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Microstructure and properties of rare earth CeO_2-doped TiO_2 nanostructured composite coatings through micro-arc oxidation

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Abstract

Rare earth cerium oxide (CeO_2) – doped TiO_2 nanostructured composite coatings were obtained through micro-arc oxidation technique on titanium substrates. The surface hardness and corrosion resistance of the substrates were improved. The results of X-ray diffraction, energy dispersive spectrum, and X-ray photoelectron spectroscopy show that the composite coatings mainly consist of rutile-TiO_2, anatase-TiO_2, and CeO_2. The CeO_2 content was increased by increasing the current density and electrolyte concentration. CeO_2 was observed on the surface as well as in the deep layers. The scanning electron microscopy results display that the number of micro-holes decreased. The holes became bigger, and a smooth area appeared around the micro-holes. The surface roughness of the composite coatings was initially reduced but subsequently increased with increasing CeO_2 concentration, while the thickness of the composite coatings increased. The results demonstrated that the surface hardness of the coatings was enhanced to 609.17 Hv at the CeO_2 concentration of 4 g/L, and the corrosion current decreased to $1.584e^{-007}$ A at 6 g/L.

Keywords: Micro arc oxidation; Pure titanium; Rare earth CeO_2; Hardness; Corrosion property

1. Introduction

Titanium and titanium alloy are used in aerospace [1], aviation [2], automation [3], chemical industry [4], and biomedicine [5], because of their high strength and low density. However, their surface hardness and corrosion resistance limit their application. Many studies aim to improve their hardness [6,7] and corrosion resistance [8,9]. Surface technologies have been developed, such as rare earth transformation coatings [10], laser surface melting [11], and organic coating [12]. TiO_2 ceramic coating has been proposed as a novel surface modification technology called micro-arc oxidation (MAO) [13]. Most investigations mainly focused on the influence of voltage on the MAO process, whereas others have indicated that the current density also has a significant effect on the MAO process [14–17]. Moreover, to improve the performance of MAO coatings further, nanoparticles such as ZrO_2 [18], Al_2O_3 [19], and TiO_2 [20] are added in the electrolyte to form composite films. However, doping coatings with cerium oxide nanoparticles on TiO_2 MAO coatings have not been evaluated.

Cerium oxide nanoparticle has many excellent properties, such as hardness [21,22] and corrosion resistance [23], and it is used in the laser treatment of alloys [24], electro-deposition [25], surface coating [26], etc. In studies that use rare earth elements to improve the performance of MAO coatings, researchers usually put the sample into the rare earth salt solution before the MAO process to obtain composite coatings [27]. Trace amounts of rare earth oxide (REO) exist on the coatings when the MAO voltage is below 140 V through energy dispersive spectrum (EDS) detection. Voltage is one of the key factors of phase transformation in the MAO process [28]. When the voltage is greater than 140 V, REO disappears from the films because MAO is a high voltage breakdown process. Surviving the violent MAO process is difficult for transformation coatings (thickness about 500 nm). Hence, the properties of the transformation and MAO composite coatings may not improve much.

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In this study, CeO_2 nanoparticles were added to the electrolyte to observe its effect on the hardness and corrosion property of the coatings with different current densities and electrolyte concentrations. A correlation between the processing parameters, structure, and the properties of the composite coatings was proposed.

2. Materials and method

2.1. Preparation of MAO coatings

Titanium plates, with dimensions of 25 mm × 15 mm × 2 mm, were used as substrates. The elemental chemical composition of the specimens is reported in Table 1. The specimens were polished using SiC sand papers from #800 to #2000 until they achieved a mirror-like finish. They were then rinsed in distilled water, cleaned ultrasonically with alcohol, and finally dried using air jets. The MAO device was made up of a 20 kW power supply (Disishukong Co., Ltd, Harbin, China) and a stirring and cooling system. The sample was connected to the positive pole of the power supply as the anode. Stainless steel sink was used as the cathode. The MAO process was carried out in deionized water with Na_2SiO_3/KOH electrolyte (Sinopharm Chemical Reagent Beijing Co., Ltd, Beijing, China) and CeO_2 nanoparticles (Nanjing Emperor Nano Material CO., Ltd, Nanjing, China). The chemical composition of the electrolyte is presented in Table 2. The average size of CeO_2 nanoparticle is 50 nm. After blending the components, the electrolyte was stirred for 30 min to disperse the CeO_2 nanoparticles and maintained at 30 ± 5 °C by using a cooling system during the MAO process. According to the research results of W. Hongbin [29] and our experiences, the frequency, duty cycle, and MAO processing time were fixed at 500 Hz, 20%, and 30 min, respectively. The current density was set at 15 or 30 A/dm^2 to observe any variation in the MAO process.

Table 1
Elemental chemical composition of the samples.

Element	Ti	Fe	O	C	N	H	Others
Wt%	99.005	0.25	0.20	0.10	0.03	0.015	0.4

Table 2
Chemical compositions, zeta potential of the electrolyte and phase contents.

Electrolyte No.	Current density A/dm^2	Na_2SiO_3 (g L^{-1})	KOH (g·L^{-1})	CeO_2 (g L^{-1})	Zeta (mV)	Anatase (wt%)	Rutile (wt%)
A	15	4	3	0	−20.68	22.4	77.5
B	15	4	3	2	−35.38	15.6	84.3
C	15	4	3	4	-	12.2	87.7
D	15	4	3	6	-	44.4	55.4
A	30	4	3	0	−20.68	18.9	81.0
B	30	4	3	2	−35.38	15.5	84.4
C	30	4	3	4	-	9.9	90.0
D	30	4	3	6	-	9.3	90.6

2.2. Analysis of composition and structure of the coatings

The phase structure of the specimens was detected using D/max-r B X-ray diffraction (XRD, Cu Kα radiation). The scattering angle 2θ was set from 10° to 90°with a step of 0.04°, an acquisition time of 1 s/step, and an energy of 40 kV, 40 mA. The Zeta potential of CeO_2 nanoparticles electrolyte was measured with a ZetaPALS Potential Analyzer (Brookhaven Instruments Corporation). The microstructure and elemental content were analyzed using a JSM-6480A scanning electron microscope (SEM) and EDS, respectively. PHI 5700 ESCA System X-ray photoelectron spectroscopy (XPS, twin anode, X-ray source, using Al Ka α¼ 1486.6 eV) was employed to probe the surface chemical composition and valence of the samples. The surface roughness and thickness of the coatings were measured using a roughness tester (TR200, cutoff length 0.8 mm) and a coating thickness gauge (TT260). The surface hardness of the coatings was evaluated using a digital micro-hardness tester (HVS-1000) in HV mode at a load of 4.900 N for 5 s. The electrochemical workstation, CHI604C, was employed to detect the corrosion resistance property of the specimens through Tafel testing. The polarization curve was measured at 3.5% NaCl aqueous solution and was conducted in the range from the initial potential (−2 V) to the final potential (+1 V) with a scan rate of 0.01 V/s and a quiescent time of 10 min. The band gap of the specimens was detected using a UV/VIS/NIR spectrophotometer (U-4100) from 200.00 nm to 1100.00 nm at a scan speed of 600 nm/min and a sampling interval of 1.00 nm.

3. Results and discussion

3.1. Structure and composition

The XRD diffraction patterns of the composite coatings obtained at a current of 30 A/dm^2 are shown in Fig. 1, where the formation of rutile-TiO_2 and CeO_2, anatase-TiO_2 is evident. The amount of anatase-TiO_2 (X_A) and rutile-TiO_2 (X_R) in the fabricated coatings was calculated by the formulae $X_A = 1/(1+1.26\ (I_R/I_A))$ and $X_R = 1/(1+0.8\ (I_A/I_R))$ [30]. The results are shown in Table 2, where I_A and I_R refer to the characteristic peak intensities of anatase (101 peak) and rutile (110 peak), respectively. A couple of features are worth noting. First, CeO_2 appeared on the coatings at 28.60°, 47.52°, and 56.48° in the XRD pattern. This phenomenon illustrates that CeO_2 particles were doped in the coatings during the MAO process. The Zeta potential measurement results of electrolyte are shown in Table 2, too. The Zeta potential of electrolyte A was -20.68 mV and of the electrolyte B was -35.38 mV. The OH^- and SiO_3^{2-} ions of electrolyte attached to the CeO_2 particles surface form negatively charged particles. The particles were drawn toward the anode by the electric field and mechanical shearing force and are then deposited in the discharge areas. This process produced the CeO_2-TiO_2 composite coatings during the MAO process. Second, peaks of rutile-TiO_2 were intensified to 84.4% in electrolyte B, which indicated that CeO_2 promoted the anatase-TiO_2 transformation