

PROCESS MONITORING OF PLASMA ELECTROLYTIC OXIDATION

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Abstract: Plasma electrolytic oxidation (PEO) is a potential technique to coat a dense ceramic oxide layer on the surface of light metals, e.g. Al, Mg or Ti. In our PEO process, Al-pieces are emerged in aqueous solutions containing dissolved silicate/alkali, e.g. KOH/NaOH and K_2SiO_3/Na_2SiO_3 . Using a DC-pulsed system with 20Hz, micro-arcs are induced at the surface of the pieces randomly and plasma is associated to cause oxidation at the surface of metals, where Al_2O_3 and Al-Si-O phase coexist. Because the role of the plasma in the physical-chemical process is less clear, an optical emission spectroscopy (OES) technique is used for the in-situ monitoring of the emitting light of the plasma in order to realize the mechanism. During the process monitoring, each whole spectrum (190nm-850nm) is acquired vs. time with a specified time interval, e.g. 1sec. By analyzing these data, we observe several peaks corresponding to the species Al(308.6nm, 394.4nm, 396.2nm), Na(589nm), K(769.9nm), H(486.8nm, 656nm) and a strong continuous spectrum coming from the thermal radiation. These profiles of these peaks vs. time are related to the corresponding profiles of the current and voltage of our system consistently. From the curve fitting of the spectrum of thermal radiation with Planck's law, the temperature of plasma is estimated to be about 5000°K.

Introduction: Plasma electrolytic oxidation (PEO), which utilizes a high voltage to induce micro-arc locally at the surface of metals, is a potential coating technique to deposit a dense ceramic oxide layer at the surface of light metals, e.g. Al, Mg or Ti [1-5]. In the process, metals are as electrodes emerged in basic aqueous solutions containing dissolved silicate/alkali, e.g. KOH/NaOH and K_2SiO_3/Na_2SiO_3 . The ceramic oxide layer of PEO coating consists of a porous outer layer and a dense inner layer, where the distribution of Al-Si-O phase gradually changes [1]. The addition of silicate in the electrolyte, e.g. K_2SiO_3/Na_2SiO_3 , leads to accelerate the coating growth, because of the incorporation of Si causing the formation of Al-Si-O phase in the ceramic layer [1]. On the other hand, Si may cause a porous structure, if the amount of Si is too much. Therefore the concentrate of the silicate in the solution is necessary to be optimized. In addition, the *pH* value of the electrolyte is also critical to the process, about 12-13 depending on the concentration of KOH or NaOH. Normally, the oxide layers formed by PEO have not only a dense structure but also an excellent adhesion to the substrate than that of the anodizing process; the tribological performance, the wear and the corrosion resistance of the coating are improved by PEO. In the ceramic layer, the composition is composed of $\alpha-Al_2O_3$, $\gamma-Al_2O_3$ and Al-Si-O phase [3].

In our PEO process, a DC-pulsed system was built up, and the frequency of pulse is tuneable. At the beginning of PEO, only the electrochemical reaction occurs, and a thin oxide layer is formed. When the thickness of the layer becomes thicker, and the applied voltage reaches a certain value, numerous events of the arc-discharge take place, due to local breakdown. During the arc-discharge, light emission from the plasma associated with bubbles generates [2]. Because the complicated process consists of plasma and electrochemical reaction, the detailed mechanism is still unravelling [1]. In this paper, we utilize the optical emission spectroscopy (OES) method [6-8] to measure the spectrum of the emitting light from the plasma in order to identify the species involving the reaction. During the process monitoring, each frame containing a whole spectrum (190nm-850nm) is acquired vs. time with a specified time interval, e.g. 1sec. The range of light from UV to NIR (190nm-850nm) almost covers the major emissions spectrum of each species, which we are concerned. The maximum sampling rate of our OES system is 20 frames/sec. However a sampling rate with one frame per sec is enough for our process monitoring, compared to the changing rate of the process. For diagnosing and analyzing the spectrum of light emission of the plasma, a database of atomic spectra (Si, O, H, Al, Na, K) and diatomic molecular spectra (OH, AlO *etc.*) were used to identify the species [9]. In addition, a

continuous spectrum of thermal radiation, mixing with these line spectra, was observed by OES, which imply the information of the plasma temperature. Since the plasma reaction takes place in the basic aqueous solution, we predict not only the atomic spectra but also certain molecular spectra could be observed by OES. In order to implement OES measurement, an observing window with quartz was designed on the tank as an access for the transmission of the emission light to the collimator and optical fiber, which guide the light to a monochromator.

Results: Al-alloy 6061 plates (Si: 0.5%, Fe: 0.7%, Cu: 0.15-0.4%, Mg: 0.8-1.2%, Zn: 0.25%, Ti: 0.15%, Mn: 0.15%) with dimension (75mm×100mm) and thickness (1mm) were used for PEO coating. The compositions of the aqueous solution are KOH (14 g/l) and K_2SiO_3 (15 g/l). Since the purity of KOH and K_2SiO_3 , we used, are 99%, there is around 1% of NaOH and Na_2SiO_3 in the aqueous solution. The peak load of the applied voltage of the DC-pulse (20Hz) is increased step by step from 0 to 400V, as shown in Fig. 1, and the corresponding current is depicted in Fig. 2. The total time of the process is about 1000sec. The average thickness of the oxide layer is about 30 μ m. Fig. 3 shows the spectrum of light emission at 590sec, and the atomic spectrum lines of Al(308.6nm, 394.4nm, 396.2nm), Na(589nm), K(769.9nm), H(H_α : 656nm, H_β : 486.8nm,) are designated in the figure. H_α and H_β are the Balmer lines of hydrogen. Besides the atomic spectra, there is a continuous spectrum of thermal radiation, which is an envelope in Fig. 3. The variations of the emission at these wavelengths are depicted in Fig. 4-9 by plotting their intensities vs. time. To exhibit the feature of the thermal radiation only, we choose an arbitrary wavelength, $\lambda=550.4$ nm, for observation, because there is no any related atomic emission in our process to interfere its intensity and it is located at the neighbourhood of the peak of the blackbody radiation.

Discussion: The atomic spectra of Al(308.6nm, 394.4nm, 396.2nm), Na(589nm), K(766.5nm, 769.9nm), H (486.8nm, 656nm) are observed in Fig. 3, and the spectra of diatomic molecular OH and AlO also possibly exist; the peak of OH (306.4nm) could overlap with Al(308.6nm), and AlO(486.6nm) with H_β . The intensities of alkali metals, Na and K, is dependent of their concentrations. We ever tested the other electrolytes with different concentrations of KOH and NaOH. We found if sodium (Na) is the major, the colour of the emitting light is more like yellow, due to Na(589nm). The thermal radiations, coming from the high-temperature plasma are also observed by OES as shown in Fig. 3. According to the curve-fitting of Planck's law, the temperature is about 5000°K, which was confirmed by Ref [10]. Since the plasma is adjacent to the oxide layer, it is inferred that parts of the former oxide layer could be fused by the high temperature, and then a new oxide is formed again.

By comparing the profiles of Fig. 4-10, the profiles of Na, K, Al and H are almost identical with that of the thermal radiation. The peaks of these profiles, Fig. 4-10, are also consistent with the current's profile, as shown in Fig. 2. However after 800sec, the profiles of Al are little different from that of alkali and hydrogen. A reasonable explanation is that there is less signal contamination from the thermal radiation for the intensities of Al's atomic spectra, since the peaks of Al(308.6nm, 394.4nm, 396.2nm) are located at the UV region. However the intensities of these wavelengths, corresponding to the line spectra of Na, K and H, include two contributions, the thermal radiation and the atomic emission. Observing Figs 1, 4-10, an obvious emission is found to abruptly occur when the applied voltage is above 350V. At the initial stage (below 350V), the voltage is not enough to cause a crucial breakdown of the oxide layer, so the light emission is very weak, even there is a certain amount of current accompanying. Notice that the emitting light is caused by the photon emission when the electrons return from the excited state to the ground state. However the population of the excited radial, neutron or iron in the plasma is unknown. For different species, their abilities of emission are also not the same. Therefore the results of OES cannot be directly interpreted.

Conclusions: The monitoring of PEO by OES was demonstrated in the research. From the spectrum analysis, the light emission of plasma by micro-discharge was identified to be composed of alkali (K, Na), H, Al, OH. The spectrum of AlO is suspected reasonably to exist at 486.6nm, where H_{β} is close to. Additionally, the continuous spectrum of thermal radiation of plasma can also be detected by OES. From the curve fitting of the envelope of the thermal radiation with Planck's law, the temperature of plasma is calculated to be about 5000 °K. These clues provided by OES is being further investigated by us for the interpretation of the reaction mechanism of PEO. How to distinguish the signals of Al and OH, as well as AlO and H_{β} is being conducted now. The verification of the existence of OH and AlO during the process, for instance, can aid us to account for the unravelling mechanism. Beside the process of PEO, the similar processes of plasma electrolysis for nitride and carbide coating can also be diagnosed by OES.

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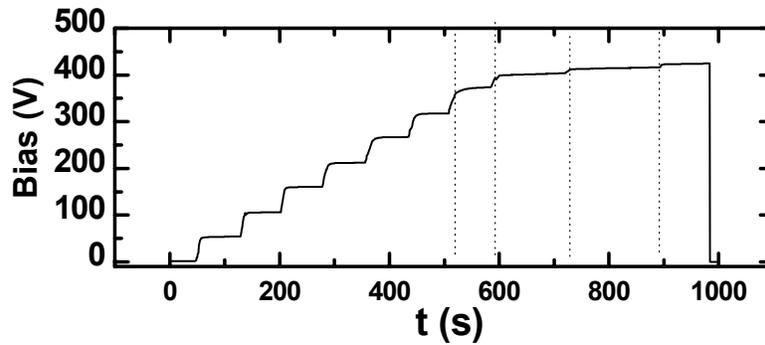


Fig. 1 The applied voltage of PEO vs. time.

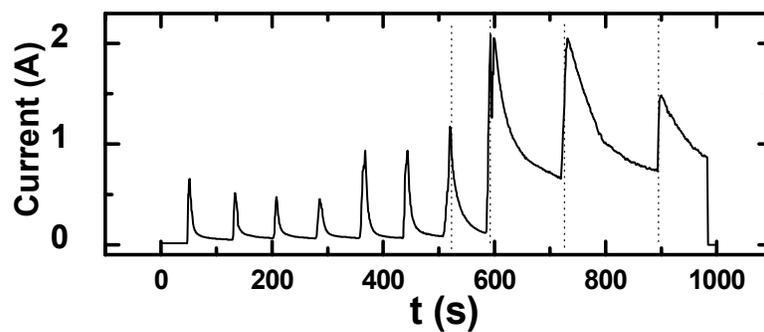


Fig. 2 The corresponding current of PEO vs. time.

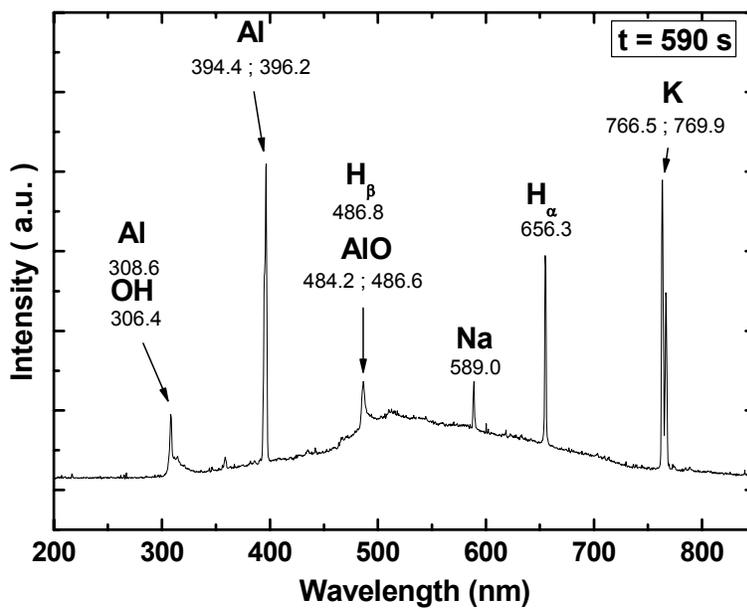


Fig. 3 The spectrum of plasma at 590sec.

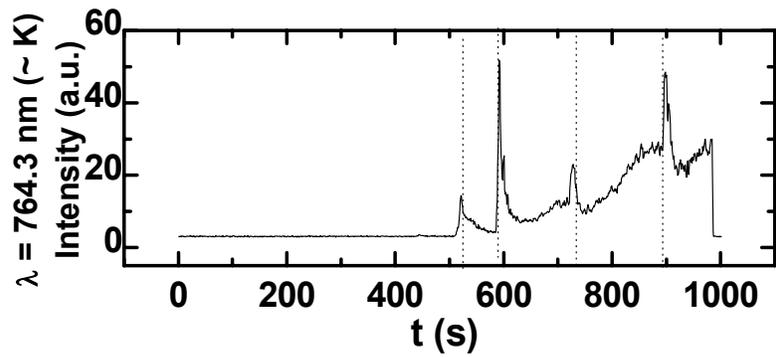


Fig. 4 The intensity of K (764.3nm) vs. time.

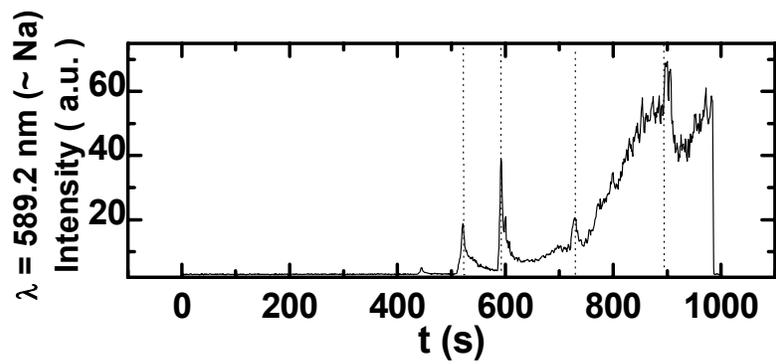


Fig. 5 The intensity of Na (589.2nm) vs. time.

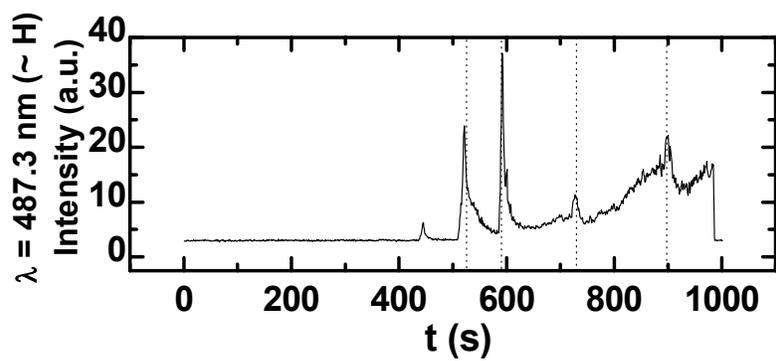


Fig. 6 The intensity of H_{β} (487.3nm) vs. time. The signal of the emission of AlO could merge into that of H_{β} at this wavelength.

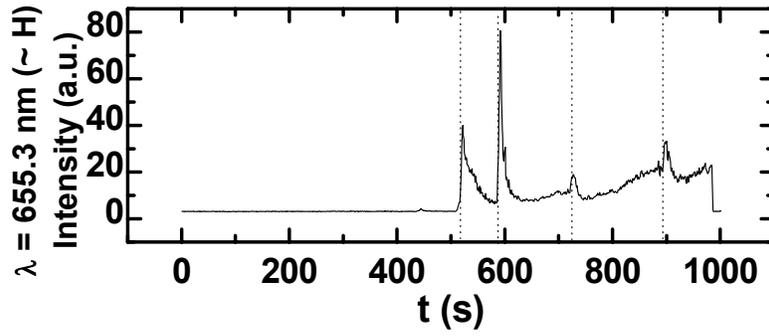


Fig. 7 The intensity of H_{α} (655.3nm) vs. time.

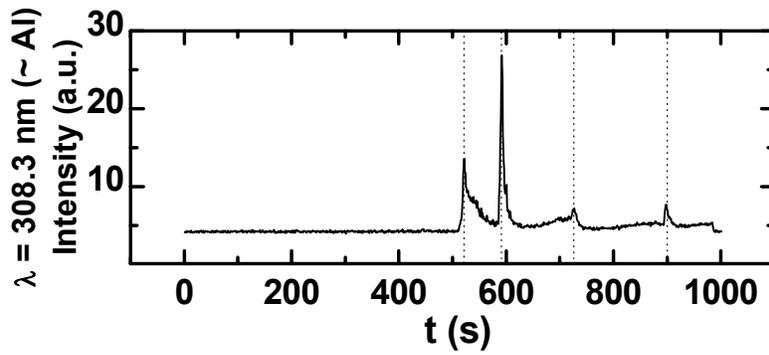


Fig. 8 The intensity of Al (308.3nm) vs. time. The signal of the emission of OH could merge into that of Al at this wavelength.

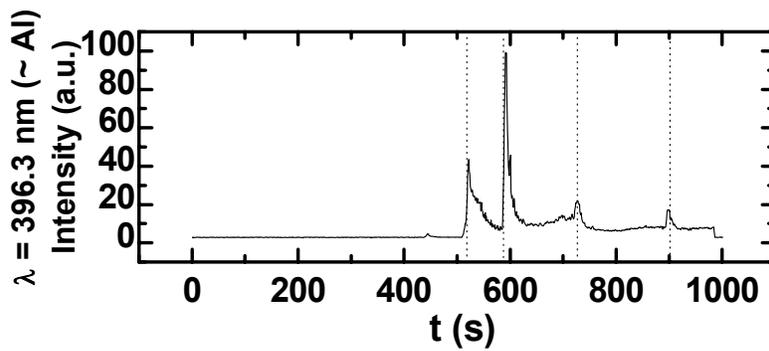


Fig. 9 The intensity of Al (396.3nm) vs. time.

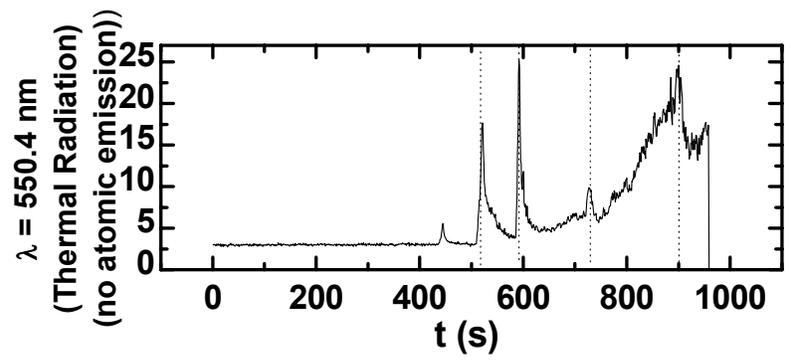


Fig. 10 The intensity of $\lambda=550.4\text{nm}$ vs. time, which can be regarded as the variation of the thermal radiation, because there is no any corresponding atomic emission in our process.