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Favorable deposition of γ-Al_2O_3 coatings by cathode plasma electrolysis for high-temperature application of Ti-45Al-8.5Nb alloys

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ABSTRACT

Cathode plasma electrolysis deposition (CPED) has been used to prepare γ-Al_2O_3 coatings on Ti-45Al-8.5Nb alloys for high-temperature application. The effect of deposition voltage and duty cycle on microstructure and high-temperature oxidation resistance of the coatings has been studied. The surface and cross-section morphologies before and after high-temperature oxidation test, chemical composition and phase identification of the coatings have been investigated by scanning electron microscopy (SEM), energy disperse spectroscopy (EDS), and X-ray diffraction (XRD). The results show that the thickness and high-temperature oxidation kinetics of as-prepared Al_2O_3 coatings initially increase and then decrease, with the increase of deposition voltage from 110 V to 150 V and duty cycle from 40% to 80%. The minimum weight gain of only 0.495 mg/cm^2 after oxidation duration of 100 h at 900 °C can be achieved for the coatings formed with deposition voltage of 130 V and duty cycle of 60%. The deposition mechanism of the coatings and effect of CPED parameters are also explained in this work.

1. Introduction

High-temperature TiAl alloys have attracted great attention due to low density, high specific strength, high Young's modulus and excellent creep resistance [1–3]. However, poor oxidation resistance over 700 °C limits their practical applications. The main reason for insufficient high-temperature oxidation resistance is the formation of TiO_2 and Al_2O_3 mixture rather than the continuous Al_2O_3, during the oxidation process [4–6]. Therefore, a highly attractive solution should be explored to promote the formation of Al_2O_3 and suppress the existence of TiO_2 on the surface of TiAl alloys at elevated temperature.

Plasma electrolysis is an advanced and environmental friendly surface modification technique [7], which includes anode process (such as plasma electrolytic oxidation (PEO)) and cathode process (such as cathode plasma electrolytic deposition (CPED)). The PEO technique, as micro-arc oxidation, is an in-situ coatings growth process on the surface of the valve metals (such as Al, Mg, Ti) through micro-arc discharge and electrochemical reaction under the very high voltage [8–10] (almost 400 V). However, the Al_2TiO_5 phase is mainly formed on the TiAl alloy by using PEO technique, which was decomposed to α-Al_2O_3 and r-TiO_2 [11–13].

CPED technology is a new method to deposit metal coatings [14], ceramic coatings [15,16] and diamond-like carbon films [17] on various kinds of metals or alloys. It have been reported that coatings prepared by CPED exhibit excellent adhesion to the substrate, high hardness and favorable corrosion, as compared to conventional method [18,19]. Research for ceramic coatings obtained by means of CPED is generally taken by using high voltage (e.g. 400 V) and long deposition time (such as 60 min) [20,21]. In this work, relatively low voltage (e.g. 130 V) and very short deposition time (e.g. 60 s) have been used for forming continuous and dense Al_2O_3 coatings on TiAl alloy substrates. It is interesting to note for the formation of γ-Al_2O_3 phase rather than α-Al_2O_3 phase by CPED. The effects of deposition voltage and duty cycle on the microstructure and high-temperature oxidation kinetics of the CPED-treated alloys have been also systematically studied.

2. Experimental

2.1. Substrate pre-treatment

Ti-45Al-8.5Nb alloy (the alloy element content has been shown in Table 1) was used as the substrate. The cylinder alloy samples with the size of φ 6 mm × 50 mm were polished with SiC paper up to a grit of #1500. The samples were ultrasonically cleaned in ethanol for 5 min sequentially, then rinsed with the ionized water, and dried up in air finally.

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Table 1
The alloy element content.

	Ti	Al	Nb	W	B	Y
Atomic percentage (%)	46.26	45	8.5	0.2	0.02	0.02

2.2. Preparation of Al_2O_3 coatings

Al_2O_3 coatings were fabricated on Ti-45Al-8.5Nb alloy by cathode electrolysis plasma deposition (CPED) in 1 mol/L Al $(NO_3)_3$ aqueous solutions (pH = 5.6). The experimental device consisted of a quartz electrolytic cell with circulating water cooling and direct-current (DC) power supply. Two paralleled graphite plates were used as anode and the cylinder alloy samples as cathode, immersed in the Al $(NO_3)_3$ electrolyte. The power voltage was adjusted in the range of 0–400 V and duty cycle was varied from 1% to 99%. The distance between cathode and anode was 150 mm, the electrolyte temperature was controlled below 60 °C, the power frequency was 4000 Hz and the deposition time for each sample was 60 s.

2.3. Characterization

The surface and cross-sectional morphologies of coatings were observed by scanning electron microscope (SEM, Zeiss Supra 55), and element compositions were determined by energy dispersive spectroscopy (EDS). Phases identification in the coatings were performed by X-ray diffraction (Ultima IV) with Cu K_α radiation ($\lambda = 0.15406$ nm), and $2\theta/\theta$ diffractograms were recorded in the scan range of 10–90°, with a step wise of 0.02°. The roughness of coatings was investigated by Olympus laser confocal microscopy.

Cyclic oxidation tests were carried out in a box-type resistance furnace at 900 °C in air for total oxidation duration of 100 h. Each sample was perpendicularly put in an yttrium crucible, removed with oxidation interval of 10 h, cooled down to room temperature for weighing, and then replaced the sample in the furnace of continued oxidation until 100 h. The weight gain of the samples were obtained by an analytical balances with an accuracy of 10^{-5} g, and the weight gain per contact area (mg/cm^2) was used to evaluate high-temperature oxidation resistance of samples. In order to ensure the reproducibility, double specimens were measured under the same condition.

3. Results

3.1. The range of parameters for CPED process

A typical current density-voltage curve of the CPED process in the Al $(NO_3)_3$ electrolyte is shown in Fig. 1(a). When the voltage is lower than about 70 V (U_1), the current density-voltage characteristics are approximately consistent with Ohm law. At the stage, a large number of hydrogen gas accumulates on the cathode surface, and meanwhile, the current density continues to rise, resulting in the local electrolyte boiling. Consequently, glow discharge initially occurs in the electrolyte. On further increase of the voltage up to about 170 V (U_2), current density begins to sharp decline, because of low electrical conductivity of the bubble [22,23]. It is found that a continuous plasma envelope is formed on the sample surface, which resultes in the rapid increase of the surface temperature with the increase of voltage. Nervetheless, the bulk temperature of the cylinder substrate remains relatively low, due to continuously cooling in the flowing electrolyte solution. Beyond this voltage zone, the continuous and steady plasma transforms to intensive arc discharge, which is harmful to deposition coatings.

Suitable deposition process parameters under the pulse frequency of 4000 Hz were shown in Fig. 1(b). When the duty cycle or voltage was too high, it was difficult to obtain Al_2O_3 coating because the strong discharge induced surface cleaning effect. Once the voltage exceeds the upper limit, the Ti-45Al-8.5Nb alloy would melts under a fixed duty cycle, just as the red region of Fig. 1(b). Meanwhile, only normal electrolysis process occurs when the duty cycle lower than the bottom limit [24], as shown in the green zone in Fig. 1(b). The continuous and stable electrolysis plasma only occurs, when the voltage and duty cycle are within suitable zone in the blue zone mentioned in Fig. 1(b).

3.2. Characterization of CPED Al_2O_3 coatings

Fig. 2 shows the surface and cross-sectional morphologies of Al_2O_3 coatings prepared by CPED with different voltages and duty cycles. When the deposition voltage is relatively low (110 V), as showed in Fig. 2(a) and (b), the surface cannot be completely covered by a thin coatings, and there are many micro-pores on the surfaces of coatings due to hydrogen evolution [25]. As the discharge voltage increases to 130 V, both average diameter of micro-pores and thickness of as-prepared coatings arise. Additionally, the coating thickness increases to 23.5 μm with the increase of duty cycle from 40% to 60% at the same voltage of 130 V, and the average diameter of the micro-pores also reaches maximum value of approximately 10 μm.

From the backscattered cross-sectional SEM images in Fig. 2(b), (d) and (f), it can be observed that the interfaces between substrate and

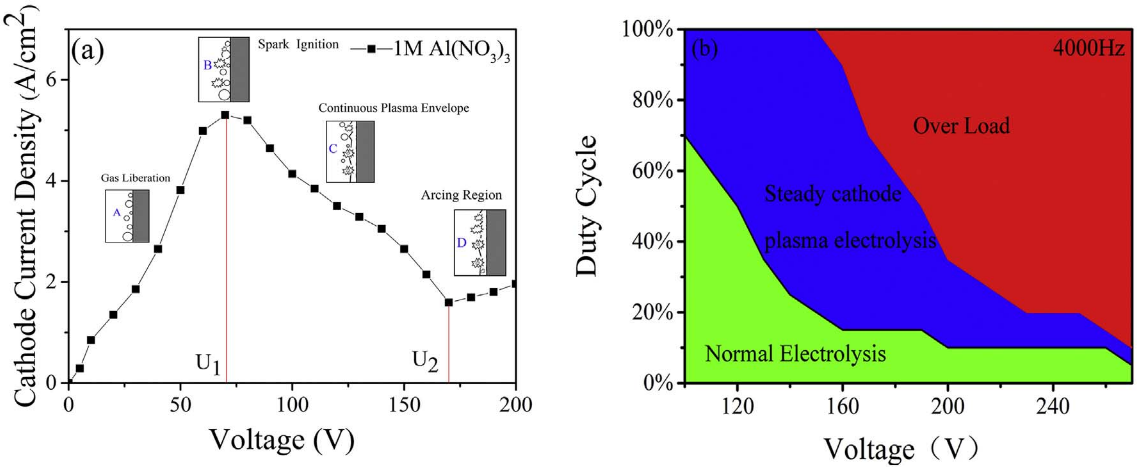

Fig. 1. (a) A typical current density-voltage curve of the CPED process. (b) Suitable deposition process parameters under the pulse frequency of 4000 Hz.