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Investigation of anodic plasma electrolytic carbonitriding on medium carbon steel

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ABSTRACT

In this paper, anodic plasma electrolytic carbonitriding (APEC/N) treatment was employed to fabricate a hardened layer on medium carbon steel. The optical emission spectroscopy (OES) and the acoustical signal characterizations of plasma discharge during APEC/N process were analyzed for the first time. The results showed that the discharge plasma was in a local thermal equilibrium (LTE) state and the electron temperature in discharge zone was 4000 K–8000 K. The high electron temperature and strong acoustical signal corresponded with the intense discharge process, while the high-frequency noise up to 20 KHz related to the discharge taking place. Beneath the oxide layer, there was a 60 μm thick carbonitrided layer, which contained Fe_3C and Fe_4N phases. After APEC/N treatment, the wear resistance of medium carbon steel was improved. The wear rate of treated steel was about 2.61×10^{-4} mm^3/N·m, which was only half of the bare steel substrate.

1. Introduction

Plasma electrolytic saturation (PES) method for the surface hardening of metals has been paid great attention over the past few years [1–5]. Comparing with the conventional chemical heat treatment process such as pack carburizing, nitriding and carbonitriding, the PES method is much more efficient and environmentally friendly. It is carried out in organic electrolyte solution without high temperature environment or vacuum condition. When the voltage is applied to the workpiece, the aqueous solution is heated to produce a continuous gaseous envelope around the electrode surface. By increasing the voltage to a critical value, the gaseous envelope is broken down, resulting in plasma discharge and diffusion of active species towards metal substrate.

Up to now, most of the PES studies set the workpiece as cathode and focus on the saturation of light elements, like carbon [2], nitrogen [3] and boron [4]. In general, the wear or corrosion resistance of the metals is improved after PES treatment. Recently, P. Belkin et al. [6–8] have tried to investigate the anodic PES process where the steel workpiece is set as anode. The feature of anodic PES treatment is the formation of the oxide layer and the presence of anode dissolution. The anodic PES treatment can avoid the overheating or melting of steel workpiece, comparing with the cathodic PES process. In their previous work [7], the thermal model for anode heating was established. The influences of electrolyte concentration, treatment temperature and discharge time on the structure characteristics of the modified layer were analyzed [8]. However, the mechanical property of the modified layer was rarely reported. In addition, the optical emission spectroscopy or acoustical signal characterization of plasma discharge is helpful for understanding the mechanism underlying PES process. This field has not been involved so far.

In this work, anodic plasma electrolytic carbonitriding (APEC/N) treatment on medium carbon steel was carried out. The spectral and acoustical signals of plasma discharge were analyzed by optical emission spectroscopy (OES) method and short-time Fourier transform (STFT) method, respectively. The electron concentration and electron temperature in plasma envelope around the steel sample were calculated to evaluate the discharge condition during APEC/N process. Meanwhile, the microstructure and tribological performance of treated samples were analyzed. The electrochemical mechanism for the formation of modified layer was discussed.

2. Material and methods

The as-received substrate material is a medium carbon steel (C: 0.42– 0.50, Si: 0.17– 0.37, Mn: 0.50– 0.80, P: ≤0.040,S: ≤0.045, wt%, Fe balance) plate with dimensions of 36 mm × 15 mm × 1 mm, and it was set as the anode. The APEC/N process was carried out in a stainless steel container which served as the cathode. A pulse DC power supply with pulse frequency of 150 Hz and duty cycle of 45% was employed. The water-based electrolyte contains 10 wt% glycerol, 10 wt% carbamide and 5 wt% sodium silicate. The latter was added in order to reduce

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the anode dissolution. The steel sample was immersed in the electrolyte, then the positive bias voltage gradually increased from zero to 280 V to trigger the plasma discharge. After a short holding time, the applied voltage sequentially increased to 450 V to sustain a stable discharge for 10 min. Finally, the power supply was turned off in a slow mode in order to protect the electronic devices against a large current surge [5]. The steel sample was slowly cooled and was then taken out from the electrolyte, followed by cleaning and drying.

During the APEC/N treatment, an optical emission spectrometer (AvaSpec-3648, Avantes Company) was employed to acquire the OES signals. The optical fiber probe was placed at 2 cm away from the steel sample. The spectral resolution was 0.08 nm and the integration time was 1 s. The system used for acoustical signal detection was set to acquire acoustic waveforms related to plasma discharge at a sampling rate of 51.2 KHz. The acoustic sensor (mode 4944, Brüel & Kjær Company) was placed at 10 cm away from the steel sample and connected to a multi-channel high-precision data acquisition module. The morphology and microstructure of treated sample were observed by scanning electron microscope (SEM, Hitachi S-4800) equipped with the energy dispersive spectroscopy. The phase constituents of the treated sample were analyzed by X-ray diffraction (XRD, X'Pert Pro MPD). In addition, a Vickers indenter with 10 g load was used to measure the microhardness distribution of the hardened layer. A ball-on-disk friction and wear tester (HT-1000, Lanzhou Zhongke Kaihua technology development Co., Ltd.) was used to evaluate the tribological performance against GCr15 steel ball with 5 N load. Furthermore, the cross-sectional profiles of wear tracks were measured by a surface profilometer (TR200, Beijing Time Lianchuang technology Co., Ltd.). All the tests were performed at ambient temperature.

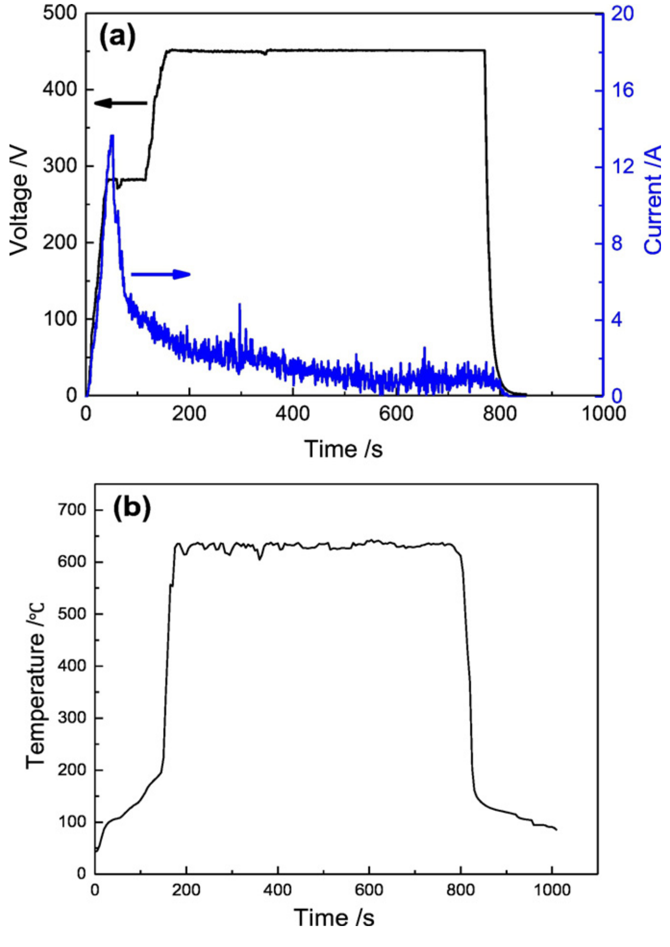

Fig. 1. (a) The voltage and current variation with time, and (b) the sample temperature variation with time during the APEC/N treatment.

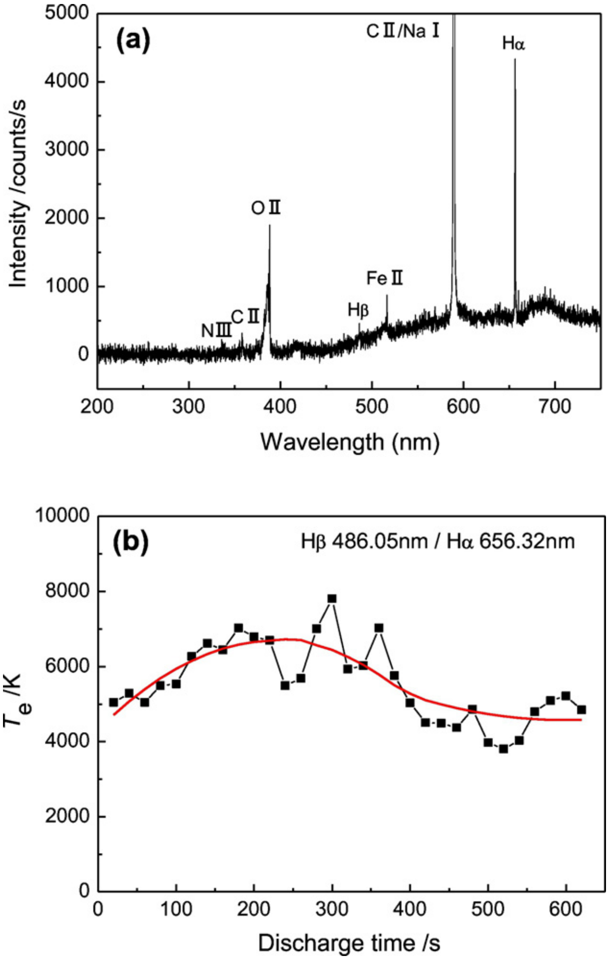

Fig. 2. (a) Typical emission spectrum of APEC/N process on medium carbon steel, and (b) electron temperature variation with discharge time.

3. Results and discussion

3.1. Current, voltage and sample temperature in the APEC/N process

The voltage and current variations with time in the APEC/N process are shown in Fig. 1a. At first, the current rises linearly with voltage to form a gaseous envelope around the steel sample surface. While the voltage reaches 280 V, this gaseous envelope is broken down, leading to the plasma discharge. Then, the current drops to 1.5 A with the voltage rising sequentially to 450 V. Finally, when the power supply is turned off, the current and voltage decrease to zero synchronously.

Fig. 1b displays the sample temperature variation with time. After the plasma discharge starts, the sample temperature rises rapidly. At 450 V, the sample temperature maintains at about 620 °C, which can promote the diffusion process of C, N atoms towards steel matrix. In addition, it is notable that the cooling rate of sample in the slow turn-off mode is about 10 °C/s, which implies that the quench-hardening effect may not take place.

Table 1
H_α and H_β lines with the wavelength (λ), transition, statistical weights of upper level (g_k), excitation energy (E) and transition probabilities (A_{ki}).

Line	λ (nm)	Transition	g_k	E (eV)	A_{ki} (10^6 S^{-1})
H_β	486.1	4d ^{2}D → 2p ^{2}P	32	2.55	8.42
H_α	656.3	3d ^{2}D → 2p ^{2}P	18	1.89	44.1