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Microstructure and high temperature properties of two-step voltage-controlled MAO ceramic coatings formed on Ti_2AlNb alloy

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ABSTRACT

A two-step voltage-controlled microarc oxidation (MAO) method has been used to produce ceramic coatings (NA-2st) on Ti_2AlNb alloy. For a comparative study, one-step voltage-controlled MAO ceramic coatings (NA-1st) were also formed on Ti_2AlNb alloy. The NA-2st coating with a relatively compact microstructure is composed of Al_2TiO_5, R-TiO_2, α-Al_2O_3 and γ-Al_2O_3 phases. The adhesive strength of MAO coatings was tested by a direct pull-off method. Isothermal oxidation tests were carried out at 800 °C in a muffle furnace in air. Normal spectral emissivity of MAO coatings was measured at 600 °C in the infrared wavelength range of 3–20 μm. High temperature tribological properties of MAO coatings were evaluated by using a ball-on-disc friction and wear tester at 600 °C. Due to its compact microstructure and high content of Al_2TiO_5 phase, the NA-2st coating exhibits better high temperature properties, such as good oxidation resistance, high infrared emissivity, low friction coefficient and small wear rate.

1. Introduction

Microarc oxidation (MAO) known as a surface modification technique has been widely applied to structural components, medical and optical catalysis devices [1–3]. MAO ceramic coating is an in-situ growth process through micro-arc discharge and electro-chemical reaction at instantaneous high voltages and high temperatures. Both microstructure and properties of MAO coatings can be tailored by electrical parameters and electrolyte compositions [3–5]. Recently, thermal control coatings are urgently needed to enhance high temperature properties of metallic substrate. However, up to now, only a few studies focus on high temperature properties of MAO coatings [6–8].

It is well-known that protective coatings used at high temperatures should have a relatively compact microstructure and adequate thickness. High current densities and voltages in a MAO procedure generally cause an increased discharge intensity, which contributes to the formation of a coarse and porous microstructure. Many efforts have been made to improve the coating performance by adjusting the current density mode during MAO process. In contrast with the constant current density mode, the optimized current density waveforms (such as a freely decaying current density in the later stage [9] and a stepped current regime [10]) can significantly improve the microstructure of MAO coatings. Furthermore, a combination of different preparation technologies is also able to improve the microstructure and properties of MAO ceramic coatings. For example, the MAO process in combination with a sol–gel treatment is capable of increasing the corrosion resistance of Mg alloy [11]. The surface mechanical attrition treatment (SMAT) in combination with the MAO process enhances the corrosion resistance of Al alloy [12]. A pre-anodization treatment followed by the MAO process could increase the density of MAO coating [13]. In addition, a two-step MAO process in different electrolytes (such as first in an alkaline aluminate electrolyte and then in an acid electrolyte) is beneficial to improving the adhesion strength of MAO coating on Ti alloy [14].

In this work, a two-step voltage-controlled microarc oxidation (MAO) method has used to produce ceramic coatings on Ti_2AlNb alloy in the electrolyte containing sodium aluminate. Ti_2AlNb alloy with an orthorhombic structure was used as the substrate. Due to its excellent integrative properties, such as high strength/weight ratio, low density, good creep resistance, and high fracture toughness [15,16], O—Ti_2AlNb alloy has become a candidate for high temperature structural materials. In order to facilitate the applications in aircraft and automobile industries, thermal control coatings are important to improve high temperature properties of Ti_2AlNb alloy [17,18]. The purpose of this study is to prepare the two-step voltage-controlled MAO coatings on Ti_2AlNb alloy, and to further evaluate the oxidation resistance, infrared emissivity and tribological properties at elevated temperatures. As comparison, the bared Ti_2AlNb alloy and the one-step voltage-controlled MAO coatings were also tested at identical test conditions.

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Table 1
Technological parameters for microarc oxidation experiments.

Technological parameters	NA-1st coating	NA-2st coating	
Voltage (V)	550	400	550
Oxidation time (min)	20	10	10
Frequency (Hz)	600	600	
Cycle duty (%)	8	8	
Temperature (°C)	30–50	30–50	
pH	12–14	12–14	

2. Experimental procedure

2.1. Materials

In the present work, orthorhombic phase Ti_2AlNb alloy with a chemical composition of Ti—21Al—25Nb (at.%) was used as the substrate. The Ti_2AlNb alloy substrate were machined into the rectangular samples with the dimensions of 18 mm × 15 mm × 3 mm for isothermal oxidation tests, the disc samples with the dimensions of Φ 30 mm × 3 mm for emissivity tests, and the rectangular samples with the dimensions of 15 mm × 15 mm × 3 mm for wear tests, respectively. Prior to the fabrication of MAO coating, the samples of Ti_2AlNb alloy substrate were ground, polished, degreased, cleaned, and dried successively.

2.2. Preparation of microarc oxidation coatings

Different microarc oxidation coatings were prepared in a home-made microarc oxidation equipment by tailoring the MAO technological parameters. The $NaAlO_2$ solution of 25 g/L was used as the electrolyte in order to increase the Al_2O_3 content in coatings. The MAO technological parameters were given in Table 1. A two-step voltage-controlled MAO coating (designated as NA-2st) was synthesized firstly at a voltage of 400 V for 10 min, and then at a voltage of 550 V for another 10 min. As comparison, the one-step voltage-controlled MAO coating (designated as NA-1st) was directly prepared at a voltage of 550 V for 20 min. After the MAO process, the coated samples were cleaned in distilled water, and then dried at room temperature.

2.3. Characterization of microarc oxidation coatings

The thickness of different MAO coatings was directly measured three times for each specimen to take average value by an eddy current coating thickness gauge with a precise calibration (Minitest 600B, Germany EPK). The surface roughness of different MAO coatings was measured seven times for each specimen to take average value with the standard deviations by a surface profilometer with a precise calibration (JB-4C, Shanghai Optical Instrument Co., China). Phase constituents of MAO ceramic coatings before and after oxidation tests were identified by a cornule X-ray diffractometer (XRD, Philips X'Pert, The Netherlands). XRD patterns were recorded in a 2θ range of 20 to 80° at room temperature with a continuous scanning mode at a step length of 0.02°, per step of 0.5 s with an incident angle of 3°. The surface and cross-section morphologies of MAO coatings before and after isothermal oxidation tests, as well as wear tests were characterized by a scanning electron microscope (SEM, FEI Quanta 200F, The Netherlands).The preparation of metallographic specimens to microscopic examinations consists of several steps, such as sectioning (cutting), mounting, grinding and polishing. The samples are surrounded and mounted by an organic resin after heating under an applied pressure.

2.4. Adhesion of MAO coatings

The adhesive strength of MAO coatings were measured by a direct pull-off tensile method in this work. Before tests, both sides of coating samples were bonded to the untreated steel by using the epoxy resin (3M Scotch-Weld Epoxy Adhesive, 3M Company). The pull-off tests were carried out on an Instron-1195 electronic tensile testing machine. The load to the coating was continually applied on the steel cylinderat a rate of 1.0 mm/min until the sample was broken. The adhesive strength was an average value of five measurements under identical test conditions.

2.5. Isothermal oxidation tests

Isothermal oxidation tests were carried out at 800 °C for 150 h in a muffle furnace in the air. Before oxidation tests, the samples of MAO coatings were firstly ultrasonic cleaned in alcohol, and were then dried in oven at 60 °C to measure the mass, and were finally placed into pre-sintered alumina crucibles. The samples were taken out of the muffle furnace at regular time intervals for mass measurements. The sensitivity of the balance used in this study was 10^{-4} g. Weight gains as a function of time were obtained for every sample.

2.6. Infrared emissivity measurements

Infrared emissivity of MAO coatings were measured at 600 °C on a self-made infrared radiometer (Harbin Institute of Technology, China) based on a Fourier transform infrared spectrometer (JASCO FT/IR—6100, Japan). The normal spectral emissivity is defined as the ratio of the radiance of the samples to that of a blackbody at identical temperature level under the same spectral and normal directional conditions. The thermal emission from the samples and the blackbody were detected and analyzed by the Fourier transform infrared spectrometer (FTIR) with a DLATGS detector at a high spectral resolution in a broad wavelength range of 3–20 μm at 600 °C.

2.7. Tribological properties of MAO coatings

Tribological properties of MAO coatings were tested on a ball-on-disk high-temperature friction and wear tester (HT–1000, Lanzhou, China) under dry sliding condition. Sintered Si_3N_4 ball with a diameter of 5.6 mm was chosen as the counterpart. The wear parameters were selected as 2 N of normal load, 3 mm of sliding radius, 400 rpm of rotational speed, 10 min of wear duration, room temperature and 600 °C of test temperature. After wear tests, the wear depths were measured across the wear tracks by a surface profilometer (JB-4C, Shanghai Optical Instrument Co., China) at different randomly selected locations.

3. Results and discussion

3.1. Microstructure of MAO coatings

Fig. 1 shows the XRD patterns of MAO coatings formed on Ti_2AlNb alloy. No diffraction peaks of Ti_2AlNb alloy substrate are detected in the XRD patterns, which means that Ti_2AlNb alloy is completely covered by the MAO coatings. From Fig. 1, the NA-1st coating consists of R-TiO_2, α-Al_2O_3, γ-Al_2O_3 and a small amount of Nb_2O_5. In contrast with the NA-1st coating, the NA-2st coating contains a lot of Al_2TiO_5 phase besides R-TiO_2, α-Al_2O_3, γ-Al_2O_3 and Nb_2O_5. Clearly, the NA-2st coating firstly forms Al_2TiO_5 phase at a relatively low voltage discharge stage, and then it generates