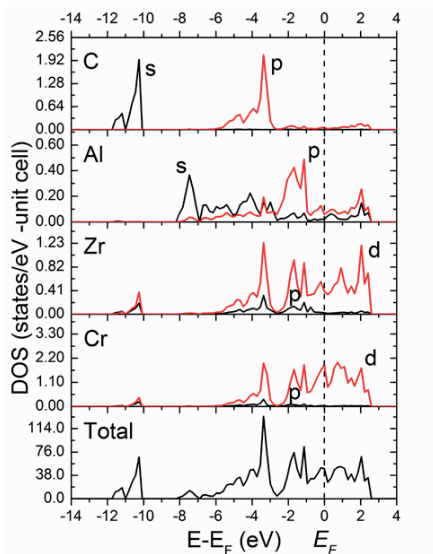
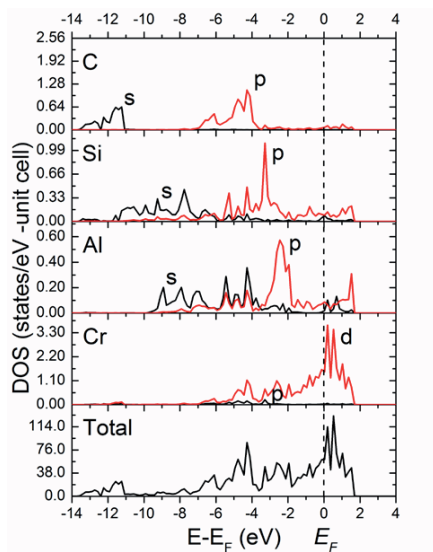


Figure 8: Total and partial density of states (DOS) for $(\text{Cr}_{0.5}\text{Zr}_{0.5})_2\text{AlC}$. The Fermi level is set to zero.



Results and discussion

Figure 9: Total and partial density of states (DOS) for $\text{Cr}_2(\text{Al}_{0.5}\text{Si}_{0.5})\text{C}$. The Fermi level is set to zero.

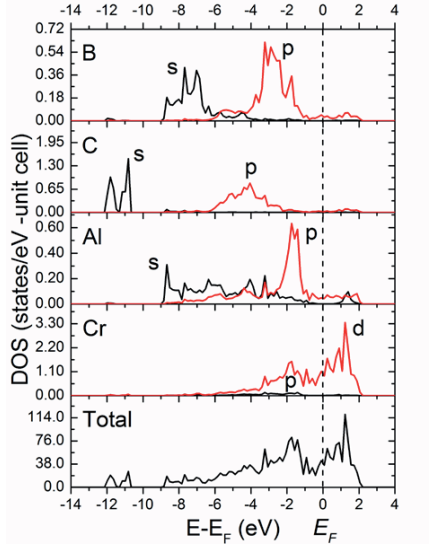


Figure 10: Total and partial density of states (DOS) for $\text{Cr}_2\text{Al}(\text{C}_{0.5}\text{B}_{0.5})$. The Fermi level is set to zero.

The correlation between the electronic structure (DOS data) and the phase stability of $M_{n+1}\text{AX}_n$ phases has been discussed in the literature: Generally, the phase stability with respect to population of bonding and antibonding/nonbonding states may be explained using crystal-orbital Hamilton population (COHP), crystal-orbital overlap population (COOP) and balanced crystal-orbital overlap population (BCOOP) analysis. A systematic COHP analysis has been carried out for $M_2\text{AlC}$ ($M = \text{Ti}, \text{V}, \text{Cr}$) [57]. Furthermore, Ti_2AlC [58] and Nb_3SiC_2 [59] have been described by COOP and BCOOP, respectively. In all these studies, the stability interpretations based on these population data are consistent with the DOS analysis. Hence, the DOS data and

interpretations describing the phase stability of the solid solutions in this work are physically sound.

4.1.3 Summary

The influence of the alloying elements on the M, A and X sites on the phase stability of $(Cr_{1-x},M_x)_2(Al_{1-y},A_y)(C_{1-z},X_z)$ ($M = Ti, Hf, Zr$; $A = Si$, $X = B$) was studied using *ab initio* calculations. Lattice parameters a and c , equilibrium volume, energy of formation and energy of mixing for $(Cr_{1-x},M_x)_2(Al_{1-y},A_y)(C_{1-z},X_z)$ ($M = Ti, Hf, Zr$; $A = Si$, $X = B$) have been calculated. Based on the energy of mixing data as well as the density of states analysis, $(Cr_{1-x},Zr_x)_2AlC$ and $(Cr_{1-x},Hf_x)_2AlC$ are predicted to be unstable, whereas $(Cr_{1-x},Ti_x)_2AlC$, $Cr_2(Al_{1-y},Si_y)C$ and $Cr_2Al(C_{1-z},B_z)$ are predicted to be stable or metastable. Implications of these results for the vapour phase condensation of self-healing Cr_2AlC based materials are discussed. Based on these results, alloying of Cr_2AlC with Si and B is expected to result in the formation of a solid solution and the self-healing behavior thereof may hence be evaluated experimentally.

4.2 Effect of Si alloying on the self-healing kinetics of Cr_2AlC : enhanced self-healing rate of $Cr_2Al_{1-x}Si_xC$ ($0 < x \leq 0.06$) films at 1120 °C in air

4.2.1 Introduction

Ternary metal carbides or nitrides with the general formula $M_{n+1}AX_n$ (M : early transition metal, A : A group element, mostly IIIA or IVA, X : C or N, $n = 1-3$) are nanolaminates with metallic ($M-A$) and covalent/ionic ($M-X$) bonding nature [4-6, 60].

Results and discussion

They have attracted a great deal of attention over the past decade due to their distinctive combination of metallic and ceramic properties [4, 60, 61]. Recently it has been reported that the $M_{n+1}AX_n$ phases Ti_3AlC_2 [17], Ti_2AlC [18, 19] and Cr_2AlC [20] show self-healing behavior: Cracks in Ti_2AlC was filled and thereby healed by the oxidation products of the M and A elements. After crack healing, the flexural strength of Ti_2AlC was restored to the level of the virgin material [19]. Hence, such materials are attractive for application as structural components or protective coatings at elevated temperatures and in harsh environments. They may significantly prolong their service lifespan if cracks can be healed *in situ*. However, the oxide scale of $Ti_{n+1}AlC_n$ phases consists of not only Al_2O_3 but also TiO_2 [16-19], where the discontinuously distributed TiO_2 may act as potential crack initiation sites. Therefore, it is anticipated that Cr_2AlC based materials are advantageous self-healing materials since $\alpha-Al_2O_3$ formation has been reported for oxidation at 1000 °C and above [10-15, 21]. Moreover, a proof-of-concept of multiple erosion damage healing of Cr_2AlC has been demonstrated experimentally [22].

However, the Al_2O_3 scale formation on Cr_2AlC is sluggish, resulting in long healing time even at elevated temperatures, which is undesired for real applications that require fast self-healing process such as in multiple erosion damage healing.

Based on the guidance provided by the *ab initio* phase stability calculations [62], Si was selected as an alloying agent for Cr_2AlC . While the synthesis of bulk $Cr_2AlSi_{0.2}C$ has been reported by Yu *et al.* [24], the oxidation behavior is unknown. In this work, the effect of Si additions on the phase formation and the oxidation kinetics of Cr_2AlC was investigated by spatially resolved analysis of the structure and composition.

4.2.2 Experiments

4.2.2.1 Characterization of the as-deposited Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films

XRD analysis of the as-deposited 23 $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films (Figure 3(b)) reveals that for films containing < 1.5 at% Si, only *MAX* phase peaks were identified, whereas for films containing ≥ 1.5 at% Si, the formation of other phases in addition to Si containing *MAX* phase was observed.

Figure 11 shows the X-ray diffractograms of the samples containing 0, 0.3, 0.7, 1.1, 1.5 and 5.6 at% Si. For samples containing 0, 0.3, 0.7 and 1.1 at% Si, the formation of $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ *MAX* phase was observed. For samples containing 1.5 and 5.6 at% Si, in addition to the *MAX* phase $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$, also diffraction peaks corresponding to $\text{Cr}_{5-x}\text{Si}_{3-z}\text{C}_{x+z}$ were identified. Pellegrini *et al.* [63] consider the $\text{Cr}_{5-x}\text{Si}_{3-z}\text{C}_{x+z}$ phase as an extension of $\beta\text{-Cr}_5\text{Si}_3$, where the carbon atoms are interstitially incorporated with a solubility range of $0.25 < x+z < 1.05$. Hence, the metastable solubility limit for Si determined by XRD analysis appears to be between 1.1 and 1.5 at% under the deposition conditions studied and the corresponding Si concentration range of the samples exhibiting diffraction peaks stemming only from $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ *MAX* phase is $0 < x < 0.06$.

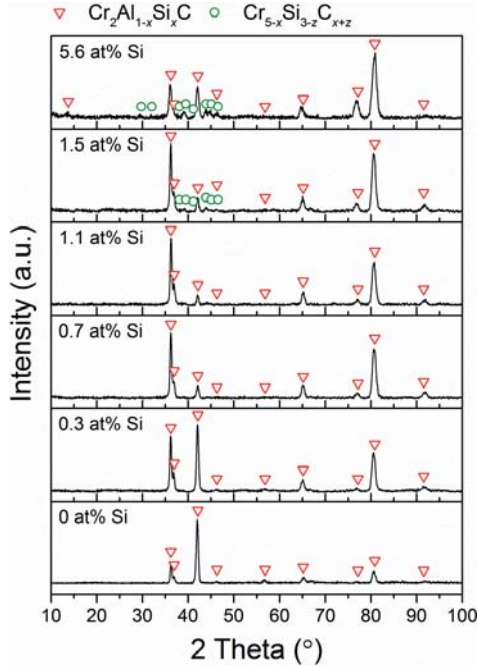


Figure 11: X-ray diffractograms of the as-deposited films containing 0, 0.3, 0.7, 1.1, 1.5 and 5.6 at% Si. The symbols were plotted according to the JCPDS data (JCPDS card no. 29-17 for $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ and no. 9-242 for $\text{Cr}_{5-x}\text{Si}_{3-z}\text{C}_{x+z}$).

4.2.2.2 Oxidation of Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.6$) films

Six $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) samples containing 0, 0.3, 0.5, 0.7, 1.1 and 1.5 at% Si were oxidized at 1120 °C in air for 4 hours. Figure 12 shows the corresponding X-ray diffractograms. For samples containing 0 and 0.3 at% Si, only $\alpha\text{-Al}_2\text{O}_3$ was identified besides the MAX phase $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$, whereas for the sample containing 0.5 at% Si, a small amount of Cr_7C_3 was identified besides $\alpha\text{-Al}_2\text{O}_3$ and the $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ MAX phase. Comparing with the sample containing 0.5 at% Si, for the sample containing 0.7 at% Si, a larger amount of Cr_7C_3 was identified besides $\alpha\text{-Al}_2\text{O}_3$ and the $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$.

Results and discussion

$x\text{Si}_x\text{C}$ MAX phase. For samples containing 1.1 and 1.5 at% Si, Cr_7C_3 as well as Cr_3C_2 were identified besides $\alpha\text{-Al}_2\text{O}_3$. Moreover, for the sample containing 1.1 at% Si, $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ MAX phase was identified whereas for the sample containing 1.5 at% Si, $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ MAX phase could not be identified. Furthermore, two tiny peaks which most likely stem from $\text{Cr}_{5-x}\text{Si}_{3-z}\text{C}_{x+z}$ were identified. It is worth noting that for the sample containing 1.1 at% Si, $\text{Cr}_{5-x}\text{Si}_{3-z}\text{C}_{x+z}$ was not identified in the as-deposited state (Figure 11). We speculate that $\text{Cr}_{5-x}\text{Si}_{3-z}\text{C}_{x+z}$ forms due to Al depletion during oxidation. Similarly, the formation of carbon containing Ti_5Si_3 was observed in the bulk $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$ ($x \leq 0.25$) after oxidation at 1000-1400 °C in air for up to 20 h [64]. No evidence for the formation of SiO_2 can be inferred from the diffraction data.

Results and discussion

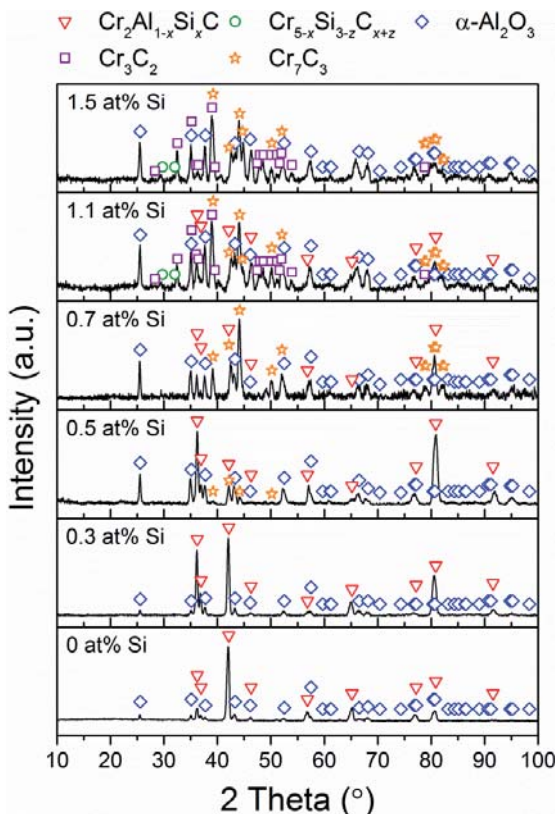


Figure 12: X-ray diffractograms of the Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ films containing 0, 0.3, 0.5, 0.7, 1.1 and 1.5 at% Si after oxidation at 1120 °C in air for 4 h. The symbols were plotted according to the JCPDS data (JCPDS card no. 29-17 for $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$, no. 9-242 for $\text{Cr}_{5-x}\text{Si}_{3-2}\text{C}_{x+z}$, no. 46-1212 for $\alpha\text{-Al}_2\text{O}_3$, no. 36-1482 for Cr_7C_3 and no. 35-804 for Cr_3C_2).

Figure 13 shows the surface oxide layer thicknesses and the relative increase in thickness of the six oxidized $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) samples versus the Si contents. The oxide layer thickness was measured from the sample cross sections by

Results and discussion

the “cut-and-weigh” method (as described in the experimental section) and the standard deviation calculated from the 6 individual thickness measurements serves as measure for the thickness distribution.

It can be seen that from 0 to 0.7 at% Si, the thickness shows a consistently increasing trend from 0.94 ± 0.05 to 1.32 ± 0.08 μm . However, for 1.1 and 1.5 at% Si, the thicknesses amount to 1.25 ± 0.03 and 1.25 ± 0.07 μm , respectively, which are slightly smaller than 1.32 ± 0.08 μm for 0.7 at% Si. Hence, the maximum oxide thickness obtained here is 1.32 ± 0.08 μm for the sample containing 0.7 at% Si. Compared with Cr_2AlC , alloying Cr_2AlC with 0.3, 0.5 and 0.7 at% Si leads to 18 ± 16 , 28 ± 18 and $40 \pm 17\%$ increase of the self-healing rate, respectively. Hence, the average thickness of the oxide layer is increased by 40% as the Si concentration is increased to sub-percentage level.

In order to identify the underlying reason for the Si induced change in oxidation kinetics, spatially resolved analysis of structure and composition of the samples containing 0.7 and 0 at% Si was performed before and after oxidation. The two compositions were selected because the minimum difference in oxide layer thickness is with 1.32 ± 0.08 μm (0.7 at% Si) and 0.94 ± 0.05 μm (0 at% Si) clearly significant. Considering the thickness variations measured along the 150 to 300 μm long interfaces, the addition of 0.7 at% Si leads to a significant increase in self-healing rate of $40 \pm 17\%$ as compared to the sample without Si additions.

Results and discussion

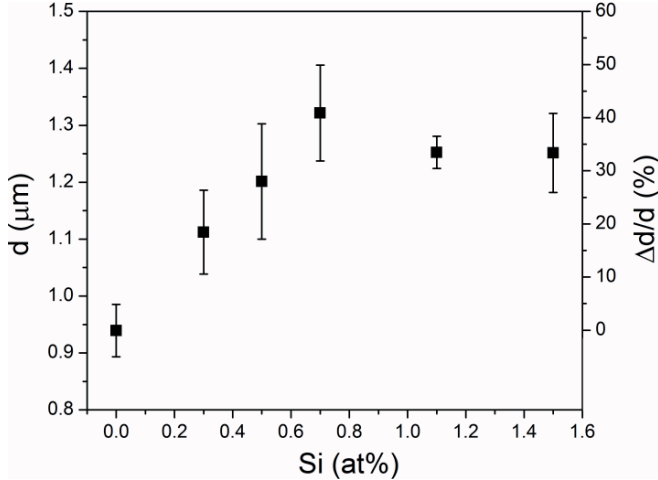


Figure 13: Surface oxide layer thickness of the Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) films oxidised at 1120 °C in air for 4 h as a function of the Si content measured in the as-deposited $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) films.

Figure 14 shows TEM bright-field images of the cross sections of the as-deposited *MAX* phase samples containing 0 and 0.7 at% Si with dimensions of about 8 μm x 8 μm. The columnar-structured grains can be clearly seen. Selected area electron diffraction (SAED) patterns (shown in inset of Figure 14) clearly show the ordering along the *c*-axis of Cr_2AlC indicating formation of the *MAX* phase rather than disordered $(\text{Cr,Al})_2\text{C}_x$ [65, 66].

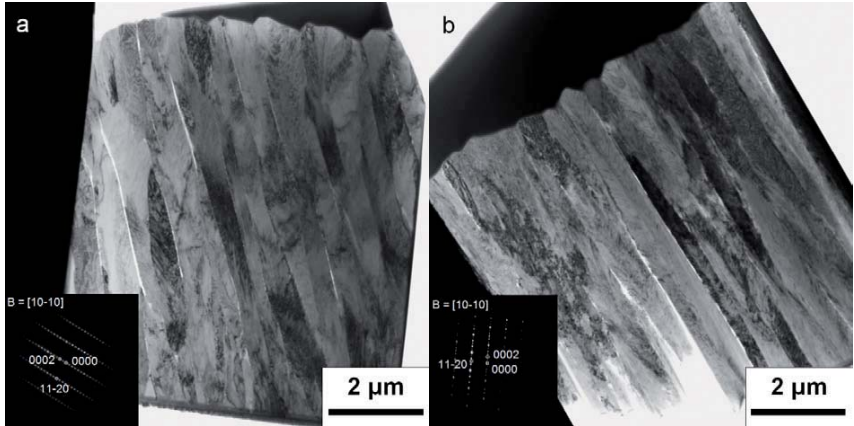


Figure 14: TEM bright-field images and SAED patterns of the cross sections of the *MAX* phase samples containing (a) 0 at% and (b) 0.7 at% Si before oxidation.

Figure 15(a) shows the STEM bright-field image of the cross section of the *MAX* phase sample without Si additions after oxidation. Due to the strong contrast difference between the *MAX* phase and its oxide, a bright-field image with optimized contrast for the oxide is shown separately (surrounded by red rectangle). The columnar *MAX* phase grains are clearly visible. In addition, several particles with brighter contrast form at columnar grain boundaries as well as within the columnar grains. According to Hajas *et al.* [13], these alumina particles are formed by internal oxidation of the film. The oxygen probably stems from oxygen incorporation during thin film growth [67, 68]. At the oxide/film interface, 14 oxide grains are distributed over a length of 6.2 μm , corresponding to 2.3 grains/ μm . The average size of oxide grains at the oxide/film interface is 370 ± 210 nm.

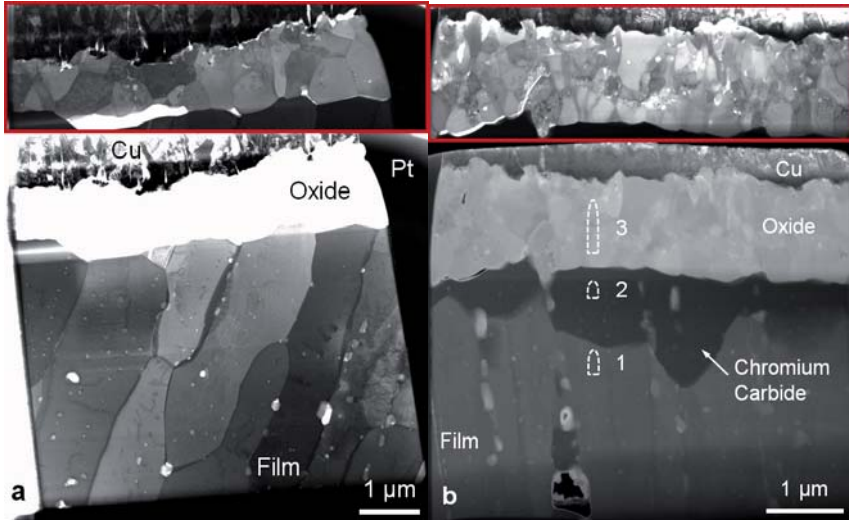


Figure 15: STEM images of the cross sections of the *MAX* phase samples containing (a) 0 at% and (b) 0.7 at% Si after oxidation.

Figure 15(b) shows the STEM dark-field image of the cross section of the *MAX* phase sample containing 0.7 at% Si after oxidation. A bright-field image of the oxide layer is shown in the inset. Similar to the oxidized *MAX* phase sample without Si additions, alumina particles appear to form at columnar grain boundaries and within the columnar grains.

Based on the EDS and XRD (Figure 12) analysis, the dark-contrast sublayer below the oxide layer consists of chromium carbide which forms due to Al depletion [13]. The absence of the chromium carbide in the oxidized *MAX* phase sample without Si additions is likely due to its slower oxidation rate compared with that of the *MAX* phase sample containing 0.7 at% Si after oxidation so that the Al depletion has not yet lead to the chromium carbide formation.

Results and discussion

However, at the oxide/film interface, 18 oxide grains are distributed over a length of 5.5 μm corresponding to 3.3 grains/ μm for the *MAX* phase sample containing 0.7 at% Si. Compared to the 2.3 grains/ μm obtained for the *MAX* phase sample without Si additions, this corresponds to a Si concentration induced increase of 43% in grain population at the interface. Hence, the presence of Si at the interface causes an increase in nucleation density of the healing agent Al_2O_3 .

Table 3 summarizes the average size of the oxide grains from the whole oxide layer and the average size of the oxide grains at the oxide/film interface of the *MAX* phase samples containing 0 and 0.7 at% Si after oxidation as obtained from Figures 15(a) and 15(b). The average size of the oxide grains from the whole oxide layer and the average size of the oxide grains at the oxide/film interface of the *MAX* phase sample containing 0 at% Si after oxidation were calculated by averaging 27 and 14 oxide grain size values, respectively. The average size of the oxide grains from the whole oxide layer and the average size of the oxide grains at the oxide/film interface of the *MAX* phase sample containing 0.7 at% Si after oxidation were calculated by averaging 38 and 18 oxide grain size values, respectively. Oxide grains with a size smaller than 10 nm were not taken into account. The calculated standard deviation serves as measure for the grain size distribution.

Table 3: Average size of the oxide grains from the whole oxide layer and the average size of the oxide grains at the oxide/film interface of the *MAX* phase samples containing 0 and 0.7 at% Si after oxidation.

<i>MAX</i> phase sample	d_{oxide}	$d_{\text{interface}}$
Cr_2AlC (0 at% Si)	$330 \pm 190 \text{ nm}$	$370 \pm 190 \text{ nm}$
$\text{Cr}_2\text{Al}_{0.97}\text{Si}_{0.03}\text{C}$ (0.7 at% Si)	$200 \pm 80 \text{ nm}$	$260 \pm 80 \text{ nm}$

Results and discussion

While all here investigated grain size distributions overlap, the average grain size of the oxide grains from the whole oxide layer and the average size of the oxide grains at the oxide/film interface is smaller for the sample containing 0.7 at % Si as compared to the sample with 0 at %. This finding is consistent with the analysis of the number of oxide grains populating the oxide/film interface as discussed in section 3.2 where the presence of Si caused a 43% increase in grain population at the interface.

Table 4 summarizes the average columnar grain widths of the *MAX* phase samples containing 0 and 0.7 at% Si before and after oxidation. The average columnar grain widths of the *MAX* phase sample containing 0 at% Si before and after oxidation were calculated by averaging 14 and 7 grain width values, respectively. The average columnar grain widths of the *MAX* phase sample containing 0.7 at% Si before and after oxidation were calculated by averaging 12 and 8 grain width values, respectively. The calculated standard deviation serves as a measure for the columnar grain width distribution and is given in table 1.

Table 4: Average columnar grain widths of the *MAX* phase samples containing 0 and 0.7 at% Si before and after oxidation.

<i>MAX</i> phase sample	Before oxidation	After oxidation
Cr_2AlC (0 at% Si)	$0.56 \pm 0.11 \mu\text{m}$	$1.01 \pm 0.27 \mu\text{m}$
$\text{Cr}_2\text{Al}_{0.97}\text{Si}_{0.03}\text{C}$ (0.7 at% Si)	$0.43 \pm 0.10 \mu\text{m}$	$0.48 \pm 0.17 \mu\text{m}$

In order to further elucidate the role of Si for the above discussed increase in self-healing kinetics the local chemical composition was analyzed by 3D APT in the sample containing 0.7 at% Si after oxidation. Three different regions were investigated: Firstly a *MAX* phase region (Figure 15(b)(1)), secondly a Al depleted chromium carbide region (Figure 15(b)(2)) and thirdly a region within the oxide top

Results and discussion

layer (Figure 15(b)(3)). The representative positions where the tips for APT were extracted are marked by dashed tip contours in Figure 15(b).

Figure 16(a) shows the 3D elemental maps of all the constituent elements from the tip extracted from the *MAX* phase region close to the chromium carbide region of the oxidized sample containing 0.7 at% Si. All elements are homogeneously distributed. The 1D concentration profile taken along the cylindrical volume of $10 \times 10 \times 200 \text{ nm}^3$ (in inset) with 1 nm bin width (Figure 16(b)) shows that the chemical composition is $51.7 \pm 1.0 \text{ at\% Cr}$, $20.3 \pm 0.8 \text{ at\% C}$, $24.8 \pm 0.9 \text{ at\% Al}$, $1.9 \pm 0.3 \text{ at\% O}$ and $1.3 \pm 0.2 \text{ at\% Si}$, which agrees well with the global Cr:Al:C stoichiometry of 2:1:1.

Results and discussion

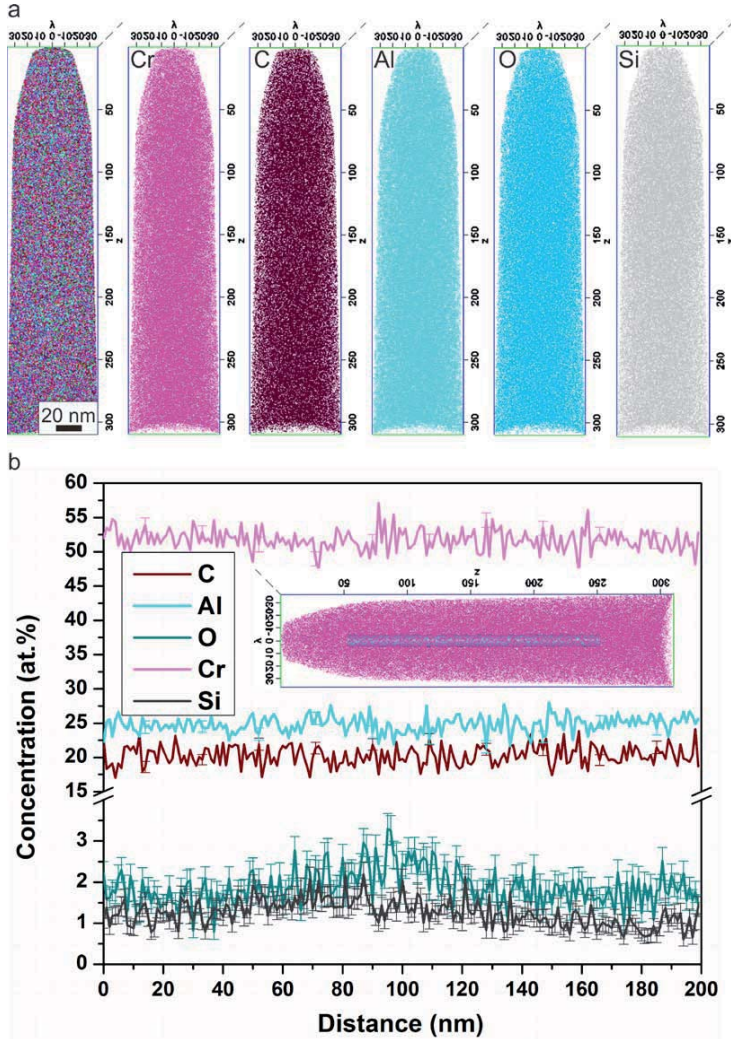


Figure 16: (a) 3D elemental maps of the tip extracted from the *MAX* phase region of the oxidized sample containing 0.7 at% Si displaying the overall distribution of constituent elements and the individual Cr, C, Al, O and Si atomic positions (from left

Results and discussion

to right). (b) 1D concentration profile taken along the cylindrical volume of $10 \times 10 \times 200 \text{ nm}^3$ (in inset) with 1 nm bin width.

Figure 17(a) shows the 3D elemental maps of all the constituent elements from the tip extracted from the chromium carbide region of the *MAX* phase sample containing 0.7 at% Si after oxidation. Two Al- and O-rich regions can be identified in the chromium carbide matrix. APT results do not indicate the presence of Si in the CrC layer. Since no solubility of Si in chromium carbide has been reported experimentally [69], the result here appears to be consistent with literature. By analyzing the elemental concentration surrounding the interface between the matrix and the Al-rich region, as marked by the square in Figure 17(b), it can be seen in the proximity histogram, Figure 17(c) that the composition in the matrix is approximately 74.7 ± 0.1 at% Cr and 24.1 ± 0.1 at% C, which is in fair agreement with the phase formation of Cr_7C_3 as identified by XRD (Figure 12).

At the interface, the Cr and C contents start to decrease while the O and Al contents start to increase. In the Al- and O-rich region, the composition is around 28.1 ± 1.1 at% Al, 56.4 ± 1.2 at% O, 5.4 ± 0.3 at% Cr and 9.9 ± 0.8 at% C; The Al:O stoichiometry is close to 2:3, indicating Al_2O_3 being the major oxide. The oxide particles exhibit a diameter of 25-40 nm, which is consistent with the size of the bright particles distributed at the chromium carbide layer observed in the STEM image (Figure 15(b)). Hence, the above discussed alumina phase formation based on 3D APT and STEM data is consistent with the internal oxidation notion from Hajas *et al.* [13].

Results and discussion

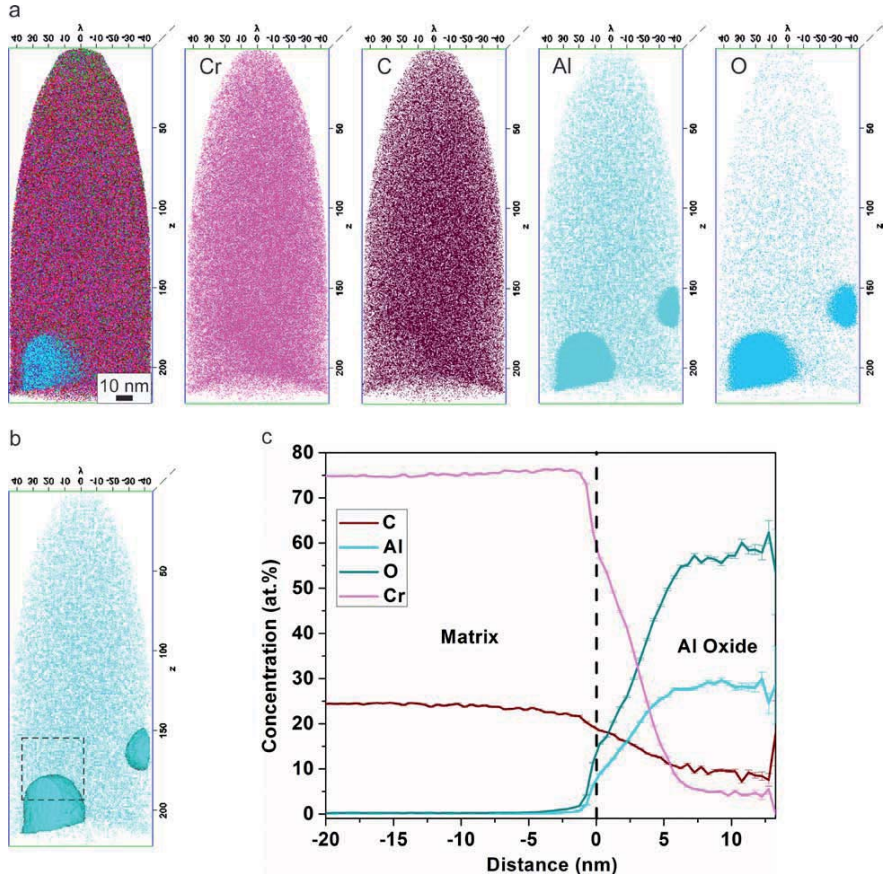


Figure 17: (a) 3D elemental maps of the tip extracted from the chromium carbide region of the MAX phase sample containing 0.7 at% Si after oxidation displaying the overall distribution of constituent elements and the individual Cr, C, Al and O atom positions (from left to right). (b) APT elemental map of Al and Al rich regions delineated by 2 at% isoconcentration surfaces and (c) proximity histogram of 0.5 nm bin width with respect to the Al rich region marked by the square in (b).

Results and discussion

Figure 18(a) shows the 3D elemental maps of all the constituent elements from the tip extracted from the oxide layer of the MAX phase sample containing 0.7 at% Si after oxidation. As shown in Figure 18(b), the 1D concentration profile taken along the cylindrical volume of $10 \times 10 \times 640 \text{ nm}^3$ (in inset) with 1.5 nm bin width indicates that the composition is around 40 at% Al and 60 at% O with traces of Cr (below 5 at%) and C (below 2 at%). Similar to the results obtained from the CrC region, no evidence for Si incorporation was obtained by APT. The Al:O stoichiometry is close to 2:3, indicating the formation of Al_2O_3 , which is consistent with XRD (Figure 15). The small amount of Cr is likely from the $(\text{Al,Cr})_2\text{O}_3$ solid solution formed in the alumina [13]. Since the average oxide grain size is $200 \pm 80 \text{ nm}$, it is likely that the concentration profile over a length of 640 nm contains oxide grain boundaries. Hence, the absence of Si in the measured cylindrical volume indicates that there is no Si present in the oxide grain or in the oxide grain boundary.

Results and discussion

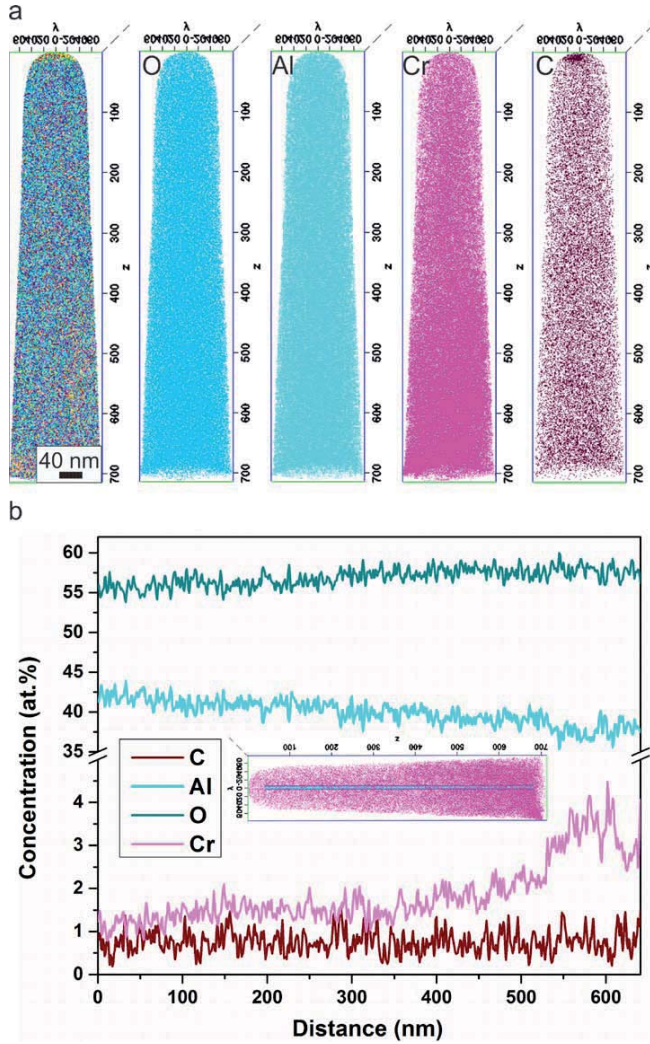


Figure 18: (a) 3D elemental maps of the tip extracted from the oxide layer of the MAX phase sample containing 0.7 at% Si after oxidation displaying the overall distribution of constituent elements and the individual O, Al, Cr and C atomic positions (from left

Results and discussion

to right). (b) 1D concentration profile taken along the cylindrical volume of $10 \times 10 \times 640 \text{ nm}^3$ (in inset) with 1.5 nm bin width.

Based on the comparative structural and compositional analysis of the as-deposited and oxidized samples containing various amounts of Si, the following can be inferred. The self-healing rate can be increased by 40% upon minor additions of Si to Cr_2AlC (Figure 13). The number of oxide grains normalized to the interface length is increased from $2.3 \mu\text{m}^{-1}$ to $3.3 \mu\text{m}^{-1}$ by the addition of 0.7 at% Si. This corresponds to a Si concentration induced increase in grain population at the interface of 43%.

No evidence for the presence of Si in the oxide layer (Figure 16) or the chromium carbide region (Figure 17) of the *MAX* phase sample containing 0.7 at% Si after oxidation was obtained by 3D APT. It is therefore reasonable to assume that the here reported Si concentration induced increase in self-healing rate is enabled by the Si concentration induced, and hence concomitant, increase in nucleation density of the oxide during the initial stages of oxidation. The increased nucleation density results in the above discussed 43% increase in grain population at the interface of the sample containing 0.7% Si compared to the sample without Si. It may be speculated that the absence of Si in the oxide layer (Figure 18) and chromium carbide region (Figure 17) of the *MAX* phase sample containing 0.7 at% Si after oxidation is due to the formation of volatile SiO_x rather than SiO_2 [70].

4.2.3 Summary

Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films were synthesized by DC magnetron sputtering at 600°C in an industrial chamber. Oxidation experiments were performed at 1120°C in air for 4 hours for the Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) films. The crystal structure, microstructure and chemical compositions of the as-deposited as

Results and discussion

well as oxidized films have been investigated by means of XRD, SEM, EDS, TEM, STEM and 3D APT.

It is shown that the self-healing kinetics of Cr_2AlC based films can be increased drastically by sub-percentage additions of Si. Detailed characterization of the *MAX* phase samples containing 0 and 0.7 at% Si before and after oxidation demonstrates that Si alloying affects the microstructural evolution during oxidation. It is observed that the average columnar grain width of the oxidized *MAX* phase sample without Si additions has increased significantly compared to that of its as-deposited state, whereas the average columnar grain width of the *MAX* phase sample containing 0.7 at% Si after oxidation show no significant difference from that of its as-deposited state. The presence of Si in Cr_2AlC appears to inhibit grain growth during oxidation. Moreover, after oxidation a significant increase of the number of oxide grains at the oxide/film interface per unit length of the interface has been observed for the *MAX* phase sample containing 0.7 at% Si compared with the *MAX* phase sample without Si additions. Furthermore, 3D APT analysis of the *MAX* phase sample containing 0.7 at% Si after oxidation reveals the absence of Si in the chromium carbide and oxide regions. Electron microscopy and atom probe tomography data support the notion that the here reported Si concentration induced increase in self-healing rate by up to 40% is enabled by the Si concentration induced, and hence concomitant, increase in nucleation density of the healing agent Al_2O_3 .

4.3 Phase formation of Nb₂AlC investigated by combinatorial thin film synthesis and *ab initio* calculations

4.3.1 Introduction

Nb₂AlC (space group $P6_3/mmc$, prototype Cr₂AlC) is a ternary compound belonging to the group of $M_{n+1}AX_n$ phases (M : early transition metal, A : A group element, mostly IIIA or IVA, X : C or N, $n = 1-3$). Their unique nanolaminated structure consisting of $M_{n+1}X_n$ layers interleaved with A-group element layers has endowed $M_{n+1}AX_n$ phases with a remarkable combination of metallic and ceramic properties [60, 71].

Similar to other $M_{n+1}AX_n$ phases, Nb₂AlC has been reported to be machinable [72], damage tolerant, thermal shock resistant [72, 73] and is also a good thermal and electrical conductor [74, 75]. The oxidation behavior of Nb₂AlC was studied by Salama *et al.* [76] in the temperature range of 650-750 °C in air. Together with these unique physical, chemical and mechanical properties combinations, its low neutron absorption renders Nb₂AlC a candidate as protective coating material for Zircaloy nuclear fuel tubes [77, 78].

Nb₂AlC bulk synthesis was reported in several studies, for example [72, 75, 79, 80], while only one study [81] on thin film Nb₂AlC synthesis is available. Jeitschko *et al.* [79] were first to report the synthesis of Nb₂AlC by a sequential annealing at 1000 °C without giving details about the formed microstructure. Salama *et al.* [72] fabricated dense Nb₂AlC with ~ 2 vol.% Al₂O₃ and ~ 1 vol.% Nb-carbides and aluminides by reactive hot isostatic pressing (HIP) of graphite, Al₄C₃ and Nb powders at 1600 °C and 100 MPa for 8 h. Using a powder mixture of Nb, Al and NbC with a molar ratio of 1:1:1, Zhang *et al.* [75] synthesized single phase Nb₂AlC by *in situ* reaction/hot-

Results and discussion

pressing at 1650 °C and 30 MPa for 90 min. Yeh *et al.* [80] conducted combustion synthesis in the self-propagating high-temperature synthesis (SHS) mode to produce Nb₂AlC from Nb₂O₅-Al-Al₄C₃ powder compacts with varying stoichiometry, and Al₂O₃, NbC as well as Nb-aluminides were identified as impurity phases. Scabarozi *et al.* [81] deposited Nb₂AlC thin films on c-axis sapphire (Al₂O₃) substrates by magnetron sputtering at temperatures ranging from 800 °C to 950 °C and observed the formation of Nb₅Al₃C_x, Nb₂C and NbC. Hence, the formation of impurity phases is generally observed during bulk and thin film synthesis of Nb₂AlC. In order to synthesize single phase Nb₂AlC, several factors such as purity and stoichiometry of the starting synthesis materials and also the synthesis method play a crucial role.

The general formula of $M_{n+1}AX_n$ phases ($n = 1-3$) implies M_2AX ($n = 1$), M_3AX_2 ($n = 2$) and M_4AX_3 ($n = 3$) stoichiometry. However, deviations from the stoichiometric compositions have been reported: The composition of bulk Ti₃AlC₂ was determined by Tzenov and Barsoum [82] to be Ti₃Al_{1.1}C_{1.8}. Mertens *et al.* [83] reported the compositional range of a single phase Cr₂AlC thin film to be $1.42 \leq \text{Cr/Al} \leq 2.03$ and $1.72 \leq \text{Cr/C} \leq 1.93$. For Nb₂AlC, Jeitschko *et al.* [79] speculated that a homogeneity range (with unspecified magnitude), which obeys the formula Nb_{2-x}Al_{1+x}C_{1-x/2}, exists. However, there is no experimental or theoretical study available to date reporting the homogeneity range of Nb₂AlC. Therefore, this work aims to explore the phase formation of Nb₂AlC thin films. In the current work, Nb-Al-C thin films were synthesized by combinatorial DC magnetron sputtering [43]. This deposition technique allows the formation of concentration gradients. Hence the relationship between chemical composition, structure and mechanical properties can be investigated efficiently if spatially resolved characterization techniques are employed [43]. Based on correlative compositional and structural data, the formation of a

Results and discussion

predominantly single phase Nb₂AlC region where 99% of the XRD intensity originates from Nb₂AlC at Nb, Al and C concentrations of 49.4 ± 0.5 at%, 24.7 ± 0.7 at% and 25.6 ± 0.9 at%, respectively, was identified. It is also shown that the small solubility of Al in Nb₂AlC can be rationalized by considering the formation of energetically favorable defects.

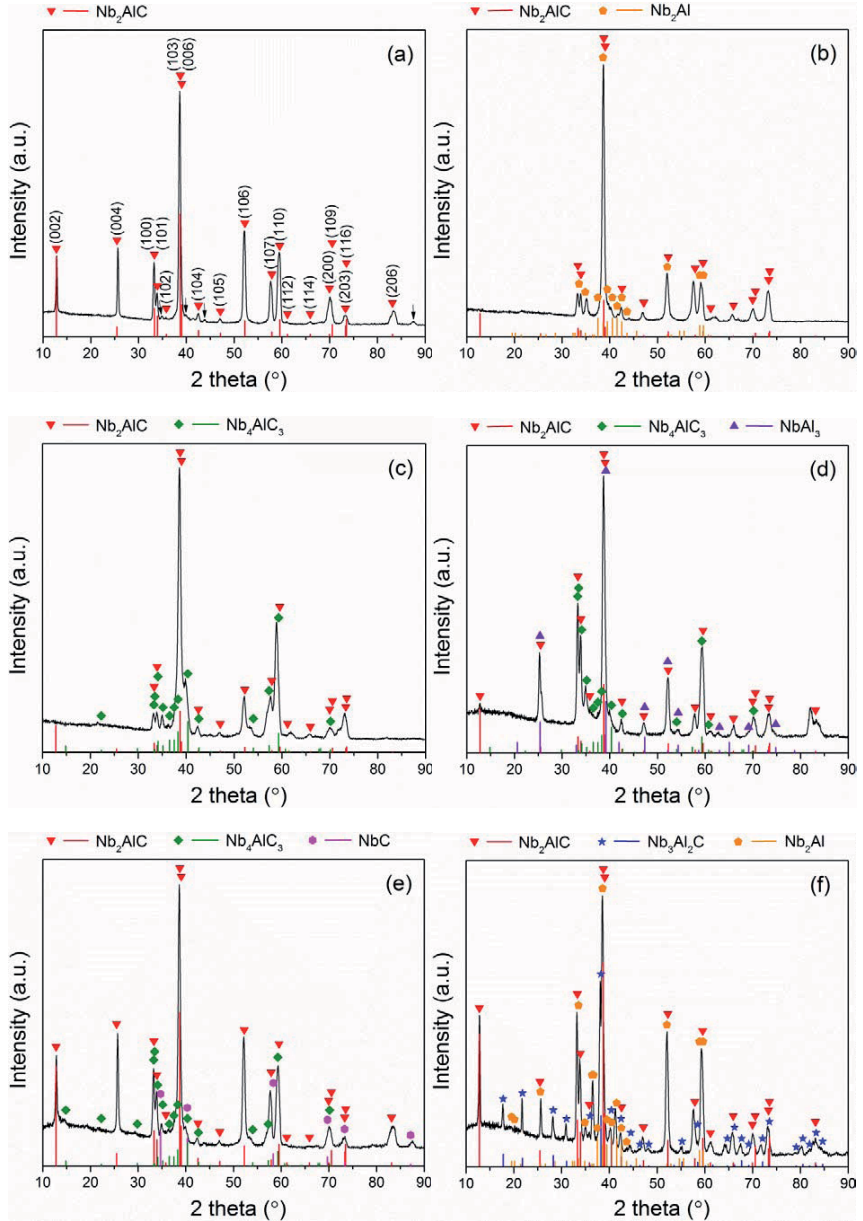
4.3.2 Experiments and *ab initio* calculations

The crystal structure and chemical composition of the Nb-Al-C thin film deposited at 870 °C were investigated by XRD and EDS, respectively. As expected, the phase formation depends on the chemical composition. Different phase formation regions were identified. Representative X-ray diffractograms for phase formation regions containing predominantly Nb₂AlC are shown in Figure 19. Based on the comparison of the phase resolved integrated diffracted intensities from the diffractogram shown in Figure 19(a), approximately 99% of the total diffracted intensity corresponds to the Nb₂AlC phase. The chemical composition measured at this grid point amounts to 49.8 at% Nb, 24.6 at% Al, 25.3 at% C and 0.3 at% O. Four low intensity peaks (as marked by the arrows in Figure 19(a)) are present besides the Nb₂AlC peaks. Based on these peaks no positive phase identification could be performed. Figure 20 shows a montage of TEM bright-field images of the as-deposited film cross section at the predominantly single phase Nb₂AlC region with length and thickness of 7 µm and 1.2 µm, respectively. The film composition of the TEM samples is indicated in Figure 21. Columnar grains with width ranging from 50-250 nm are clearly visible. The representative SAED pattern shown in Figure 20(a) clearly indicates that only Nb₂AlC is formed. Figure 20(b) shows an enlarged view of the interface region from the sample shown in Figure 20(a). In the SAED pattern of the interface, the diffraction

Results and discussion

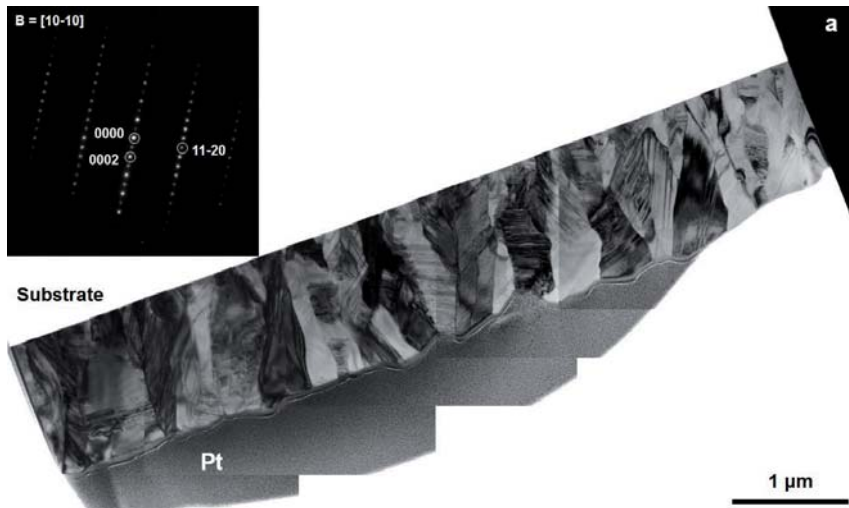
spots originating from the film are marked by red circles. The same diffraction spots are marked on the SAED pattern of the film. It can be seen that all diffraction spots in the SAED pattern of the interface originate only from the substrate and the Nb_2AlC $M_{n+1}\text{AX}_n$ phase thin film. A second cross-sectional sample (not shown here for brevity) prepared 15 μm away from the sample shown in Figure 20(a) was analyzed by TEM and SAED showing also no evidence for the formation of impurity phases can be found in the film as well as at the interface between film and substrate. Therefore the detection of the low intensity peaks (besides the Nb_2AlC peaks) by XRD indicates that the single phase Nb_2AlC region is smaller than the by XRD irradiated surface area of 2.4 mm^2 . Additional diffraction measurements were conducted using a pinhole collimator with a smaller diameter (0.3 mm), resulting in an irradiated area of 0.9 mm^2 instead of 2.4 mm^2 , and by aligning the long axis of the irradiated area with the longitudinal direction of the Nb_2AlC phase region on the wafer (*c.f.* asterisks in Figure 4). The diffracted intensity of Nb_2AlC increased from 99% to 99.6% due to the change of diffraction optics and geometry, indicating that the single phase region is smaller than 0.9 mm^2 .

Results and discussion



Results and discussion

Figure 19: Representative X-ray diffractograms for different phase formation regions: (a) Nb_2AlC (JCPDS card no. 30-33), (b) Nb_2AlC and Nb_2Al (JCPDS card no. 14-458), (c) Nb_2AlC and Nb_4AlC_3 [84], (d) Nb_2AlC , Nb_4AlC_3 and NbAl_3 (JCPDS card no. 13-146), (e) Nb_2AlC , Nb_4AlC_3 and NbC (JCPDS card no. 38-1364) and (f) Nb_2AlC , $\text{Nb}_3\text{Al}_2\text{C}$ (JCPDS card no. 30-32) and Nb_2Al phase regions. The lines were plotted according to the JCPDS and literature data. The symbols were plotted indicating the peaks which are present. The Nb_2AlC peaks were indexed according to the JCPDS database.



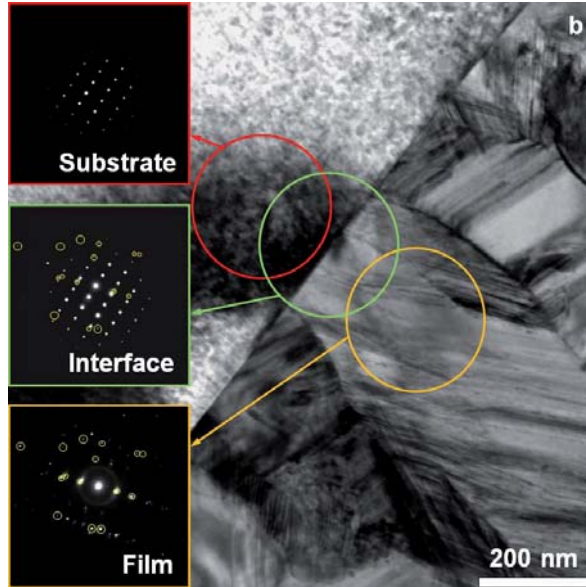


Figure 20: TEM bright-field images and SAED patterns of the cross section of the Nb-Al-C film deposited at 870 °C from the single phase Nb_2AlC region: (a) overview of the cross-sectional sample, (b) enlarged view of the interface region from the sample shown in (a). In the SAED pattern of the interface, the diffraction spots originating from the Nb_2AlC film are marked by circles. The same diffraction spots are marked in the SAED pattern of the $\text{Nb}_2\text{AlC } M_{n+1}\text{AX}_n$ phase thin film.

Figure 21 shows the resulting Nb-Al-C ternary phase formation diagram including the predominantly single phase Nb_2AlC region (highlighted). Besides the predominantly single phase Nb_2AlC region, it can be seen in Figure 21 that with variation of the chemical composition, five different phase formation regions can be distinguished, i.e. two two-phase regions ($\text{Nb}_2\text{AlC} + \text{Nb}_2\text{Al}$ and $\text{Nb}_2\text{AlC} + \text{Nb}_4\text{AlC}_3$) and three three-phase regions ($\text{Nb}_2\text{AlC} + \text{Nb}_4\text{AlC}_3 + \text{NbAl}_3$, $\text{Nb}_2\text{AlC} + \text{Nb}_4\text{AlC}_3 + \text{NbC}$ and $\text{Nb}_2\text{AlC} + \text{Nb}_3\text{Al}_2\text{C} + \text{Nb}_2\text{Al}$).

Results and discussion

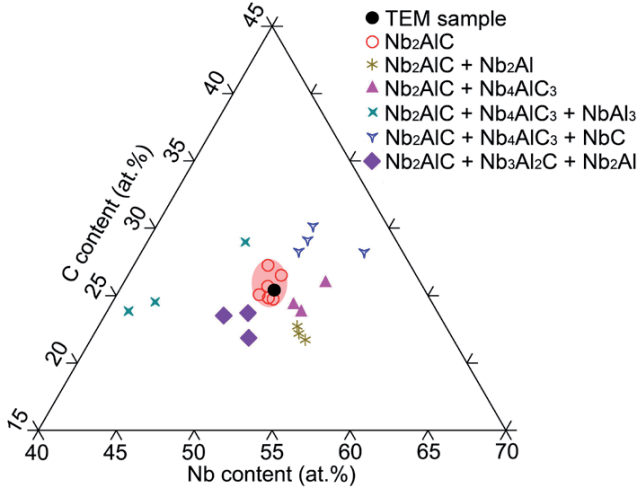


Figure 21: Nb-Al-C ternary phase formation diagram focusing on the predominantly single phase Nb_2AlC region (highlighted) plotted based on the X-ray diffraction and chemical analysis of the Nb-Al-C thin film deposited at 870 °C.

As marked in Figure 21, the predominantly single phase Nb_2AlC region contains seven individual samples (grid points). The average chemical compositions of the predominantly single phase Nb_2AlC region is 49.4 ± 0.5 at% Nb, 24.7 ± 0.7 at% Al, 25.6 ± 0.9 at% C and 0.3 ± 0.02 at% O. The compositional variations here only account for measurement statistics. Mertens *et al.* [83] deposited a Cr-Al-C thin film at 850 °C and reported single phase Cr_2AlC composition regions with $1.42 \leq \text{Cr/Al} \leq 2.03$ and $1.7 \leq \text{Cr/C} \leq 1.93$. The maximum deviation from the stoichiometric composition for Al was 6.3 at% for Cr_2AlC [83] and only 1 at% for Nb_2AlC . In order to explore the underlying chemical difference between the Al solubility in Nb_2AlC and Cr_2AlC , *ab initio* calculations were performed considering one Al atom substituting one M ($M = \text{Nb}, \text{Cr}$) atom in identical supercell configurations with $M/\text{Al} = 1.82$. The

Results and discussion

defect formation energy of Al substituting Nb and Cr is calculated to be $\Delta E_{f, \text{Al} \rightarrow \text{Nb}} = 1.5 \text{ eV defect}^{-1}$ and $\Delta E_{f, \text{Al} \rightarrow \text{Cr}} = 1.0 \text{ eV defect}^{-1}$ in Nb_2AlC and Cr_2AlC , respectively. It can be seen that the defect formation energy of Al substituting Nb is higher than for Al substituting Cr, indicating that Al over-stoichiometry is energetically less likely in Nb_2AlC than in Cr_2AlC . Hence, the limited solubility of Al in Nb_2AlC can be readily understood based on energetic considerations. Furthermore, the defect formation energy may serve as indicator for the magnitude of the A-element homogeneity range in $M_{n+1}AX_n$ phases. The methodology of predicting defect formation energies for Al substituting transition metals in $M_{n+1}AX_n$ phases was shown to correlate with experimentally determined Al solubility ranges for both, Nb_2AlC and Cr_2AlC .

To explore the effect of substrate temperature on the structural evolution, XRD detector scans with 10° incidence angle were performed covering a 2θ range of 10° to 100° . Diffractograms of samples with Nb:Al:C ratios of 2:1:1 deposited at 710, 750, 800 and 870 $^\circ\text{C}$, respectively, are shown in Figure 22. Besides the Nb_2AlC peaks, additional peaks with an integrated relative intensity of $< 2.4\%$ are present for samples deposited at temperatures $\geq 750^\circ\text{C}$. It can be seen that for samples deposited at 870 $^\circ\text{C}$ (Figure 22(a)) and 800 $^\circ\text{C}$ (Figure 22(b)), all peaks listed in JCPDS card no. 30-33 are present. For the sample deposited at 750 $^\circ\text{C}$ (Figure 22(c)), all Nb_2AlC peaks listed in JCPDS card no. 30-33 are identified except the (002) basal plane peak. For the sample deposited at 710 $^\circ\text{C}$ (Figure 22(d)), the (002) and (104) Nb_2AlC peaks cannot be identified. Since the $M_{n+1}AX_n$ phase formation can be inferred based on the presence of the (002) peak [65, 66], additional XRD measurements were performed with an incidence angle $\theta = 6.4^\circ$ and a 2θ range of 3 to 32° in order to resolve the (002) peak specifically. The XRD frames measured by the area detector are shown as insets in Figure 22. The diffraction rings located at

Results and discussion

the center of the circular frames originate from (002) diffraction as indicated in the images for samples deposited at 870 °C (Figure 22(a)), 800 °C (Figure 22(b)) and 750 °C (Figure 22(c)). The (002) diffraction ring for the sample deposited at 710 °C (Figure 22(d)) is not visible in the diffraction experiment. This indicates that the lowest formation temperature for Nb₂AlC observed here is between 710 and 750 °C. Moreover, the diffraction rings are discontinuous, suggesting texturing. With the temperature increasing from 750 °C to 870 °C, the full width at half maximum (FWHM) of the (106) Nb₂AlC peak decreases from 0.719° to 0.571°, indicating increased crystallinity of Nb₂AlC. Hence, we have selected the sample deposited at 870 °C for lattice parameter and elastic property measurements. The lattice parameters of Nb₂AlC were determined to be $a = 3.110 \pm 0.001$ Å and $c = 13.873 \pm 0.006$ Å, using a least square fitting procedure of eight lattice spacings obtained from the X-ray diffractograms of 7 samples from the predominantly single phase Nb₂AlC region deposited at 870 °C. The calculated lattice parameter values are $a = 3.14$ Å and $c = 13.91$ Å, with deviations of 1 % and 0.3 % from the experimentally determined a and c values, respectively. Hence, experimental and calculated lattice constants are in very good agreement. Moreover, experimental and calculated values are also in good agreement with reported literature values (with differences smaller than 0.5% and 0.7% for the experimental and calculated values, respectively) as shown in Table 4.

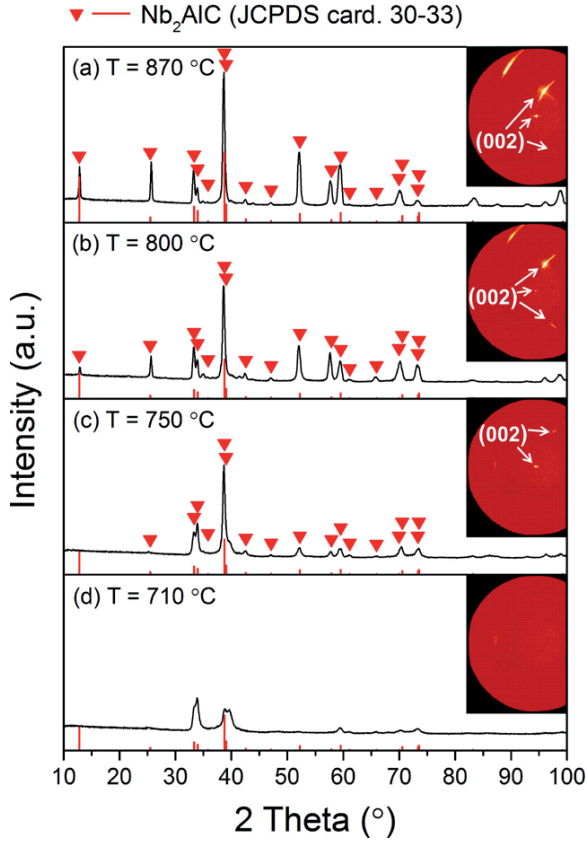


Figure 22: X-ray diffractograms of samples with Nb:Al:C ratios of 2:1:1 deposited at (a) 870 °C, (b) 800 °C, (c) 750 °C and (d) 710 °C. The XRD frames measured by the area detector are shown as insets. The (002) diffraction ring sections are indicated by arrows.

Table 4. The lattice parameters as well as equilibrium volumes obtained from experiment and calculation are listed together with data from literature.

Results and discussion

a (Å)		c (Å)		V (Å ³)	
Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
3.110 ± 0.001	3.14	13.873 ± 0.006	13.91	116.2 ± 0.05	118.8
3.107 [72]	3.16 [78]	13.888 [72]	14.01 [78]	116.1 [72]	121.2 [78]
3.106 [85]	3.12 [85]	13.888 [85]	13.87 [85]	116.0 [85]	116.9 [85]
3.1 [79]		13.8 [79]		114.9 [79]	
3.103 [73]		13.93 [73]		116.2 [73]	

The elastic moduli of samples from the predominantly single phase Nb₂AlC region were obtained from 175 nanoindentation measurements. An average elastic modulus of 274 ± 62 GPa was determined. The scatter of 22.6% is assumed to be due to the surface roughness ($R_a = 40$ nm). The calculated elastic modulus of Nb₂AlC is 295 GPa, which is in very good agreement with the experimental results. The elastic modulus of bulk Nb₂AlC reported in the literature from both experiment [74, 75] and theory [42, 86] ranges from 242 to 299 GPa. The hardness of Nb₂AlC is calculated from the load-displacement curves to be 11 ± 3 GPa, while the hardness of bulk samples reported in the literature exhibits lower values (6.1 [72] and 4.5 [75] GPa). Comparing the hardness of other $M_{n+1}AX_n$ phase thin films with that of bulk samples, similar differences are commonly observed: 13 ± 2 GPa [7] for Cr₂AlC thin films compared with 3.5 GPa [87] for bulk, 11.5 ± 1.7 GPa [8] for V₂AlC thin films compared with 4 GPa [71] for bulk and 20 GPa [88] for Ti₃AlC₂ thin films compared with 2.7-3.2 GPa [89] for bulk. This behavior was previously attributed to be due to the hardening effect originating from the significantly smaller grain size (around tens

of nanometers) compared to bulk samples which have an average grain size around micrometers or larger [8].

4.3.3 Summary

The relationship between chemical composition and phase formation in the Nb-Al-C system was studied by combinatorial thin film synthesis and *ab initio* calculations. Thin films with lateral chemical composition gradients were synthesized by DC magnetron sputtering using elemental targets at substrate temperatures of 710-870 °C. Analysis of the phase formation at different substrate temperatures revealed that Nb₂AlC forms between 710 and 750 °C under the deposition conditions studied here. A predominantly single phase Nb₂AlC region where at least 99% of the X-ray diffraction intensity originates from Nb₂AlC was identified. The average chemical composition of the predominantly single phase Nb₂AlC region is measured to be 49.4 ± 0.5 at% Nb, 24.7 ± 0.7 at% Al, 25.6 ± 0.9 at% C and 0.3 ± 0.02 at% O. Furthermore, selected area electron diffraction analysis reveals a single phase Nb₂AlC region. It is suggested that the higher defect formation energy of Al substituting Nb compared with Al substituting Cr may explain the limited solubility of Al in Nb₂AlC compared with Cr₂AlC. This energetics consideration may serve as indicator for the magnitude of the A-element homogeneity range in $M_{n+1}AX_n$ phases. The lattice constants of Nb₂AlC determined from experiment and calculation are $a = 3.110 \pm 0.001$ Å, $c = 13.867 \pm 0.006$ Å and $a = 3.14$ Å, $c = 13.91$ Å, respectively. The deviations between the experimental and calculated a and c lattice constants are 1 % and 0.3 % respectively, being in very good agreement. The elastic modulus of Nb₂AlC measured by nanoindentation is 274 ± 62 GPa, which also agrees very well with the calculated elastic modulus of 295 GPa from *ab initio* calculations.

Conclusions

In this thesis, the phase stability of $(\text{Cr}_{1-x}\text{M}_x)_2(\text{Al}_{1-y}\text{A}_y)(\text{C}_{1-z}\text{X}_z)$ ($M = \text{Ti, Hf, Zr}$; $A = \text{Si, X} = \text{B}$, space group $\text{P6}_3 / \text{mmc}$, prototype Cr_2AlC) was studied using *ab initio* calculations. Based on the energy of mixing data as well as the density of states (DOS) analysis, $(\text{Cr}_{1-x}\text{Zr}_x)_2\text{AlC}$ and $(\text{Cr}_{1-x}\text{Hf}_x)_2\text{AlC}$ are predicted to be unstable, whereas $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$, $\text{Cr}_2(\text{Al}_{1-y}\text{Si}_y)\text{C}$ and $\text{Cr}_2\text{Al}(\text{C}_{1-z}\text{B}_z)$ are predicted to be stable or metastable. Among the three theoretically predicted promising alloying elements (Ti, Si and B) for Cr_2AlC , Si was selected for further experimental study.

The alloying scheme was realized via combinatorial DC magnetron sputtering using a split compound target consisting of the upper part Cr:Al:C stoichiometry of 2:1:1 and the lower part Cr:Si:C stoichiometry of 2:1:1 in an industrial chamber. Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x < 1$) films were synthesized at 600 °C. Oxidation experiments were performed at 1120 °C in air for 4 hours for the Cr_2AlC and $\text{Cr}_2\text{Al}_{1-x}\text{Si}_x\text{C}$ ($0 < x \leq 0.06$) films. The crystal structure, microstructure and chemical composition of the as-deposited as well as oxidized films have been investigated by means of XRD, SEM, EDS, TEM, STEM and 3D APT. It is found that the self-healing kinetics of Cr_2AlC based films can be increased drastically by sub-percentage additions of Si. Detailed characterization of the MAX phase samples containing 0 and 0.7 at% Si before and after oxidation demonstrates that Si alloying affects the microstructural evolution during oxidation. It is observed that the average columnar grain width of the oxidized MAX phase sample without Si additions has increased significantly compared to that of its as-deposited state, whereas the average columnar grain width of the MAX phase sample containing 0.7 at% Si after oxidation show no significant difference from that of its as-deposited state. The presence of Si in Cr_2AlC appears to inhibit grain growth during oxidation. Moreover, after oxidation a significant increase of the

Conclusions

number of oxide grains at the oxide/film interface per unit length of the interface has been observed for the MAX phase sample containing 0.7 at% Si compared with the MAX phase sample without Si additions. Furthermore, 3D APT analysis of the MAX phase sample containing 0.7 at% Si after oxidation reveals the absence of Si in the chromium carbide and oxide regions. Electron microscopy and atom probe tomography data support the notion that the here reported Si concentration induced increase in self-healing rate by up to 40% is enabled by the Si concentration induced, and hence concomitant, increase in nucleation density of the healing agent Al_2O_3 .

In the last part of the thesis the relationship between chemical composition and phase formation of Nb-Al-C thin films was studied by combinatorial thin film synthesis and *ab initio* calculations. Thin films with lateral chemical composition gradients were synthesized by DC magnetron sputtering using elemental targets at substrate temperatures of 710-870 °C. Analysis of the phase formation at different substrate temperatures revealed that Nb_2AlC forms between 710 and 750 °C under the deposition conditions studied here. A predominantly single phase Nb_2AlC region where 99% of the X-ray diffraction intensity originates from Nb_2AlC was identified. The average chemical composition of the predominantly single phase Nb_2AlC region is measured to be 49.4 ± 0.5 at% Nb, 24.7 ± 0.7 at% Al, 25.6 ± 0.9 at% C and 0.3 ± 0.02 at% O. Furthermore, selected area electron diffraction analysis reveals a single phase Nb_2AlC region. It is suggested that the higher defect formation energy of Al substituting Nb compared with Al substituting Cr may explain the limited solubility of Al in Nb_2AlC compared with Cr_2AlC . This energetics consideration may serve as indicator for the magnitude of the A-element homogeneity range in $M_{n+1}\text{AX}_n$ phases. The lattice constants of Nb_2AlC are $a = 3.110 \pm 0.001$ Å and $c = 13.867 \pm 0.006$ Å determined from X-ray diffraction analysis with deviations of 1 % and 0.3 % from the

Conclusions

ab initio calculated a and c values respectively, being in good agreement. The elastic modulus of Nb_2AlC measured by nanoindentation is 274 ± 62 GPa, which also agrees well with the calculated elastic modulus of 295 GPa from *ab initio* calculations.

These conclusions show that combining combinatorial thin film synthesis with high-throughput characterization techniques and quantum mechanical calculations enables knowledge-based materials design: Based on the phase stability predictions from the *ab initio* calculations, promising alloying elements were selected and hence combinatorial synthesis can be employed to synthesize the desired thin films covering the whole alloying concentration range. Then key experiments could be conducted to evaluate the phase stability predictions made and to identify the effect of the alloying element concentration on the self-healing kinetics of Cr_2AlC (c.f. chapter 4.2). Further experiments are described in the future work section of this thesis.

5 Future work

Based on the above conclusions, there are several future research directions possible. It has been shown that Ti, Si and B are promising alloying elements in Cr_2AlC from the theoretical predictions. Besides Si, the effect of Ti and B as alloying elements for Cr_2AlC on the self-healing kinetics should be evaluated in the future. It can be expected that the study of the effect of different alloying elements on the self-healing kinetics of Cr_2AlC will contribute to the identification and understanding of the basic physical and chemical design principles for tuning the self-healing kinetics of Cr_2AlC .

It was shown that alloying Cr_2AlC with Si affects the microstructural evolution and oxidation kinetics. The enhancement of the self-healing rate is suggested to be due to the Si concentration induced and hence concomitant increase in nucleation density of the healing agent. Hence, further detailed study should be conducted in order to find out how Si affects the oxidation kinetics. It is expected that the Si distribution can be unveiled by analyzing the Si concentration within the Cr_2AlC grains as well as at the grain boundaries of the as-deposited and oxidized films by means of 3D APT. Moreover, electron energy loss spectroscopy (EELS) analysis is expected to find out how Si is incorporated in the film before and after oxidation. Hence, combining 3D APT and EELS analysis the effect of Si on the film grains is likely to be discovered. Moreover, further detailed study on the oxidation of the Si containing Cr_2AlC films especially its initial stages of oxidation is expected to elucidate the correlation between the chemistry and microstructure of the film and nucleation and growth process of the oxide. It is expected that 3D APT analysis and *in-situ* X-ray photoelectron spectroscopy study during oxidation at the interface between the film and oxide will contribute to understanding the chemistry of the initial stages of

Future work

oxidation. In addition, thermal gravimetric analysis should be performed at different temperatures. Then combining with compositional analysis and microscopic observations, it is anticipated that eventually a growth rate law can be described in terms of the amount of oxide, time and temperature.

As a first step for extending the study of self-healing materials to other $M_{n+1}AX_n$ phase systems, Nb_2AlC thin films have been successfully synthesized via combinatorial approach. The next step would be to synthesize homogeneous single phase Nb_2AlC thin films. Since it was found that the chemical compositions of the Nb_2AlC thin films are rather close to the stoichiometric composition, it is of crucial importance to develop the synthesis recipe which can produce the right film composition and hence the single phase Nb_2AlC . This may be realized by means of tuning the stoichiometry of the target material and the atomic diffusion process during synthesis. Further studies would be on the self-healing kinetics of Nb_2AlC with respect to the time, temperature and alloying elements if needed.

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