Effect of Si Alloying on the Self-healing Kinetics of Cr_2AlC

and

Phase Formation of Nb_2AlC Thin Films

Von der Fakultät für Georessourcen und Materialtechnik der
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Abstract

In the first part of this thesis, 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, space group $P6_3/mmc$, 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, $(Cr_{1-x},Zr_x)_2AlC$ 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. The density of states analysis reveals that small differences in the position of the Fermi level alters the phase stability: $(Cr_{1-x},Zr_x)_2AlC$ and $(Cr_{1-x},Hf_x)_2AlC$ are predicted to be unstable or metastable as the Fermi level lies at a peak position. While the Cr dominated DOS for $(Cr_{1-x},Ti_x)_2AlC$ 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 $Cr_2Al_{1-x}Si_xC$ ($0 < x < 1$) 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 $Cr_2Al_{1-x}Si_xC$ ($0 < x \leq 0.06$) 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 ± 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 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. Furthermore, selected area electron diffraction analysis reveals the local formation of single phase Nb_2AlC. The limited Al solubility in Nb_2AlC compared with Cr_2AlC can be readily understood by comparing the defect formation energy of Al substituting Nb and Cr in Nb_2AlC and Cr_2AlC, 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 Nb_2AlC determined experimentally are in very good agreement with the *ab initio* calculated data.

Zusammenfassung

Im ersten Teil der Arbeit wird die Phasenstabilität von $(Cr_{1-x},M_x)_2(Al_{1-y},A_y)(C_{1-z},X_z)$ (M = Ti, Hf, Zr; A = Si, X = B, Raumgruppe $P6_3/mmc$, Prototyp Cr_2AlC) mittels *ab initio*-Berechnungen untersucht. Auf der Grundlage von Daten zur Mischungsenergie sowie Zustandsdichteanalysen (density of states analyses, DOS) werden $(Cr_{1-x},Zr_x)_2AlC$ and $(Cr_{1-x},Hf_x)_2AlC$ als instabile Phasen vorhergesagt, während $(Cr_{1-x},Ti_x)_2AlC$, $Cr_2(Al_{1-y},Si_y)C$ und $Cr_2Al(C_{1-z},B_z)$ als stabile bzw. metastabile Phasen errechnet werden. Die Zustandsdichteanalysen zeigen, dass geringe Unterschiede in der Position der Fermi-Level die Phasenstabilität beeinflussen: $(Cr_{1-x},Zr_x)_2AlC$ und $(Cr_{1-x},Hf_x)_2AlC$ werden als instabil bzw. metastabil vorhergesagt, da das Fermi-Niveau in einem Hochpunkt liegt, während für die Cr-dominierten Zustandsdichten im $(Cr_{1-x},Ti_x)_2AlC$ 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 $Cr_2Al_{1-x}Si_xC$ ($0 < x < 1$)-Dünnschichten wurden mittels DC-Magnetronsputterns bei 600°C in einer Industrieanlage synthetisiert und anschließend bei 1120°C/4h 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 ± 17%. Die Daten der Elektronenmikroskopie und Atomsondentomographie unterstützen das Konzept, dass die hier berichtete Si-Konzentrationinduzierte 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-Magnetronsputterns mit elementaren Targets bei Substrattemperaturen von 710-870°C abgeschieden. In Bezug auf die Phasenbildung in Nb_2AlC 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 Nb_2AlC 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 $(Cr_{1-x},M_x)_2(Al_{1-y},A_y)(C_{1-z},X_z)$

(M = Ti, Hf, Zr; A = Si, X = 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. Primetzhofer, 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_2AlC (M = 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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