## ARTICLE IN PRESS

Surface & Coatings Technology xxx (2017) xxx-xxx



Contents lists available at ScienceDirect

## Surface & Coatings Technology



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

## Preparation and properties of ceramic coatings by cathode plasma electrolytic deposition on titanium alloy

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#### ARTICLE INFO

Article history: Received 6 January 2017 Revised 8 April 2017 Accepted in revised form 12 April 2017 Available online xxxx

Keywords: Titanium alloy Cathode plasma electrolytic deposition Alumina Zirconium lanthanum Composite coatings

### ABSTRACT

The ceramic composite coatings consisting of Al<sub>2</sub>O<sub>3</sub> bond-coat (70–90  $\mu$ m) and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> top-coat (300–330  $\mu$ m) were prepared by two-step cathode plasma electrolytic deposition (CPED) on titanium alloy. Compared with single La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating, the bonding strength of the composite coatings was improved by 40%, owing to the anchorbond of Al<sub>2</sub>O<sub>3</sub> coating and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating. High temperature cyclic oxidation at 700 °C was adopted to investigate the high temperature corrosion resistance of the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating and the composite coatings. The results revealed the composite coatings possessed the best high-temperature oxidation and spallation resistance. Deposition processes of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating and Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> composite coatings were illustrated through current density-time curves.

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#### 1. Introduction

Titanium (Ti) alloys are attractive materials due to their high relative strength, low density and good corrosion resistance [1]. However, the high affinity of Ti towards oxygen is one of the main factors that limit the applications of these alloys at high temperature. The Ti alloys degrade quickly during oxidation process because of the formation of non-protective oxide scales. Therefore it is necessary to make some surface modifications to enhance the high temperature oxidation resistance and the heat insulation of the Ti alloys without altering the bulk properties.

So far, many techniques have been developed to prepare coatings on Ti alloys. Hot-dip aluminizing and interdiffusion treatment [2–4] have been used to develop a TiAl<sub>3</sub>-rich coating, which can markedly decrease the oxidation rate of Ti alloys. But the thermal insulation effect of these coatings is poor. Plasma spraying (PS) and electron-beam physical vapor deposition (EB-PVB) [5] are the relatively mature coatings preparation technologies. Thermal barrier coatings (TBCs) with good heat insulation properties can be prepared by these two methods. However, both of them are not suitable for preparing coatings on the samples with complex shapes. Micro arc oxidation (MAO) is an electrochemical formation of anodic films on valve metals by spark/arc microdischarges. The compositions and structures of MAO coatings are greatly influenced by substrate. Though Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and other particles could be doped [6–8], the coatings prepared by MAO on Ti alloys are mainly composited of TiO<sub>2</sub>, which causes them poor oxidation resistance. In

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http://dx.doi.org/10.1016/j.surfcoat.2017.04.033 0257-8972/© 2017 Elsevier B.V. All rights reserved. addition, these coatings are not easy to thicken due to the mechanism of MAO.

Cathode plasma electrolytic deposition (CPED) is a new method of surface treatment. Compared with the traditional coatings preparation methods, the CPED method has advantages of fast deposition rate, large coating thickness and simple equipment requirements [9,10]. Moreover, the coating composition can be well designed to generate most of the types of deposits and almost not affected by substrates in the CPED method. Ceramic coatings, metal coatings and composite coatings can be prepared by this method on various electrically conductive substrates (including Ti, Mg, Al, C, SiC, Fe, Ni, and et al.) [11-15]. But due to the high current density in the CPED process and strong edge effects of coatings, this method hasn't got much attention of researchers. Recently, our group has found that the current density of CPED can be significantly reduced by adding water-soluble polymer and modifying the electrolyte [16,17]. On this basis, the zirconium lanthanum coating (La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating), alumina coating (Al<sub>2</sub>O<sub>3</sub> coating) and other ceramic coatings can been uniformly deposited by CPED.

As we all know, La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> is an excellent material with low thermal conductivity, good high-temperature phase stability and low sintering tendency [18–21]. However, the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating prepared by CPED usually has poor bonding strength with the Ti alloy substrate. In addition, the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating also exhibits poor high temperature oxidation and spallation resistance. Given the shortages of single La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating mentioned above, Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> double layer composite coatings were prepared by two-step CPED on Ti alloy. The microstructure, bonding strength, high temperature oxidation and spallation resistance of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating and Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> composite coatings were investigated. The formation mechanisms of the coatings were discussed.

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### 2. Experiments

#### 2.1. Coating preparation

The schematic diagram of CPED device for preparing coatings is shown in Fig. 1. A platinum electrode was worked as anode with a dimension of 120 mm  $\times$  50 mm  $\times$  0.3 mm. The sample of Ti alloy (6.3% Al, 4.2% V, 0.15% O, 0.11% Fe, 0.03% C, 0.02% N, 0.001% H, balance Ti, wt%) was used as cathode. A pulsed electrical power supply (TN-KGZ01) was connected in the electrolytic bath. Frequency was set as 500 Hz and duty ratio 60%. A thermostatic water bath was used to control temperature of the electrolyte under 50 °C.

The compositions of solutions and CPED parameters for preparing La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating and Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> composite coatings (Al<sub>2</sub>O<sub>3</sub> coating as the bond-coat) are showed in Table 1. Sample 1 is the Ti alloy with single La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating prepared by CPED. Sample 2 is the Ti alloy with composite coatings prepared by two steps CPED, including Al<sub>2</sub>O<sub>3</sub> coating prepared as the bond-coat and then La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating prepared as the top-coat. For Al<sub>2</sub>O<sub>3</sub> coating preparation, the aqueous solution mainly consisted of Al(NO<sub>3</sub>)<sub>3</sub> $\cdot$ 9H<sub>2</sub>O. The voltage was increased from 0 to 120 V at a rate of 1 V/s and then controlled at 120 V for about 15 min. For La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> coating preparation, the aqueous solution mainly consisted of  $Zr(NO_3)_4 \cdot 5H_2O$  and  $La(NO_3)_3 \cdot 6H_2O$ . The voltage value was increased from 0 to 120 V at the rate of 1 V/s and held at 120 V for about 60 s. Then, the voltage value was increased by 5 V every 60 s. The deposition time was controlled about 10 min. In order to control the process of plasma discharge ignition and ensure the coatings more uniform, 25 g/L polyethylene glycol (PEG, as a surface modification agent) was added in solutions. Moreover, the solutions were treated by heating at 80 °C for 4 h [17].

In the CPE process, the cathode material in solution was covered with bubbles firstly. Then increase the voltage until bright micro-arcs can be observed on the surface of cathode, as shown in Fig. 1. After the electrochemical reactions, a ceramic coating on the surface of cathode material could be observed. Then the obtained sample was washed with distilled water and dried at room temperature.

#### 2.2. Coating characterization

Morphologies and elementary compositions of the samples were characterized by scanning electron microscope (SEM, FEI Quanta250 Environmental Scanning Electron Microscope). Phase structures were characterized by X-ray diffraction (XRD, using a Cu K $\alpha$  radiation DMAX-2500RB, scanning from 10° to 90°, with step of 0.02°, scan rate

Table 1	
The compositions of solutions and C	CPED parameters to prepare coatings.

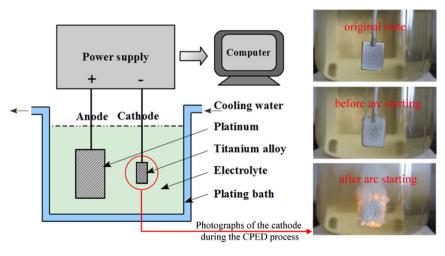
Sam	ple	Al(NO <sub>3</sub> ) <sub>3</sub> ∙9H <sub>2</sub> O mol/L	La(NO <sub>3</sub> ) <sub>3</sub> ∙6H <sub>2</sub> O mol/L	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O mol/L	Time min
1		/	0.67	0.67	10
2	Step-1	0.8	/	/	15
	Step-2	/	0.67	0.67	10

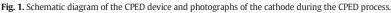
 $2^{\circ}$ /min). Surface roughness was tested by the equipment Taylor Hobson PGI-400, and roughness parameter chosen for this characterization was Ra (roughness average).

Bonding strength was performed to evaluate the bonding force between coating and substrate according to the Chinese Testing Standard GB/T 5210-2006. The coated samples were glued to uncoated similar counterparts (cylinders  $\phi$ 4.5 mm) and then tested in tension in a universal testing machine with drawing rate of 1 mm/min. The value of the tensile load was registered and transformed into an adhesion value, and the bond strength was calculated by the relation of load and area. The pairs were glued together with glue of AAA (cohesive strength ~70 MPa, from Shanghai Research Institute of Synthetic Resins) on the top surface, fully cured in an autoclave, and kept for 24 h at 65 °C before tensile testing. The morphologies and elementary compositions of the samples before and after the bonding strength test were characterized by stereoscopic microscope (KEYENCE VHX-2000) and the SEM mentioned above.

High temperature cyclic oxidation tests were carried out to investigate the kinetics of oxidation and spallation resistance of coatings in air furnace at 700 °C for 100 h. Before the oxidation test, the mass of sample + crucible ( $W_0$ ) and the mass of crucible ( $W'_0$ ) were weighed by the analytical balance (Mettler AE240, China) respectively. Then the sample and crucible were put into the furnace, and taken out after 10 h. After air cooling to the room temperature, the spalling oxide + crucible ( $W_1$ ) and the mass of sample + spalling oxide + crucible ( $W_1$ ) and the mass of spalling oxide + crucible ( $W'_1$ ) were weighed by the analytical balance again. The weight gain was equal to  $W_1 - W_0$ , and the spallation was equal to  $W'_1 - W'_0$ . Then the cycle was repeated 10 times in turn.

The evolutions of voltage (*V*) and cathode current density ( $i_c$ ) with time (t) towards different samples were measured. The voltage value was increased from 0 to 120 V at the rate of 1 V/s and held at 120 V for about 60s. Then, the voltage value was increased by 5 V every 60 s. Final voltage was controlled at 145 V and total time about 10 min. The  $i_c$  and *V* were recorded and plotted as the  $i_c$ -t and *V*-t curves by computer.





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