Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Effect of Si additions on the Al_2O_3 grain refinement upon oxidation of Cr_2AlC MAX phase

Lin Shang[a,*], Pradeep Konda Gokuldoss[a,*], Stefanie Sandlöbes[b], Moritz to Baben[a,c], Jochen M. Schneider[a]

[a] Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, D-52074 Aachen, Germany
[b] Institut für Metallkunde und Metallphysik, RWTH Aachen University, Kopernikusstr. 14, D-52074 Aachen, Germany
[c] GTT-Technologies, Kaiserstr. 103, D-52134 Herzogenrath, Germany

ARTICLE INFO

Article history:
Received 6 October 2016
Received in revised form
26 November 2016
Accepted 30 November 2016
Available online xxx

Keywords:
$M_{n+1}AX_n$ phases
Oxidation
Alloying
Atom probe tomography
Combinatorial magnetron sputtering

ABSTRACT

The effect of Si additions on the oxidation behavior of Cr_2AlC based coatings is investigated. Oxidation experiment was performed at 1120 °C in air for 4 h for Cr_2AlC and $Cr_2Al_{1-x}Si_xC$ ($0 < x \leq 0.06$) coatings. The crystal structure, microstructure and chemical composition of the as-deposited as well as oxidized coatings have been investigated. Alloying Cr_2AlC with up to 0.7 at.% Si causes an increase in Al_2O_3 scale thickness by up to 40 ± 17%. Electron microscopy and atom probe tomography data support the notion that the here reported Si concentration induced 40% increase in Al_2O_3 layer thickness (during oxidation at 1120 °C for 4 h) is enabled by the Si concentration induced, and hence concomitant, increase in nucleation density of Al_2O_3.

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 [1–4]. They have attracted a great deal of attention over the past decade due to their distinctive combination of metallic and ceramic properties [1,2,5]. Recently it has been reported that the $M_{n+1}AX_n$ phases Ti_3AlC_2[6], Ti_2AlC [7,8] and Cr_2AlC [9] show self-healing behavior: Cracks in Ti_2AlC were 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[8]. Hence, such materials are attractive for application as structural components or protective coatings at elevated temperatures and in harsh environments. They may significantly prolong the service lifespan if cracks can be healed in situ. However, the oxide scale of $Ti_{n+1}AlC_n$ phases consists not only of Al_2O_3 but also of TiO_2 [6–8,10], where the discontinuously distributed TiO_2 may act as potential crack initiation sites. Therefore, it is anticipated that Cr_2AlC based materials are better self-healing materials since α-Al_2O_3 formation has been reported for oxidation at 1000 °C and above [11–17]. Moreover, recently the proof-of-concept for multiple erosion damage healing of Cr_2AlC has been demonstrated experimentally [18].

However, the Al_2O_3 scale formation on Cr_2AlC is sluggish, resulting in long healing times even at elevated temperatures, which is undesired for 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 [20], 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. [21], the oxidation behavior is unknown. In this work, the effect of Si additions on the phase formation and the surface oxidation of Cr_2AlC was investigated by spatially resolved analysis of the structure and composition.

* Corresponding authors.
E-mail addresses: pradeep@mch.rwth-aachen.de, kg.prad@mpie.de (P. Konda Gokuldoss).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.050
0955-2219/

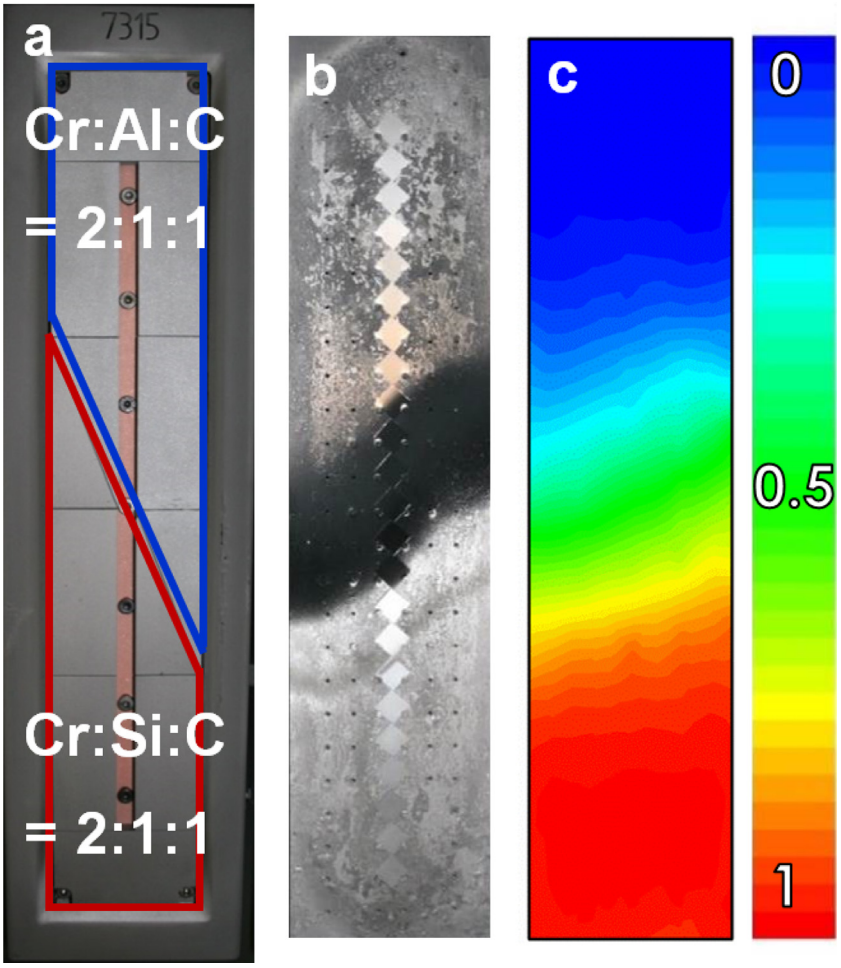

Fig. 1. (a) Photograph of the split Cr-Al-C/Cr-Si-C target. (b) Photograph of the 23 coated substrates on the sample holder located along the vertical axis of the target. (c) Si concentration gradient x ($0 < x < 1$) in the as-deposited coatings measured along the vertical axis of the target.

2. Experimental section

2.1. Sample fabrication

Cr_2AlC and $Cr_2Al_{1-x}Si_xC$ ($0 < x < 1$) coatings were synthesized by DC magnetron sputtering in an industrial chamber (CC800/9, CemeCon AG, Wuerselen, Germany). A compound target with a size of 50 cm × 8.8 cm × 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 coatings. A split compound target displayed in Fig. 1(a) was used to deposit the $Cr_2Al_{1-x}Si_xC$ ($0 < x < 1$) coatings shown in Fig. 1(b). The split target with a size of 50 cm × 8.8 cm × 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. 1(b) the 23 polycrystalline α-Al_2O_3 substrates (KERAFOL Keral 99, 1.5 cm × 1.5 cm × 0.038 cm, as-fired, roughness R_a = 0.2 μm) 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 h with a target power density of 2.2 W/cm^2. The geometric arrangements of the Si and Al rich target segments displayed in Fig. 1(a) results in a Si concentration gradient in the as-deposited coatings which was measured along the vertical target axis by energy dispersive X-ray spectroscopy (EDS) as depicted in Fig. 1(c).

2.2. Oxidation

Oxidation was performed using a furnace (HTF-1700, Carbolite) at 1120 °C in air for 4 h for Cr_2AlC and $Cr_2Al_{1-x}Si_xC$ ($0 < x \leq 0.06$) coatings. The heating and cooling rates were 50 and 10 °C/min, respectively.

2.3. Characterization

Characterization of $Cr_2Al_{1-x}Si_xC$ ($0 < x < 1$) coatings was performed using measurement grid points along the Si gradient with 7 mm in spacing resulting in 3 points measured per deposited coating.

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 Cr_2AlC and $Cr_2Al_{1-x}Si_xC$ ($0 < x < 1$) coatings. 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 (EDS) and scanning electron microscopy (SEM) (JEOL JSM-6480 with attached EDAX Genesis 2000) was used for compositional and microstructural investigations, respectively. For chemical composition analysis, a Cr-Al-Si-C coating sample quantified by wavelength dispersive X-

Please cite this article in press as: L. Shang, et al., Effect of Si additions on the Al_2O_3 grain refinement upon oxidation of Cr_2AlC MAX phase, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.050