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Preparation and characterization of carburized layer on pure aluminum by plasma electrolysis

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ABSTRACT

Plasma electrolytic carburizing (PEC) was employed to fabricate a carburized layer on pure aluminum in glycerol electrolyte. The near surface temperature of the aluminum workpiece at different voltages was measured and the electron temperature during cathodic plasma discharge was calculated in terms of optical emission spectroscopy (OES). At 340 V, the temperature of Al workpiece reached 450 °C, but the electron temperature in the discharge envelope fluctuated around 7000 K. The microstructure and phase constituents of the carburized layer were analyzed by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Its tribological property was measured by a ball-on-disc friction and wear tester under dry sliding against GCr15 steel ball. The corrosion behaviors were evaluated by electrochemical methods and scanning electrochemical microscopy (SECM). It was found that the depth of carburized layer was about 2 μm and its hardness was two times higher than that of the Al substrate. Besides, the friction coefficient of carburized layer containing Al_4C_3 phase decreased to 0.55, while that of the Al substrate is 0.95. The corrosion current density and scanning probe current of PEC treated aluminum were respectively 1/3 and 1/5 that of the aluminum substrate. After PEC treatment, the wear and corrosion resistances of pure aluminum were improved.

1. Introduction

Aluminum and its alloys are extensively used in automotive, marine and aerospace industries, but their insufficient wear resistance is a limiting factor. Fariaut et al. [1] employed laser induced plasma to fabricate a carburized layer of about 2 μm on aluminum alloy to improve its wear resistance, but the operating device was complex and expensive. Chemical heat treatment such as carburizing and nitriding is widely used to improve the surface hardness of steel materials. In recent years, plasma electrolytic saturation (PES) technology as an efficient and environmentally friendly approach has been successfully applied to pure iron, carbon steel, austenitic stainless steel and titanium [2–5]. In the PES process, the workpiece as cathode is immersed in organic electrolyte solution at ambient temperature [6]. Specific processing methods, such as plasma electrolytic carburizing (PEC) [7], plasma electrolytic carbonitriding (PEC/N) [4] and plasma electrolytic borocarburizing (PEB/C) [8], can be achieved based on different electrolyte compositions. All of these methods operate on similar process principles, where a continuous vapor envelope around the workpiece is broken down at a critical voltage, leading to a plasma discharge in the near-cathode region. In the plasma envelope around the metal, organic electrolyte is decomposed into active radicals and ions, which are accelerated to generate an enhanced interstitial diffusion into metal matrix.

Up to now, most PES papers focus on the metals with high melting point, such as steel and titanium [3,4,7,8]. The PES process on low melting point metals like aluminum is seldom studied, because the high heat flux during plasma discharge might melt the metal. Aliofkhazraei et al. [9] tried to prepare a carburized layer on 6082 aluminum alloy by PEC method, using a rectangular pulsed voltage of 400 V with a frequency of 10 kHz and a duty cycle of 5%. They believed that the use of higher frequency and lower duty cycle would lead to the best carbon diffusion phenomenon and limit the destructive intensity of sparks. It was suggested that the minimum possible duty cycle and maximum frequency should be used in order to avoid local surface melting of low melting point metals. So it is interesting to examine the feasibility of PEC method on aluminum with lower frequency and higher duty cycle. In addition, the temperature plays a key role in carbon diffusion and formation of carburized layer on metals [10,11]. It is important to measure the temperature in the interior of metal close to surface and evaluate the electron temperature in the plasma discharge envelope around the metal. This is beneficial for understanding the formation mechanism of carburized layer on low melting point metals. However, the temperature near

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the metal surface or in the discharge envelope during PEC process has rarely been reported before.

In this work, a carburized layer on pure aluminum was rapidly fabricated by PEC method with lower frequency and higher duty cycle in glycerol electrolyte. The dependence of sample temperature on applied voltage was measured by a thermocouple. Meanwhile, optical emission spectroscopy was utilized to characterize the discharge phenomenon during PEC process. The microstructure and phase constituents of PEC treated aluminum were analyzed. The wear and electrochemical corrosion behaviors of carburized layer were evaluated. Besides, the formation mechanism of carburized layer on aluminum was discussed.

2. Experimental details

Commercially pure aluminum (Si: 0.06, Fe: 0.36, Cu: 0.02, Mn: 0.02, Mg: 0.02, Zn: 0.005 wt.%, Al balance) plate with sizes of 40 mm × 20 mm × 1 mm was used as substrate material. The plate was mechanically polished with 1000-grit emery paper, and then was cleaned in ethanol and dried. The PEC process was carried out in a stainless steel container. The Al sample and stainless steel container were used as cathode and anode respectively. Meanwhile, a pulsed DC power supply was employed. The pulse frequency and duty ratio were fixed at 150 Hz and 45%, respectively. The pure aluminum sample was immersed in an aqueous solution containing 80 vol.% glycerol at ambient temperature. Besides, a little KCl was added into the electrolyte as an electrically conductive component. The negative bias voltage was initially set at 150 V to produce a continuous vapor envelope around the aluminum sample. Then the applied voltage was gradually increased and the vapor envelope was broken down at critical voltage, resulting in the plasma discharge. A stable discharge lasted 5 min at 340 V, and then the power supply was turned off. The active species in the plasma discharge process were detected using optical emission spectroscopy (OES, AvaSpec-3648). In addition, while the applied voltage was increasing, the temperature close to the surface of aluminum sample was measured by a thermocouple. The thermocouple was inserted into a small hole in Al sample. The distance of the hole bottom to the lower surface of sample was 0.2 mm with tolerance of ± 0.05 mm. Schematic diagram of PEC treatment and temperature measurement was described in Ref. [11]. The temperature fluctuation of measured sample was among 20 °C, which was determined by repeated measurements.

The cross-sectional microstructure and composition profile of PEC treated Al sample were observed by a scanning electron microscope equipped with energy dispersive spectroscopy (SEM & EDS, Hitachi S-4800). The phase constituents of PEC sample were analyzed by X-ray diffraction (XRD, X'Pert Pro MPD). The surface hardness was measured by a Vickers microhardness tester with 10 g load. A HT-1000 ball-on-disk friction and wear tester (Lanzhou Zhongke Kaihua technology development Co., Ltd) was used to evaluate the wear performance of Al samples before and after carburization. The wear test was carried out under dry sliding against GCr15 steel ball of 4 mm in diameter with 1.5 N load and lasted for 5 min at ambient temperature. The wear track diameter and rotation velocity were 8 mm and 300 rpm respectively. Each wear test was repeated three times and the average was taken. Besides, the cross-sectional profiles of wear tracks were measured by a surface profilometer (TR200, Beijing Time Lianchuang technology Co., Ltd). An electrochemical workstation (PARSTAT 2273, Princeton Applied Research) was used to evaluate the corrosion resistance of PEC samples in 3.5 wt.% NaCl aqueous solution. Potentiodynamic polarization tests were performed at a scan rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) tests were performed at the open circuit potential with an AC amplitude of 10 mV over the frequency range of 1 MHz to 0.01 Hz. Furthermore, scanning electrochemical microscopy (SECM, CHI920D) was used to examine the corrosion behavior of carburized layer in localized region. The electrodes include a platinum microelectrode as the probe, an Ag/AgCl reference electrode and a platinum wire counter electrode. Scans were conducted parallel to the sample surface and the probe tip was set at a height of about 10 μm over the surface. Line scanning current curve and area scanning map along the cross-section of PEC treated aluminum were obtained.

3. Results and discussion

3.1. Sample temperature and applied voltage relationship

Temperature plays a key role on the diffusion process of carbon into a metallic matrix. Conventional pack carburizing processes for steel or titanium alloy are usually carried out at high temperatures up to 1000 °C [12,13]. For PEC treatment, the sample temperature depends on applied voltage. As shown in Fig. 1, the temperature close to the surface of aluminum rises slowly when voltage is below 200 V. It is due to the heating effect of current and no spark appears in this stage. When the applied voltage exceeds 200 V, the temperature rises rapidly because the vapor envelope around aluminum sample is broken down and then plasma discharge generates large amounts of heat [14]. At 340 V, the sample temperature reaches 450 °C. After that, the temperature just increases a little though the voltage continues to rise. This could be due to the local melting of aluminum sample, whose melting point is only 660 °C. Therefore, the 340 V can be chosen as the optimal voltage for PEC treatment as it provides the maximum temperature for carbon diffusion. In other words, when the voltage is lower than 340 V, carburizing process will be insufficient and the carburized layer is difficult to form. When the voltage is higher than 340 V, high heat flux can destroy the Al sample and carburizing process can not proceed.

3.2. Microstructure and constituent analysis of PEC treated aluminum

Fig. 2 is the surface micrograph of PEC treated aluminum with 5 min discharge in glycerol electrolyte. Some particles and channels can be observed on the sample surface. They are caused by intense plasma etching during discharge process, which are similar to the surface morphology of PEC treated steel [15]. The cross-sectional micrograph and composition profile of PEC treated aluminum sample are shown in Fig. 3. The bright area in Fig. 3a is a carburized layer with a thickness of about 2 μm. As determined by EDS analysis in Fig. 3b, the carbon content in the carburized layer is much higher than that in the aluminum substrate. EDS point analysis shows that the carbon content in the carburized layer is 38.85 at.%. It indicates that carbon atoms have successfully diffused into the aluminum. Furthermore, it is found that the carbon content gradually decreases from the surface of PEC sample to the interface between the Al substrate and carburized layer, while the aluminum content increases correspondingly.

Fig. 4 displays the XRD pattern of the PEC treated aluminum sample. In addition to the aluminum phase, some Al_4C_3 peaks at 43.4°, 70.6°, 76.1° and 86.4° are detected. This means that the carbon species,

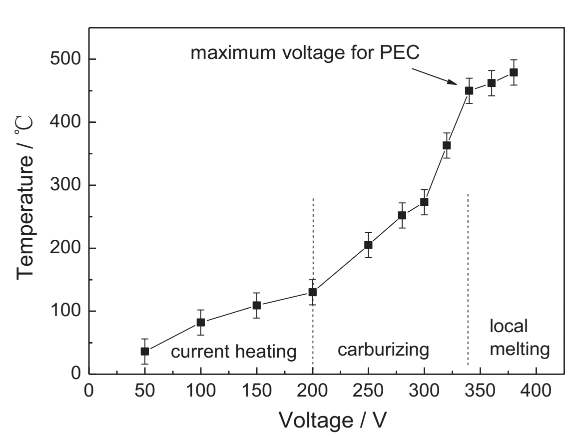

Fig. 1. Dependence of sample temperature on applied voltage during PEC process.