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Improving the high-temperature oxidation resistance of a β - γ TiAl alloy by a Cr₂AlC coating

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ABSTRACT

A Cr_2AlC coating was deposited on a $\beta-\gamma$ TiAl alloy. Isothermal oxidation tests at 700 °C and 800 °C, and thermocyclic oxidation at 800 °C were performed in air. The results indicated that serious oxidation occurred on the bare alloy. Thick non-protective oxide scales consisting of mixed $TiO_2 + \alpha - Al_2O_3$ layers formed on the alloy surface. The coated specimens exhibited much better oxidation behaviour by forming an Al-rich oxide scale on the coating surface during the initial stages of oxidation. This scale acts as diffusion barrier by effectively blocking the ingress of oxygen, and effectively protects the coated alloys from further oxidation.

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1. Introduction

In recent years, γ -TiAl intermetallic alloys have received significant attention, since they possess some potential to replace the heavy Ni-based alloys in particular applications [1–3]. These alloys combine good mechanical properties up to moderately elevated temperatures (750 °C) with a low density and are therefore considered for light-weight aerospace and automotive applications. Strength is one of the primary properties of a TiAl alloy that requires improvement. Hot-forging as normally carried out for ordinary metallic materials has been reported to result in higherstrength TiAl alloys [4]. However, forging of conventional γ -TiAl alloys is difficult due to their ordered intermetallic structure. To solve this problem, the so-called β - γ TiAl alloys have been developed [4–6]. The introduction of β phase in the γ -TiAl alloys improves the deformability remarkably, making the conventional or hot-die forging process much easier. For example, a work piece of β - γ TiAl alloy with composition of Ti-42Al-10V (at.%) dies could be forged into a turbine blade within 1 s by utilizing preheated to a temperature of only 200 °C. This improvement makes this kind of alloys very attractive for several applications, such as gas turbine blades [4,5].

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However, one of the major concerns for structural applications of TiAl alloys is the low oxidation resistance at high temperatures due to the fact that they do not form long-lasting protective alumina scales [7–10]. Additionally, some β -forming elements in the β - γ TiAl alloys, such as V and Mo, form low-melting-point oxides, e.g., V_2O_5 (690 °C) and MoO $_3$ (795 °C), respectively, which are detrimental for oxidation resistance. Therefore, the oxidation behaviour of these TiAl alloys should be even worse than that of the γ -TiAl alloys without V and Mo additions. So far, it seems that only few reports have been dedicated to the oxidation behaviour and protection of β - γ TiAl alloys.

As a member of $M_{n+1}AX_n$ (abbreviated as MAX, where M is an early transition metal, A is an IIIA- or IVA-group element, and X is C or N) phases [11], Cr_2AlC compound possesses nanolaminate microstructure of metal carbide separated by single layers of Al atoms [12]. The activity and diffusivity of Al is large enough to form a continuous protective alumina scale on the surface during exposure at high temperature. Therefore, Cr_2AlC bulk materials exhibited excellent high-temperature oxidation [13–16] and hot corrosion resistance [16]. In a previous study [17], a Cr_2AlC coating was deposited onto a near- α Ti alloy. The coating demonstrated good oxidation resistance at temperatures up to 700–800 °C.

In this work, we deposited a Cr_2AlC coating on a $\beta-\gamma$ TiAl alloy to test the capability of these ternary phases as oxidation-resistant coatings. Isothermal oxidation tests at 700 °C and 800 °C, and thermo cyclic oxidation at 800 °C of the bare alloys and coated

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specimens were performed in air. Characterization and evaluation of the coating was conducted by using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX).

2. Experimental details

The β – γ TiAl alloy with the base-line composition of Ti–Al–V–Mo was manufactured as extruded bars. The bars were cut into coupons of size Φ 20 mm \times 2 mm, and then ground up to 2500 grit and cleaned. The coating was deposited by co-sputtering from three single elemental targets of Cr, Al, and C in an industrially sized coater (CC800/9 HPPMS, CemeCon AG, Germany). The samples were hanging in a threefold planetary rotation system in the coater in order to cover all the surfaces of the samples with Cr₂AlC coatings. However, due to deposition problems, the coatings on the edges and corners were a bit thinner, about 3–4 μ m. Table 1 shows the conditions selected in this study for the deposition process of the coating [17].

Intermittent isothermal oxidation tests were conducted in static air at 700 °C and 800 °C in alumina crucibles placed in a muffle furnace. The oxidation specimens were taken out of the furnace and cooled to room temperature at various intervals for mass change measurement. The total mass of a specimen together with the crucible was recorded. Furthermore, thermocyclic oxidation tests were conducted at 800 °C in a thermal cyclic test rig. Each cycle consisted of 50 min heating and 10 min cooling. The masses of the specimens were recorded at different numbers of cycles. The sensitivity of the balance used for the isothermal and cyclic oxidation tests was $10^{-5}\,\mathrm{g}$.

Phase compositions of the Cr_2AlC coatings before and after oxidation tests were identified by XRD (D8-Discovery Brucker, Cu K α) using a fixed incident angle of 20° . The morphology and composi-

Table 1Conditions for the coating deposition parameters in this study.

Base pressure	$8\times 10^{-3}Pa$
Working pressure	0.35 Pa
Working gas	Ar
Substrate temperature	500℃
Substrate Bias voltage	−90 V
Power for Cr source	537 W
Power for Al source	480 W
Power for C source	1300 W
Rotational velocity of substrate	1 rpm
Thickness of coating	5–6 μm

tion of the coatings and the oxide scales were assessed by using SEM (Vega & Mira, 15 kV) and EDX (Oxford, 15 kV). No Au or C coatings were used on SEM samples. In the EDX measurements, a bulk Cr₂AlC material was used as the standard for quantification of Cr, Al and C elements in the as-deposited and oxidized Cr₂AlC coatings.

3. Results

3.1. As-deposited Cr₂AlC coating on the Ti-Al-V-Mo alloy

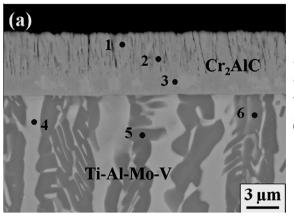
Fig. 1 shows a back-scattered electron (BSE) image of the cross-section of the Cr_2AlC coating deposited on the Ti-Al-V-Mo alloy and the corresponding XRD pattern. The Cr_2AlC coatings display a columnar structure (Fig. 1a), which can be classified as a V-shape growth type [17]. According to the EDX measurements, the chemical composition of the coating (Table 2) is close to stoichiometric Cr_2AlC : Cr 44–46 at.%, Al 25–27 at.%, and C 26–30 at.%. The thickness and chemical composition of the Cr_2AlC coating was nearly homogenous, except for the specimen edges/corners. The micrographs in Fig. 1 show that the Ti-Al-V-Mo alloy is composed of two characteristic zones: (a) white zones of β phase (point 4, rich in V and Mo), and (b) darkish zones of γ or $\gamma + \alpha_2$ phases (points 5 and 6).

3.2. Isothermal and cyclic oxidation kinetics

Fig. 2a and b shows the mass gain of the bare and coated TiAl alloy during interrupted isothermal oxidation at 700 °C and 800 °C. The oxidation behaviour of the Ti–Al–V–Mo bare alloy exhibits linear kinetics, which indicates a continuous oxidation during its exposure at high temperatures. Rather high weight gains of $\sim\!0.09~\text{mg/(cm}^2~\text{h})$ and $\sim\!0.5~\text{mg/(cm}^2~\text{h})$ were observed during oxidation at 700 °C and 800 °C, respectively. On the other hand,

Table 2 Chemical compositions (analyzed by EDX) of the points in Fig. 1a.

Analyzed point	Chemi	Chemical composition (at.%)					
	С	Al	Cr	Ti	V	Mo	
1	30	25	45	-	-	-	
2	27	27	46	-	-	-	
3	26	26	46	2	-	_	
4	-	36	-	46	13	5	
5	-	46	-	48	5	1	
6	-	44	-	47	7	2	



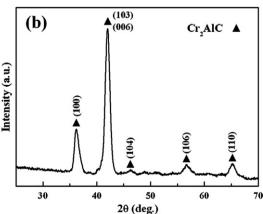


Fig. 1. Cross-sectional BSE-mode SEM image of the as-deposited Cr₂AIC coating on the Ti-Al-V-Mo alloy (a) and the corresponding XRD pattern (b).

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