Materials Chemistry and Physics 134 (2012) 484–492

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

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

A spectroscopic and microstructural study of oxide coatings produced on a Ti–6Al–4V alloy by plasma electrolytic oxidation

R.O. Hussein, X. Nie, D.O. Northwood*

Department of Mechanical, Automotive and Materials Engineering, University of Windsor, Windsor, ON, Canada N9B 3P4

ARTICLE INFO

Article history:
Received 3 August 2011
Received in revised form 30 January 2012
Accepted 3 March 2012

Keywords:
Ti–6Al–4V alloy
Plasma electrolytic oxidation (PEO)
Ceramic coatings
Corrosion

ABSTRACT

In this study, we have used PEO (plasma electrolytic oxidation) for the production of oxide coatings on a Ti–6Al–4V alloy at two different current modes, namely pulsed unipolar and bipolar. Optical emission spectroscopy (OES) in the visible and near UV band (280–800 nm) was used to characterize the PEO plasma. The emission spectra were recorded and the plasma temperature profile versus processing time was constructed using a line intensity ratios method. The aim of this work was to study the effect of the process parameters, including current mode and pulse duration time, on the plasma characteristics, surface morphology and microstructure and corrosion resistance of oxides grown on Ti–6Al–4V by PEO process. Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDS) and X-ray diffraction (XRD) were used to study the coating microstructure, morphology and phase composition. The corrosion resistance of the coated and uncoated samples was examined by potentiodynamic polarization in a 3.5% NaCl solution. It was found that the plasma temperature profiles are significantly influenced by changing the current mode from unipolar to bipolar. The strongest discharges that are initiated at the interface between the substrate and the coating can be reduced or eliminated by using a bipolar current mode. This produces a thinner, denser and more corrosion-resistant coating.

1. Introduction

Titanium alloys (especially the Ti–6Al–4V alloy) are very attractive materials due to their outstanding strength-to-weight ratios, good fatigue strength and toughness, low elastic modulus, good biocompatibility and corrosion resistance and anti-magnetic properties [1]. The Ti–6Al–4V alloy is the most widely used of the titanium alloys, especially in the aerospace industry. However, the poor tribological behavior caused by high and unstable friction coefficients [2], and the poor corrosion resistance in some aggressive environments, have critically limited extensive application of titanium in various industry sectors. Titanium and Ti alloys are remarkably resistant to corrosion owing to the formation of stable, self healing oxide films on their surfaces. The major corrosion problem with Ti alloys may be in acidic environments, particularly when the acid concentration and temperature increase [3]. In this case, the oxide film on Ti deteriorates and dissolves and the unprotected metal is oxidized to the soluble trivalent ion [1].

The properties and potential applications, of titanium and its alloys have been augmented by surface engineering [4]. Major techniques for the surface modification of titanium alloys have included: ion implantation, laser surface treatment, electroplating and physical vapor deposition (PVD) coatings, but all of them have particular limitations [5–8]. Among the newer surface modification techniques, plasma electrolytic oxidation (PEO) has recently been successfully applied to titanium alloys [9–20].

PEO coatings are much harder than the anodized coatings and can be used to protect a variety of light metals (Ti, Al and Mg) and their alloys [21,22]. Also, the PEO process typically uses a dilute alkaline solution, which is benign to the environment. The coatings are typically 5 to a few hundred microns in thickness, with crystalline and amorphous phases containing both metal substrate and electrolyte components [23,24]. However, as the coating thickness increases, the PEO coating forms a porous and rough out-layer on the top of a dense layer. Depending on the current mode as well as the current pulse timing, the outer layer thickness can be reduced. The improved surface performance that can be obtained yields numerous real and potential applications for the PEO technology in the aerospace industry (fasteners, landing gear, blades, discs and shafts of aircraft engines), the automotive industry (seat frames, doors, pistons and cylinder liners), and the gas and oil industries (gears and rotary pumps). PEO has also attracted interest for improved, high added value, biocompatible coatings on titanium in dental and orthopaedic implants, reinforcing the durability, low material, dissipation and antibacterial properties of the metal

---

* Corresponding author. Tel.: +1 519 253 3000x4785; fax: +1 519 973 7007.
E-mail addresses: husseinr@uwindsor.ca (R.O. Hussein), dnorthwo@uwindsor.ca (D.O. Northwood).

0254-0584/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2012.03.020

[25,26]. PEO treatments also improve titanium resistance to corrosion and wear [10,27].

With the aim of improving the characteristics of the ceramic coatings, many attempts have been made to improve the supplied current regimes, including different forms and duration of the current pulses. Different current modes have been utilized in the PEO processing including DC, AC, unipolar and bipolar current modes [28]. Recent studies on the effect of power supply modes on PEO coating properties have paid more attention to the bipolar current mode [29]. A number of researchers [29,30] have tried to modify the morphology and structures of oxide coatings by control of the sparking during the PEO process.

Spectral diagnostic techniques are an effective way of studying the physical phenomenon in the PEO process by investigating the emission spectra of the plasma. Optical emission spectroscopy (OES) has previously been applied to the PEO process for the detection and analyses of light that is emitted from the plasma species for Al [31,32] and Mg [30,33,34] alloys. The optical emission spectra were recorded and plasma temperature profile versus processing time relationships were calculated [31]. The two main difficulties encountered in the application of OES to PEO characterization are the aqueous solution nature of the substrate environment and the random appearance of the discharges across the substrate surface. The discharging duration time and the space of the sparks increase with the process treatment time. To study the plasma discharge behavior with the process evolution, the collective behavior of the plasma discharges over the entire surface and during the whole treatment process, rather than the individual, instantaneous discharges [34], is needed to be recorded. Hence, the measured plasma spectra represent the time integrated radiation recorded by the spectrometer. Based on such OES results, and with an assumption of local thermodynamic equilibrium (LTE) [35], plasma electron temperatures for an Al 1100 alloy have been calculated using the relative intensities of spectral lines 396.2 nm and 309.1 nm of the same atomic or ionic species [31,36]. Evaluations based on the spectroscopic method for the Al 1100 alloy show electron temperatures to be in the range of 4000–7000 K for a unipolar current mode and in the range of 4000–5500 K for bipolar current mode [37]. Kalpkiv et al. [32] measured the plasma temperature for the commerciality pure Al, to be in the range of 6899–7700 K from intensity ratio of Al I to Al II lines. Using the intensity ratio of the 383.8 nm (Mg I) to 518.3 nm (Mg I) spectra, Hussein et al. [33] determined plasma electron temperatures to be in the range of 3300–7000 K for PEO coating of an AJ62 Mg-alloy.

In this paper, the PEO plasma of a titanium alloy is studied by emission spectroscopy. The effect of current modes with different electrical charge ratios, C_R, on the plasma and on the oxide coatings on Ti–6Al–4V alloy substrate is analyzed. The optical emission spectra were recorded and plasma temperature profile versus processing time was constructed. It is interesting to note that this is only the second report of the spectroscopic characterization of the plasma for the PEO processing of Ti and its alloys [38], but the first to use the Ti spectral lines. Finally, the effect of the discharge behavior on the formation and structure of the coating surface layers was determined.

2. Experimental procedures

Ti–6Al–4V titanium alloy (87.7–91% Ti, 5.5–6.7% Al, 3.5–4.5% V) specimens with dimensions of 25 mm × 25 mm × 5 mm were used as the test coupons for the coating process. After machining, the specimens were ground with various grades of silicon carbide paper from 240 to 1200 grade. Then, the samples were degreased with acetone before the PEO treatment to ensure a similar initial surface condition for each sample. A PEO coating unit as described in Ref. [31] was used to produce the oxide coatings on the Ti coupons. For the PEO processing, the Ti–6Al–4V coupons screwed onto a Ti rod acted as the anode and a stainless steel plate as the cathode. The electrolyte used for the PEO process was composed of sodium aluminate ($8\,\mathrm{g\,l^{-1}}$ $Na_2Al_2O_4$), potassium phosphate ($1\,\mathrm{g\,l^{-1}}$ $K_4P_2O_7$) and potassium hydroxide ($0.3\,\mathrm{g\,l^{-1}}$ KOH) to balance the pH at 13. This electrolyte was chosen on the basis of previous studies on PEO processing of Ti–6Al–4V [9]. The temperature of the electrolyte was kept at $25 \pm 2\,^{\circ}\mathrm{C}$ using a water cooling system.

The PEO coating process was carried out using two different current modes [37]: a unipolar pulsed-DC mode and a bipolar current mode, comprising both a positive component and a negative component. The process parameters, such as the frequency, the duration of each pulse and the resting gap (break) between the positive and negative pulses are listed in Table 1. As described by Hussein et al. [37] the charge ratio parameter (C_R) is introduced to describe the ratio of the positive to the negative charge quantities:

$$C_R = \frac{q_+}{q_-} = \frac{\int_0^{T_{on}} I^+ dt}{\int_{T_{on}}^{T_{on}+T_{off}} I^- dt} \tag{1}$$

where I^+ and I^- represent the values of the positive and negative currents, respectively. Both pulse duration and current density were chosen based on our previous work on Mg alloy [33].

In this experiment, one spectrometer formed the main visible spectroscopy diagnostic tool. This spectrometer has 4 channel slots, each of which covers a certain wavelength region. The image of the substrate surface was transmitted and focused through a quartz window and lenses to the entrance slit of the spectrometer. Optical emission spectra were recorded within the wavelength range of 300–900 nm.

In dense plasmas, Stark broadening (caused by the fluctuating electric field produced by the ions and electrons) is often the dominant line broadening mechanism. For most diagnostic applications the relationship between full half-widths FWHM (full width at half maximum intensity) $\Delta\lambda_{1/2}$ in nm and electron concentration N_e in m^{-3} is given by [39]:

$$\Delta\lambda_{1/2} = 4.80\left(\frac{N_e}{10^{23}}\right)^{0.68116} \tag{2}$$

The hydrogen lines H_β are wide so that they are easy to record and process without perturbing the plasma.

The plasma studied here falls into the category of an optically thin plasma [35]. The relative intensities of spectral lines of the same atomic species can be used to calculate the plasma electron temperature using the expression [35]:

$$kT = \frac{E_{m(2)} - E_{m(1)}}{\ln((I(1)A_{mn}(2)g_m(2)\lambda_0(1))/(I(2)A_{mn}(1)g_m(1)\lambda_0(2)))} \tag{3}$$

where kT is the thermal energy, $I(1)$ and $I(2)$ relative line intensities of lines of the same species in question, $A_{mn}(i)$ the transition probabilities, m the upper and n the lower level of the respective lines, $g_m(i)$ the statistical weight of the upper levels, $E_m(i)$ energies of the upper levels of lines and λ_0 (i) the wavelengths of the line centers in vacuum. Eq. (3) is valid if the level populations of the lines in question are populated according to the Boltzmann law: in other words, at least partial thermodynamic equilibrium (LTE) must exist for these levels.

The emission intensity of the plasma species was monitored as a function of time using the OES system. Four different spectral lines were recorded simultaneously, which eliminates discrepancies that may otherwise happen if the spectra are recorded at different times. The spectral lines (Table 2) at 521.0 nm (Ti I), 399.8 nm (Al I), 486.1 nm (H_β), and 589.5 nm (Na I) were recorded. Atomic and ionic spectral lines were identified using the NIST online spectral database [40].