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Influence of $FeSO_4$ concentration on thermal emissivity of coatings formed on titanium alloy by micro-arc oxidation

Hui Tang[a], Tiezhu Xin[b], Qiu Sun[a], Chuangui Yi[a], Zhaohua Jiang[a], Fuping Wang[a,*]

[a] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China
[b] School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

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ABSTRACT

Ceramic coatings with high emission were fabricated on Ti6Al4V alloy by microarc oxidation (MAO) with additive $FeSO_4$ into the electrolyte. The microstructure, chemical composition and chemical state of the coatings were determined by SEM, XRD, EDS and XPS, respectively. The bonding strength between the coating and substrate was studied by tensile strength test, together with the thermal shock resistance of the coating. The results showed that Fe content in the coating layer significantly affect its thermal emissivity. The relative content of Fe in the coatings surface increased at first and then decreased with increasing the concentration of $FeSO_4$ in electrolytes, so does the emissivity of the coatings. The bonding strength became weaker with increasing the concentration of $FeSO_4$. In addition, the coating remains stable over 40 cycles of thermal shocking. The coating formed at 3 g/L $FeSO_4$ demonstrates the highest an average spectral emissivity value around of 0.87, and bonding strength higher than 33 MPa.

1. Introduction

High friction heat coming from the acute friction between vehicle's surface and atmosphere causes severe increase of surface temperature during hypervelocity flights, which leads to reduce the lifetime and performance of the space vehicles material. A thermal protection system (TPS) is demanded to avoid aerodynamic heating, which can decrease the surface temperature, prevent the heat transferring inward and protect the electron apparatus [1–3]. TPS usually bases on materials with high temperature stability and excellent thermal insulation [4]. Moreover, the materials must possess high thermal emission. It can effectively radiate the heat on the surface of vehicle back into space.

The existing of traditional thermal protection system on metal surface, contains a ceramic coating filled with highly emissive materials. Silicone adhesives are adopted to bond the coating and metal. The bond strength between the ceramic coating and the metal substrate is weak, so it is high instability. And the coating may be cracked and destroyed under thermal stress, due to its different expansion/contraction coefficients from metals. Ceramic coating formed by micro-arc oxidation technology can alleviate this problem, and result in formation of coating layer with super bonding strength, excellent mechanical and thermal properties.

Recently, micro-arc oxidation (MAO), which is also commonly called "plasma electrolytic oxidation (PEO)", has attracted more attention in virtue of its convenience and effectiveness to prepare oxide ceramic coatings with porous structure on the surface of Ti, Al, Mg and their alloys, In addition, MAO is a room-temperature electrochemical process that is suitable for the formation of uniform coatings on the substrate with complex geometries and the MAO coatings offer a good combination of wear resistance, corrosion resistance and bonding strength. In MAO process, the elements in substrate and electrolyte were incorporated into coatings, so functional coatings can be prepared by changing electrolytes and the power parameter in MAO processing [5–7].

Due to high thermal stability, oxidation resistance and low thermal conductivity, Fe_2O_3 is used as infrared radiation materials in industrial furnace for energy saving [8,9]. Fe_2O_3 also possesses high emission in near and middle infrared [10]. For these reasons, Fe_2O_3 also can be used as thermal protective materials in vehicle.

In this paper, ceramic coatings were prepared by microarc oxidation on the surface of Ti6Al4V alloy. $FeSO_4$ was added into the electrolyte in order improve the thermal emission of the coating. The influence of $FeSO_4$ concentration on the morphology, bonding strength and thermal shock resistance of the coatings was studied in detail also.

* Corresponding author. Tel.: +86 451 86418409; fax: +86 451 86418409.
E-mail address: hitth001@yahoo.cn (F. Wang).

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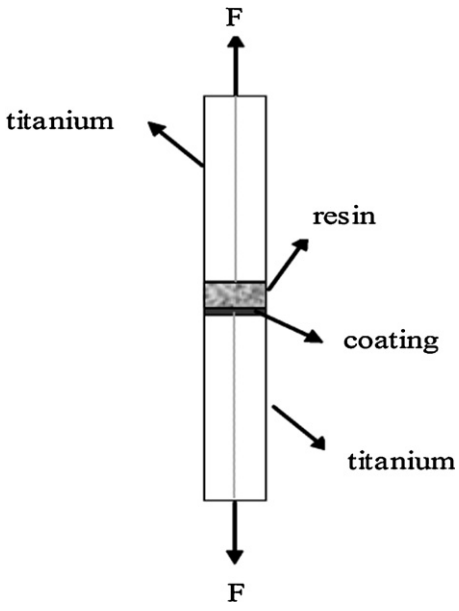

Fig. 1. Schematic diagram of the tensile strength test.

2. Experiment

A 20-kW AC microarc oxidation device was used to fabricate ceramic coatings on the Ti6Al4V surface. Ti6Al4V discs with a diameter of 30 mm and thickness of 6 mm were used as the substrate. The surface of the discs was polished with waterproof abrasive paper up to 1200 grits, make the roughness of the surface Ra = 0.2 μm, and then ultrasonically cleaned in distilled water followed in acetone. The discs were used as anode, a watercooled electrolyser made of stainless steel, which also served as cathode. The reaction temperature was controlled to below 30 °C by adjusting stirring and the cooling water flow. The electrolyte was prepared from the solution of Na_3PO_4 (7 g/L), with $FeSO_4$ 0 g/L, 2 g/L, 3 g/L, 5 g/L, respectively. Noted as MAO0, MAO2, MAO3, and MAO5. During the MAO treatment, a constant voltage mode was applied. The anodic voltage was kept constantly at 350 V and the cathodic voltage was controlled at 0 V, the frequency was 100 Hz; the duration time for the MAO treatment was 10 min.

Phase composition of the coatings was examined with a RICOH D/max-rB automatic X-ray diffractometer (XRD, D/max-rB, Japan) using a Cu Ka source. Surface morphologies of the produced coatings were studied by scanning electron microscopy (SEM, S-4800, Hitachi Co., Japan). The element distribution on the surface of the coating was investigated by energy dispersive spectroscopy (EDS, Oxford Model 7537, England). X-ray photoelectron spectroscopy (XPS; PHI 5700, America Physical Electronics, USA) was performed on a PHI 5700 system at a base pressure of less than 10^{-7} Pa, using Mg Ka radiation 12.5 kV and 20 mA. The roughness of the coatings was measured by current-based roughness gauge (TR-200, Time Company, China). The average roughness of each sample was obtained from 8 measurements at different positions.

The tensile strength of coatings was investigated by the direct pull-off method and impact tests [11]. In pull-off tests, the side of a MAO treated sample was bonded to the side of an untreated sample using epoxy resin and then a force applied to coating–substrate interface to determinate the force for detachment, as shown in Fig. 1. The pull-off test was carried out on Instron-4467 device.

During the thermal shock tests, coated samples are heated up to 500 °C at which temperature they are held for 2 min to make body temperature uniform. Then the specimens were quickly taken out and immersed in the cooling water. The tests were repeated 40 cycles, observe carefully the coatings surface and identify whether visual cracks or large area flakes are produced.

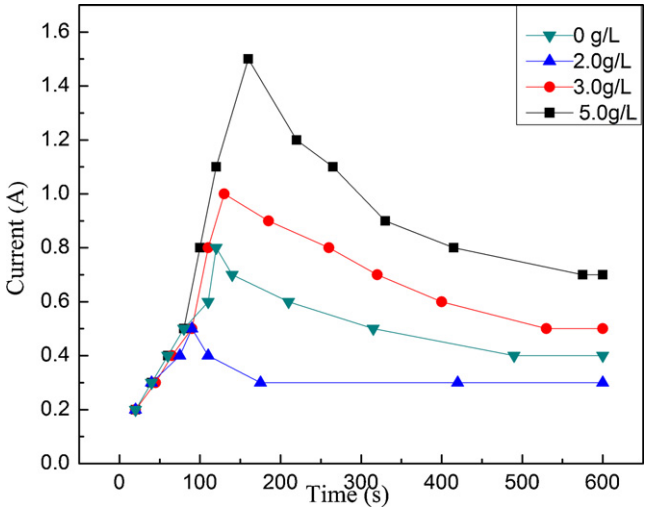

Fig. 2. Current–times curve obtained during the evolution of coating under different concentrations of $FeSO_4$.

Fourier transform infrared (FTIR) spectrometer was used to measure the emission of the coatings in vertical directions at 700 °C. The spectrometer uses a simple Michelson interferometer that consists of a corner cube mirror and a KBr beam splitter. The spectral range between 0.6 μm and 25 μm is covered by a photovoltaic HgCdTe and a silicon photodiode detector. A chamber with circulating water was designed for supporting the heater. Detailed information about the equipment can be found in other references [12].

3. Results and discussions

3.1. Current density–time response

Fig. 2 shows the plot of the current–time response during the MAO treatment process on Ti6Al4V at 350 V. For all the samples, the trend of the current–time curves was the same. As is known, there are three main steps underlying the formation of MAO coatings [13]. Firstly, an oxide film develops on the surface by conventional anodizing. This stage is characterized by a current increased rapidly, and accompanied by gas evolution. Secondly, the current decreased quickly and a few white sparks can be seen on the surface of sample. The final stage is characterized by the current decreased slowly and the yellow sparks covers the whole surface. The current remains stable eventually.

Furthermore, it can be noted that the maximum current and final current were found to be significantly influenced by the concentration of $FeSO_4$ in the electrolyte, with increasing the concentration of $FeSO_4$, the largest current and the final current became larger. The distinct deviations in the above observed behavior may be attributed to different conductivity of the four electrolytes, which is increased with the increasing concentration of $FeSO_4$. It is similar to the previous research results [14]. And this implies that the addition of $FeSO_4$ into the electrolyte, could cause the change of MAO process and subsequently lead to the differences in the formation and the characteristics of the oxidation coating as well.

3.2. Surface microstructure characterization

Fig. 3 shows the morphologies of the oxide coatings formed in four electrolytes. All the coatings have a porous surface microstructure and some volcano top-like pores. The molten oxide particles