



Direct growth of oxide layer on carbon steel by cathodic plasma electrolysis

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ABSTRACT

In this paper, we reported a novel oxidation phenomenon on carbon steel which served as cathode during plasma electrolysis process in organic solution. The optical emission spectroscopy was collected and the electron temperature in plasma discharge region was calculated. The morphology and composition of oxide layer, as well as the decomposition mechanism of electrolyte were analyzed. The results showed that the plasma discharge region contained many active oxygen species with a high electron temperature of about 11,000 K, which promoted the oxidation reaction on steel cathode. Moreover, the oxide layer displayed an enhanced mechanical property and can improve the wear resistance of carbon steel significantly. This work provides a feasible and efficient approach for the performance improvement of steel materials.

1. Introduction

In recent decades, plasma electrolysis technology, a hybrid of traditional electrolysis and atmospheric plasma process, has attracted more and more attention in the field of coating preparation and surface modification for metal materials due to its high efficiency and low cost [1,2]. Till now, plasma electrolytic oxidation (PEO) has been successfully applied to many valve metals such as aluminum, magnesium, titanium and zirconium [3–6], and has significantly improved their wear or corrosion resistance. In the PEO process, the workpiece as anode is immersed in the inorganic electrolyte solution at ambient temperature. By increasing the voltage between workpiece and counter electrode, the anodic passive film is broken down, leading to a plasma discharge and in-situ ceramic film growth. However, the PEO process cannot take effect on steel materials directly, due to the loose characteristic of Fe₂O₃ phase. For this, researchers [7,8] have tried to introduce Al element into the electrolyte solution, forming Al₂O₃ phase to improve the insulativity of PEO coating. The mechanism of this method is essentially the same with PEO process on aluminum or aluminum alloys and the electrolyte composition is complex.

Unlike the PEO process, plasma electrolytic saturation (PES) process sets the workpiece as cathode and immerses it in the organic electrolyte solution. At a low voltage, a gaseous envelope containing electrolyte vapor is formed around the cathode surface instead of a loose layer of oxides. This gaseous envelope with low electrical conductivity separates the cathode from the electrolyte, and it can be broken down as the

voltage increasing, which results in the plasma discharge. By the plasma discharge near cathode, the organic electrolyte is decomposed into active radicals and ions, which can be accelerated to generate an interstitial diffusion into metal matrix. Up to now, the cathode plasma electrolysis technology has been applied to steels to improve their wear resistance. Specific processing methods like plasma electrolytic carburizing (PEC) [9], plasma electrolytic carbonitriding (PEC/N) [10] and plasma electrolytic borocarburing (PEB/C) [11] can be realized by adjusting the electrolyte composition and electrical parameters. On the other hand, it is known to all that reduction reaction occurs on the cathode in traditional electrolysis process. However, compared with the traditional electrolysis, plasma electrolysis is characterized by its high deviation of the chemical yields that are expected on the basis of Faraday's law and may include some novel products such as O₂ at the cathode, H₂ at the anode [12]. Consequently, it may be possible to prepare an oxide layer on steel surface when it serves as cathode in plasma electrolysis process. This new approach based on cathode plasma electrolysis process is still in the exploring stage. Jin et al. [15] have employed cathodic plasma electrolysis method to fabricate an oxide layer on 304 stainless steel, but the oxide mechanism is not clearly clarified.

In this paper, we use optical emission spectroscopy (OES) method to examine the cathodic plasma electrolysis oxidation (CPEO) process. The active species in plasma envelope were determined and plasma electron temperature was calculated to evaluate the oxidation environment. Meanwhile, the morphology, composition and mechanical performance

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of CPEO treated steel under different discharge time were analyzed. The electrochemical mechanism for the formation of CPEO layer was discussed.

2. Experimental details

The T8 carbon steel (C: 0.75–0.84, Si: ≤0.35, Mn: ≤0.40, P: ≤0.035, S: ≤0.030, wt%, Fe balance) sheet of 1 mm thick was cut into coupons with 55 mm × 15 mm dimensions. The specimens were mechanically polished with 1000-grit emery paper, followed by ultrasonically cleaned in ethanol for 15 min and drying. For the CPEO process, the carbon steel specimens were set as cathode, while a stainless steel container containing an electrolyte of 80 vol% glycerol and 20 vol % deionized water served as anode. Besides, a little KCl was added into the electrolyte as a conductive additive. A pulsed DC power supply with the pulse frequency of 150 Hz and the pulse width of 3 ms was employed. Initially, the negative bias voltage was set at 150 V, and the electrolyte was heated by current to produce a continuous gaseous envelope around the cathode. At 300 V, the gaseous envelope was broken down and plasma discharge took place. Then the voltage was gradually increased to 400 V to sustain a stable discharge for 5 min and 8 min, respectively. The schematic illustration of the experimental apparatus is shown in Fig. 1.

During the CPEO process, the OES signals were collected by a fiber optic spectrometer (Avantes AvaSpec-3648) which consisted of a 3648 pixels CCD detector array. The spectral resolution was 0.08 nm and the integration time was set as 1 s. The optical fiber probe was placed at 2 cm away from the steel sample. The morphology, microstructure and composition of the prepared oxide layer on carbon steel were analyzed by scanning electron microscope (SEM, Hitachi S-4800) equipped with energy dispersive spectroscopy (EDS, Horiba Scientific), X-ray diffraction (XRD, PANalytical X'Pert Pro MPD) using a Cu K α radiation and Raman spectroscopy (Horiba LabRAM Aramis) with laser excitation at 633 nm, respectively. The adhesive strength between the coating and the substrate was measured by a scratch tester (Lanzhou Zhongke WS-2005) based on the acoustic emission testing technology. The scratches were made under linearly increasing load with a loading rate of 50 N/min and a scratch length of 4 mm. The tip radius of diamond indenter was 0.2 mm with a taper angle of 120°. Each sample was tested for three times and the average value was used as the indicator of the adhesive strength. Besides, a Vickers indenter with 10 g load was used to measure the microhardness distribution of the oxide layer. A ball-on-disk friction and wear tester (Lanzhou Zhongke HT-1000) was used to evaluate the tribological performance of the oxide layer with 10 N load against ZrO₂ ceramic balls at ambient temperature. Furthermore, the cross-sectional profiles of wear tracks were measured by a surface profilometer (Beijing Time TR200).

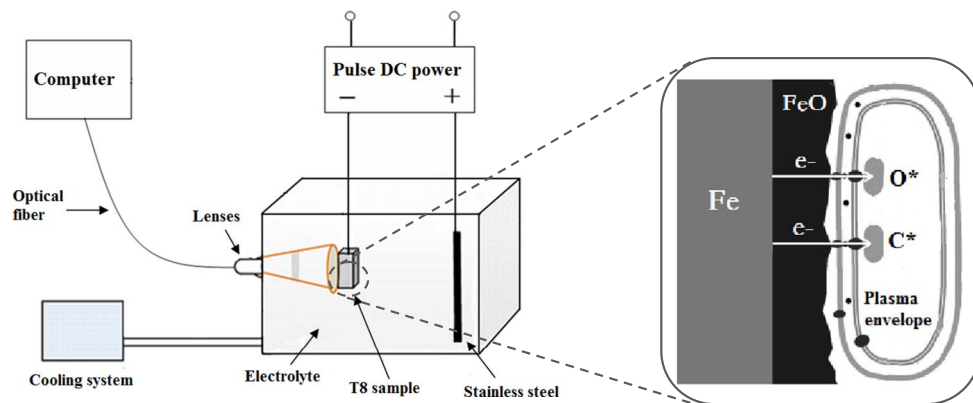


Fig. 1. Schematic illustration of the experimental apparatus for CPEO on T8 steel.

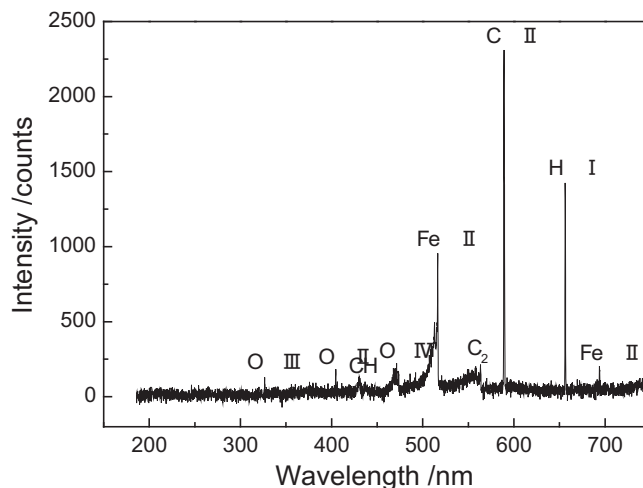
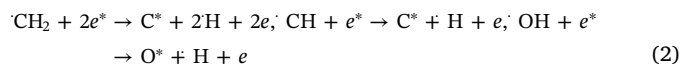
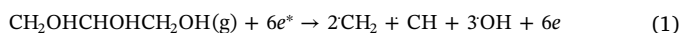


Fig. 2. Typical emission spectrum of CPEO process in glycerol aqueous solution.

3. Results and discussion

3.1. Spectroscopic investigation of the plasma discharge during CPEO process

Fig. 2 shows a typical emission spectrum of CPEO process in the near ultraviolet and visible regions. The emission spectrum of plasma discharge can indicate the active species which emit the light [16,17]. During CPEO process, Fe II (from steel substrate) and C II, H I, C₂, CH, O II, O III, O IV (from electrolyte) can be identified by the spectral analysis software (PLASUS SPECLINE 2.1). Among them, the notation H I means a neutral hydrogen atom, while the Fe II, C II and O II are singly ionized atoms. This suggests that active Fe, C, H, O radicals and ionic components have taken part in the discharge reactions. Besides, there exist some secondary and third ionization of oxygen atoms (O III, O IV) which possess highly oxidative activity. C₂ and CH are part of the decomposition products of glycerol molecules. During plasma discharge, glycerol molecules can be dissociated to some fragments by the intense collision with high energy electrons [18]. Some of them can be captured by OES, while others cannot due to the short lifespans [19]. The fragmentation pathways are proposed as below.



In order to further investigate the plasma characteristics of CPEO process, we employ the H I line (656.31 nm) to calculate the electron

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