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Preparation of thermal control coatings on Ti alloy by plasma electrolytic oxidation in K_2ZrF_6 solution

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ABSTRACT

Ceramic coatings with high emission and low absorptance were prepared on Ti6Al4V alloy by plasma electrolytic oxidation (PEO) in zirconate electrolyte. The effects of current density and working frequency on the structure and thermal control properties of the coatings were investigated. The phase composition, microstructure, thickness and roughness of coatings were examined by XRD, SEM, EDS, thickness measurement gauge and roughness measuring instrument, respectively. Thermal control properties of the coatings were studied with a UV–VIS–NIR spectrophotometer and an infrared reflectometer. The results show that the coatings are porous and composed of a large amount of $KZr_2(PO_4)_3$, and a little monoclinic ZrO_2, tetragonal ZrO_2 and ZrP_2O_7 as well. The thickness of the coatings increases with the increase of the current density or the decrease of the working frequency while the roughness of the coatings increases with the increase of the current density and the working frequency. The increase of current density reduces the absorptance, but improves the emissivity; the increase of working frequency improves the absorptance, but does not change emissivity apparently. The coating prepared at 10 A/dm^2, 50 Hz and 50 min, has the lowest solar absorptance (0.34) and the highest infrared emissivity (0.9).

1. Introduction

A thermal control system ensures operational functionality of devices and instruments of the spacecraft when running in orbit with the harsh environment temperature changes [1]. A thermal control coating is a conventional method to balance the temperature of the surface by adjusting the absorptance–emissivity ratio of the coating surface. Currently, there are two kinds of thermal control coatings: (1) a low absorptance–emissivity ratio coating and (2) a high absorptance–emissivity ratio coating. The low absorptance–emissivity ratio coatings are generally white coatings, optical solar reflectors or ceramic coatings [1–4], which are usually prepared by chemical vapor deposition, electron beam physical vapor deposition, magnetron sputtering, ion implanting, plasma spray and sol–gel [5–8]. These methods are usually of high cost or confirm weak adhesion between the coating and the substrate.

Plasma electrolytic oxidation (PEO), also called micro-arc oxidation (MAO), is becoming a universal coating technique to improve corrosion resistance and abrasion resistance for magnesium, aluminum and titanium and their alloys in recent years [9–12]. Furthermore, the prepared coatings exhibit good adhesion to the substrate, and the composition and structure and color of the coatings can be adjusted by the doping of the electrolytes or the changing of the process parameters. Therefore, PEO technique presents a promising application prospect in the field of thermal control coatings [4,11–14].

Zirconate is usually regarded as a candidate material for high temperature applications due to its low thermal conductivity, large thermal expansion coefficient, high temperature resistant performance, strong sintering resistance and high stability at high temperature [15,16]. Presently, there are only a few instances of research work with the PEO technique in zirconate solution [17–20]. In this work, K_2ZrF_6 and NaH_2PO_4 solution was used as electrolytes for the PEO process on Ti6Al4V to prepare high emissivity and low absorption coatings. The composition, the structure and the thermal control properties of coatings were also investigated.

2. Experimental details

2.1. Preparation of PEO coatings

Plate samples of Ti6Al4V (wt.%: 89.3 Ti, 6.26 Al, 4.01 V, 0. 03 Fe, 0.10 C, 0.03 N), with dimensions of 25 mm × 20 mm × 0.8 mm were prepared by a wire-electrode cutting machine. The samples were polished using SiC papers and washed in distilled water, served as the positive electrode. A water cooled electrochemical bath made of stainless steel served as the counter electrode. An in-house manufactured pulsed electrical source of 10 kW was employed for the plasma electrolytic oxidation process in a galvanostatic regime. The electrolyte solution contained 6 g/L K_2ZrF_6 and 5 g/L NaH_2PO_4. The electric parameters and the treatment time are

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Table 1
The technique parameters of PEO process.

Variables	Current density (A/dm^2)	Frequency (Hz)	Time (min)
Current density	6	50	50
	8	50	50
	10	50	50
	12	50	50
Frequency	8	50	50
	8	275	50
	8	500	50

shown in Table 1. During PEO treatment, the electrolyte temperature was maintained below 30 °C using a cooling water flow. After the treatment, the coatings were flushed with distilled water and dried in air. Three samples were made under each condition to ensure the reliability of the experiments.

2.2. Coating characterizations

The surface and cross-sectional morphologies and elemental compositions of the coatings were examined by a JSM-6480 scanning electron microscopy (SEM, Japan's Hitachi LTD) equipped with energy dispersive spectroscopy (EDS, JED-2200, Japan). The phase composition of coatings was examined by TTR-III type X-ray diffraction (XRD, D/max-rB, Ricoh, Japan), using a Cu Kα radiation as the excitation source. The coating thickness was measured with an eddy current coating thickness measurement gauge (TT260, Time Group Inc., China). The thickness was the average of ten measurements made at different locations of the sample. The coating roughness was examined with a surface roughness measuring instrument (TR200, Time Group Inc., China).

2.3. Thermal control property evaluation of the coatings

The emissivity of the coatings was measured by a TEMP 2000, a portable infrared emissivity spectrometer in the range 250 nm–2500 nm at room temperature. The Perkin Elmer Lambda 950 UV–Vis–NIR spectrophotometer was used to measure the absorptance of PEO coatings. Thermal shock resistance tests were carried out in a muffle furnace at 500 °C and in the water at room temperature. During the thermal shock test, coated samples were kept for 3 min to make the sample temperature uniform in the muffle. Then the coated samples were taken out from the furnace and quenched into the water. The tests were repeated for 50 cycles. After the thermal shock tests, the surface states of the coatings were observed and the thermal control properties of the coatings were measured.

3. Results and discussion

3.1. Thickness and roughness of the coatings

The coatings prepared on titanium alloy by the PEO technique demonstrate a roughness of Ra 8.1 to 11.6 μm and appear white in color. Fig. 1 shows the thickness of coatings produced under different current densities and working frequencies. The thickness and roughness of the coatings increase with an increase of the current density. During the experimental process, the number of micro-arc discharge locations was increased and the anode micro-arc discharge intensity was enhanced with the increasing current density, which would lead to the increase of the sintered particles on the coating surface in size and number. Thus the thickness and roughness of the coatings are increased. On the other side, the thickness decreases while the roughness increases with an increase of the working frequency. The increase of the frequency relates to a shorter duration of the anode process per pulse and the accumulative action time is effectively increased. The qualitative experimental observation is that the discharging sparks become more dispersed and smaller with the increase of the working frequency, which illustrates that the energy per pulse provided by the power source is decreased. Therefore, the amount of the sintered substance is comparatively decreased, which gives rise to the decrease of the thickness. Also, the decrease of the sintered substance may be liable for the formation of more micro-sized pores, which consequently results in the increase of the roughness.

3.2. Surface morphologies and elemental analysis of the coatings

Fig. 2 shows the surface morphologies of the coating produced under different current densities and working frequencies. No matter what experimental conditions are, there are a great number of micron-sized pores distributing randomly on the surface of these coatings. Micro-sized pores are formed by molten oxide and gas bubbles during the discharge breakdown process. The electron avalanches are generally responsible for the pore formation, which takes place at the voltage higher than the breakdown potential of the oxygen gas layer or the surface oxide layer [21].

The pores are increased in size with the increase of the current density, the largest pores of the coating (in panel (c) produced under 12 A/dm^2) are of around 75 μm. The increase of the current density leads to an enhanced discharging energy, which contributes to the enlarged pore sizes during the PEO process. Besides, as the discharge intensity increases continuously, the accumulated production mass of oxide increases, which induces a gradually increasing particle size and overlaps the pores nearby [22]. Panels (b), (d) and (e) present that

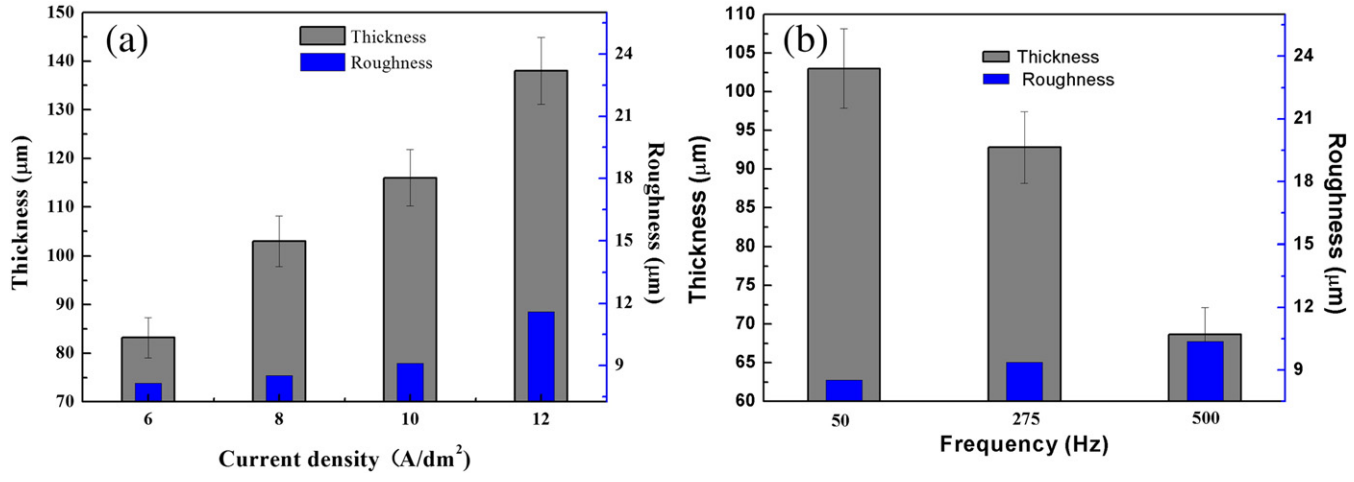

Fig. 1. Thickness and roughness of the coating prepared under different current densities and working frequencies.