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Spectroscopic characterization of plasma during electrolytic oxidation (PEO) of aluminium

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ABSTRACT

We present results of an optical emission spectroscopic study of Plasma during Electrolytic Oxidation (PEO) of aluminium in citric acid and in sodium–tungstate water solutions. The line shape analysis of the first two hydrogen Balmer lines indicates presence of two PEO processes characterized by relatively low electron number densities $N_e \approx 0.8 \times 10^{15}\,cm^{-3}$ and at $2.5 \times 10^{16}\,cm^{-3}$. Apart from these two N_e values, $N_e \approx 6.0 \times 10^{16}\,cm^{-3}$ is determined from the width of the Al II 704.2 nm line. Three considerably different N_e values imply presence of three types of discharge during PEO of aluminium. The electron temperature T_e is determined from relative line intensities of the O II ($T_e \approx 38{,}300$ K) and W I ($T_e \approx 3300$ K) lines. The use of two databases of transition probabilities for O II lines introduces systematic difference of reported T_e results.

1. Introduction

Plasma electrolytic oxidation (PEO) is high-voltage anodizing process which produces a stable oxide coating on the surface of number metals, such as aluminium, titanium, magnesium as well as their alloys, see e.g. Ref. [1] and references therein. This process leads to the local formation of plasma, as indicated by the presence of micro-discharges on the metal surface accompanied by gas evolution. Short-lived micro-discharge events determine thermal and chemical conditions and play an important role in the phase formation, composition and morphology of such oxide coating [2,3].

Several attempts have been made to characterize spectroscopically PEO of aluminium and its alloys. The main difficulty in application of Optical Emission Spectroscopy (OES) for PEO characterization comes from space and time inhomogeneity of micro-discharges appearing randomly across the anode surface. Thus, the PEO spectra represent time integrated radiation recorded by spectrometer–detector system. The results of spectroscopic observation are even more complex to analyze if one takes into account that the radiation intensity is rather low and long exposure times are required. For this reason high light power spectrometers with low spectral resolution are usually employed for spectra recordings. Consequently, fine details of spectral line shape of hydrogen lines and narrow line-widths of non-hydrogenic lines are not widely used for PEO characterization.

The most popular application of OES for PEO diagnostics is spectra characterization and observation of temporal evolution of spectral lines in a visible and near UV spectral region [4–9]. Relative line intensity measurements are used [5,9,10] to determine electron temperature T_e[11]. For electron number density N_e measurements the Inglis–Teller method [12] was applied in Ref. [10], while in Ref. [9] Stark widths of Mg II and Si II lines [11] are used for the same purpose. The H_β line width in conjunction with theoretical calculations [11] was used to determine N_e in Ref. [5].

The present status of N_e characterization of PEO is best illustrated by the scatter of reported N_e values: (1.5–2.4) $\times 10^{16}\,cm^{-3}$[5], $5 \times 10^{16}\,cm^{-3}$[10] and ~$5 \times 10^{17}\,cm^{-3}$ in Ref. [9]. Similar situation is with reported T_e results: T_e in the range (4500–10,000) K was determined from the intensity ratio of two Al I lines 396.2 nm and 309.1 nm [5–7], the ionization temperatures in the range (6800–7700) K were measured from intensity ratio of Al I and Al II lines [10]. Two lines intensity ratio was used also for T_e measurements in Ref. [9] where $T_e = 3480$ K was determined from the H_β and the H_α line while two lines of Mg II and two lines of Si II gave 17400 K. It is interesting to note that none of the preceding authors used O II lines for T_e measurement. In this work, numerous O II lines are detected and used for T_e characterization. Further, it should be pointed out that it is difficult to trace the source of sometimes large differences of reported N_e and T_e results and compare them with this work since different discharge conditions are used.

The aim of this work is to determine N_e in PEO using line shape OES techniques. The line intensity ratio within single ionization stage of O II and W I will be used for T_e measurements. An attempt is made to correlate results of N_e with recently proposed PEO model [5,14].

2. Experimental

In the experiment, high purity aluminium samples (99.999%) were used as anode material. Before PEO has started, aluminium was

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degreased in acetone, ethanol and distilled water, using ultrasonic cleaner, and dried in a warm air stream. PEO process was carried out in an electrolytic cell with flat glass windows [15]. Platinum wires were used as cathodes. Water solution of 0.01 M sodium–tungstate (pH = 8.6) or 0.01 M citric acid (pH = 2.8) was used as electrolyte. The electrolyte was prepared using double distilled and deionised water and PA (pro analysis) grade chemical compounds. PEO process was carried out at current density of 50 mA/cm^2. During PEO, electrolyte circulated through the chamber–reservoir system. The temperature of the electrolyte was kept at (19.0 ± 0.5) °C during experiment.

In order to optimize recording of spectral line shapes in our laboratory, three spectrometers were used. To study the H_α line shape details high spectral resolution is required, for the weak H_β high resolution and high light power instrument is needed, while for recording of Al II 704.2 nm line high resolution combined with high light sensitivity spectrometer-detection system should be used. Therefore, the PEO spectra were recorded with three available grating spectrometers equipped with CCD for radiation detection. The lowest dispersion system (Hilger 0.3 m with 1200 grooves/mm grating) equipped with thermoelectrically cooled ICCD (−40 °C) was used for spectra recording in a wavelength range 380 nm−850 nm [16], see typical spectra in Fig. 1.

The H_α line in Fig. 2a was recorded with 2 m Ebert spectrometer (Carl Zeiss, Jena PGS 2, f/28, inverse linear dispersion 0.74 nm/mm, grating blaze wavelength 550 nm) while the H_β line in Fig. 2b was recorded with 0.67 m Czerny–Turner spectrometer (McPherson, Model 207, f/4.7, inverse linear dispersion 0.83 nm/mm). Both spectrometers were equipped with thermoelectrically cooled (−10 °C) CCD detector. The instrumental profiles of both high dispersion instruments were very close to Gaussian with the Full Width at Half Maximum (FWHM) of 0.026 nm and 0.030 nm for 2 m and 0.67 m spectrometers, respectively. The Al II lines in Fig. 3 were recorded also with 2 m spectrometer, but with grating blazed at 750 nm. In all experiments the image of anode surface was projected with unity magnification to the entrance slit of spectrometer with an achromatic lens having focal length 75.8 mm. The spectra from PEO were always recorded seven minute after the beginning of PEO with integration times from 10 s to 30 s, depending on spectrometer–detector system used. In order to measure relative line intensities for T_e measurements, the sensitivity of 0.67 m spectrometer–detector system was calibrated against standard tungsten strip lamp.

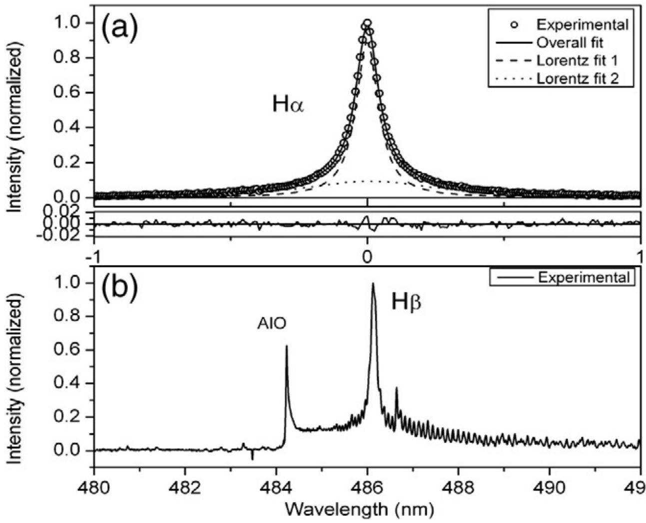

Fig. 2. a) The H_α line experimental profile fitted with two Lorentzians and residue plot; b) The H_β line profile. Experimental conditions: same as in Fig. 1.

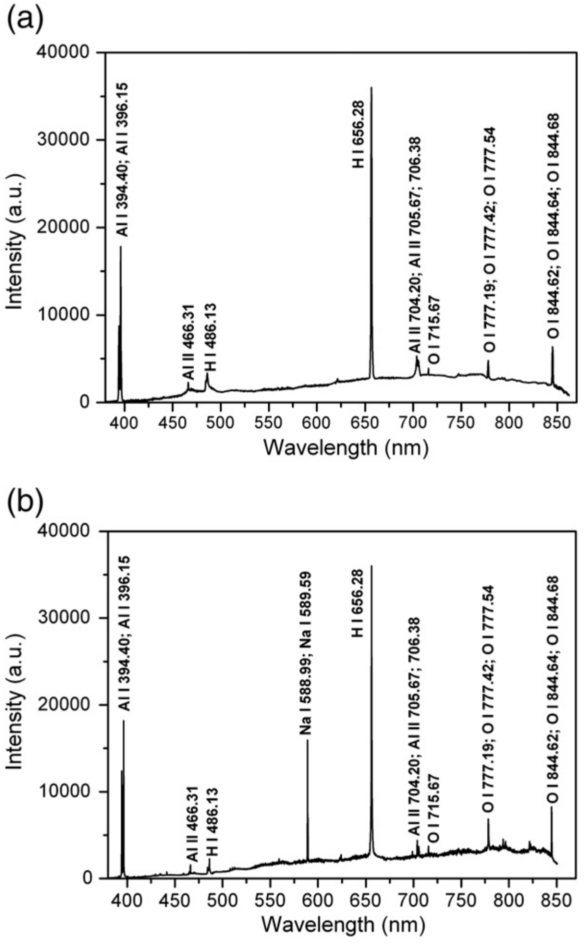

Fig. 1. Typical PEO emission spectrum in a) citric acid and b) sodium-tungstate, recorded with 0.3 m spectrometer. Experimental conditions: current density of j=50 mA/cm^2, electrolyte temperature 19.0 °C.

3. Results and discussion

Typical optical emission spectrum of micro-discharges during PEO of aluminium in citric acid is presented in Fig. 1a. The species that are identified originate either from aluminium electrode or from the electrolyte. The strongest lines belong to hydrogen Balmer lines H_α (656.28 nm), H_β (486.13 nm), Al I at 394.40 nm and 396.15 nm and O

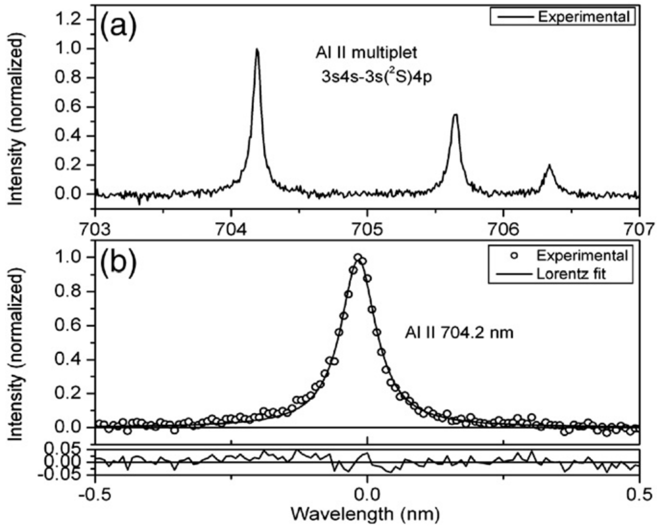

Fig. 3. a) The recording of Al II 3s4s–3s(^{2}S)4p multiplet 3; b) Experimental profile and best fit of the Al II 704.2 nm line. Experimental conditions: same as in Fig. 1.