Effects of Hybrid Voltages on Oxide Formation on 6061 Al-alloys During Plasma Electrolytic Oxidation

Kai Wang[a], Bon Heun Koo[a],*, Chan Gyu Lee[a], Young Joo Kim[a], Sunghun Lee[b], Eungsun Byon[b]

[a]School of Nano & Advanced Materials Engineering, Changwon National University, Changwon 641-773, Korea

[b]Surface Technology Research Center, Korea Institute of Materials Science, Changwon 641-010, Korea

Abstract

Plasma electrolytic oxidation (PEO) is carried out on 6061 Al-alloys in a weak alkaline electrolyte containing NaOH, Na_2SiO_3 and NaCl. Centered on the correlation of composition and structure, analyses by means of X-ray diffration (XRD), scanning electron microscope (SEM) and energy dispersive spectrometry (EDS) are conducted on the specimens, which have been PEO-treated under hybrid voltages of different direct current (DC) values (140-280 V) with constant alternate current (AC) amplitude (200 V). Attention is paid to the composition, properties and growth mechanism of oxide layers formed with hybrid voltages. Moreover, the main effects of DC value are discussed. Ceramic layers with a double-layer structure which combines hard outer and soft inner layers are found to be consist of α-Al_2O_3, γ-Al_2O_3 and mullite. With the DC values increasing, the growth of the ceramic layers tends to have increasingly obvious three-stage feature.

Keywords: plasma electrolytic oxidation; oxide layer; aluminum alloys; alkaline electrolyte; hybrid voltages

1. Introduction

Al-alloys with a wide variety of properties have found broad applications in engineering structures thanks to their importance in reducing construction weights. The requirements for the components made with Al-alloys very often include high wear resistance. In this respect, as a new electro-chemical surface treatment technology for generating anti-abrasive oxide layers on light metals/alloys such as Al, Mg, Ti and their alloys[1], plasma electrolytic oxidation (PEO) is counted among the most promising ways out. In addition, some researches[2-4] pointed out that PEO layers are able to achieve an ideal balance among wear resistance, corrosion resistance, mechanical strength, interfacial adhesion and thermal property. Till now, some achievements have been made on the practical application of PEO-treated machine parts out of various materials[5-6].

However, while most researchers laid their attention on the traditional parametric fators, such as direct current (DC), mains frequency alternate current (AC) or pulsed voltages, the problem of compound voltage, despite its complicacy and urgency to be solved, has not been in-depth investigated yet. To do this, it must be required to clearly understand the relationships between the kinetics of the PEO formation and voltage-dependent surface morphology and composition of ceramic layers.

In present work, PEO was undertaken on 6061 Al-alloy in a weak alkaline-silicon-chlorine electrolyte. As hybrid voltages, different DC voltages with a constant AC amplitude were used to investigate the characteristics of PEO layer including the effects of hybrid voltage on surface morphology, composition and microhardness of the treated ceramic layers.

2. Experimental

Specimens out of 6061 Al-alloy (composition: Mg, 1 wt%; Si, 0.65 wt%; Fe, 0.7 wt%, Cu, 0.3 wt%; Cr, 0.2 wt%; Mn, 0.15 wt%; Ti, 0.15 wt%; and Al, balance), 30 mm diameter×16 mm high, with a surface finish of $R_a \leq 0.1$ μm were used as substrates. Prior to PEO treatment, the samples were degreased, ultrasonically cleaned in acetone, thoroughly dried, and then immersed in an alkaline aqueous electrolyte (pH = 9-10) containing NaOH (2 g/L), Na_2SiO_3 (8 g/L) and NaCl (0.5 g/L). The PEO process was carried out at room temperature in a 2-litre water-cooled stainless steel tank,

*Corresponding author. Tel.: +82-19-550-7624.

E-mail address: bhkoo@changwon.ac.kr

which served as a counter-electrode with the metallic samples immersed in the electrolyte as an anode. The PEO treatment was carried out in 5 min in a combination of different AC 60 Hz frequency power supply with a DC power supply ($U_{DC}+U_{AC}$). In the experiments, in order to control the PEO conditions, the DC value (U_{DC}) and the AC amplitude (U_{AC}) were variable: U_{DC} = 140-280 V, U_{AC} = 140-220 V. Previous work pointed out that U_{AC} = 200 V is the most suitable. This article will focus on the effects of DC values. In the process, the AC amplitude was slowly increased to 200 V to keep the current density at 3-4 dA/cm^2 throughout the experiment, and then the DC value was increased gradually so as to maintain the reset current density even as the layer thickness was gradually increasing. The plasma began to discharge onto the surface at U_{DC} = 140 V with U_{AC} = 200 V.

The different phases present in the layer were investigated with Philips-X'Pert system X-ray diffraction (XRD) (Cu Kα radiation) and the scans were performed with 0.02° θ step size in the 2θ range of 30°-90°. The microstructures of surface and cross-sectional morphology of treated samples were examined on a JSM 5610 scanning electron microscopy (SEM). The element distribution in the layer was investigated with Oxford 6587 energy dispersive spectrometry (EDS). The layer microhardness was measured at 10 surface sites of each sample on VLPAK2000 Mitutoyo Hardness Test Machine under 0.1 N load in 30 s dwell time, and then the average was calculated.

3. Results and Discussion

Fig.1 shows the surface features of the PEO-treated samples under different DC values. The micrographs clearly indicate the presence of discharge channels with an appearance of dark circular spots and the crater-like microstructures distributing all over the surface. It is also apparent that the diameter of the crater-like discharging channels increase with DC values, yet the number of discharging channels decreases. According to the growing trend of channel diameter, can be divided three stages: (1) growing stage from DC 140 V to 180 V, (2) intimidate stable stage from DC 200 V to 240 V, and (3) steady stage from DC 260 V to 280 V.

As shown by the XRD patterns (see Fig.2), mullite, α-Al$_2$O$_3$ and γ-Al$_2$O$_3$ are the main phases which constitute the surfaces of oxide layers formed with different DC values. With lower DC values (140-180 V), γ-Al$_2$O$_3$ phase dominates the surface. With the DC value increasing, the amount of α-Al$_2$O$_3$ increases. In his study on the formation of meta-stable alumina phase for the plasma spraying technique, R. McPherson[7] found that high cooling rate is in favor of the formation of α-Al$_2$O$_3$ during the solidification of alumina droplets. In the plasma electrolytic process, the molten alumina is injected into the electrolyte solution through the discharging channel when plasma sparks develop, so the outer alumina in contact with the electrolyte is quenched at a high cooling rate, which favors

the formation of α-Al$_2$O$_3$ outside. With the DC value increasing, the temperature around the discharging channel can exceed 1 000 °C; γ-Al$_2$O$_3$ phase will transform into α-Al$_2$O$_3$, a stable alumina phase characteristic of high hardness[8].
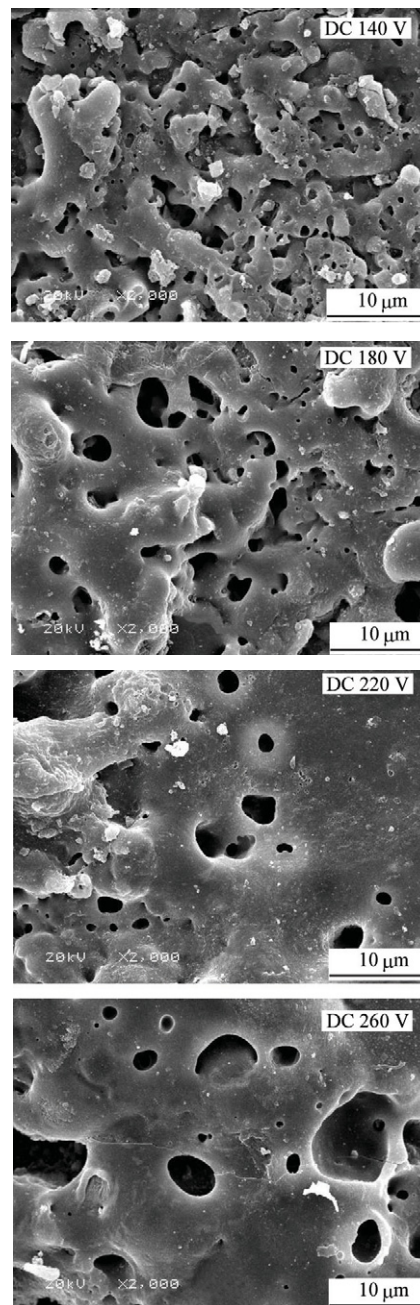

Fig.1   SEM surface morphology of PEO-treated samples with different DC values.

The cross-sectional SEM micrographs of the layers formed with different DC values are presented in Fig.3, which shows variation of layer thickness. In a layer, there can be discovered a two-layer structure consisting of inner layer and outer layer. Inner layer is denser, finer and less porous without obvious gas cavities in it while outer layer is quite the opposite with other defects included. Still, no distinct interface can be found
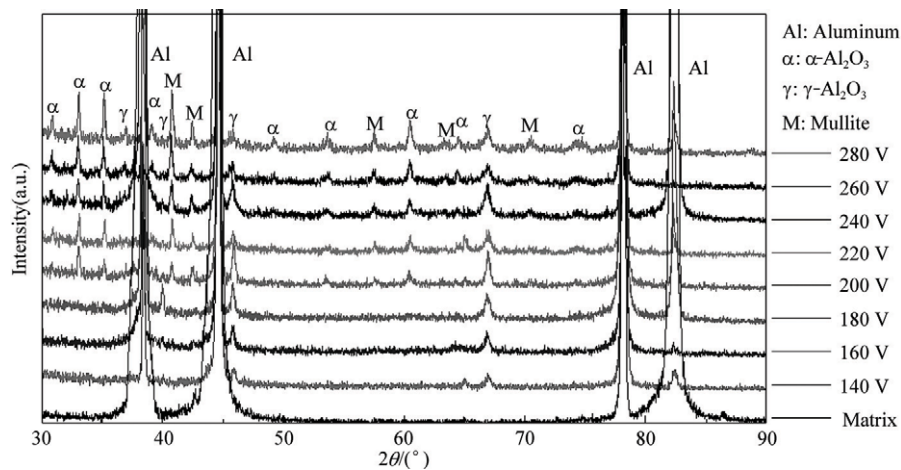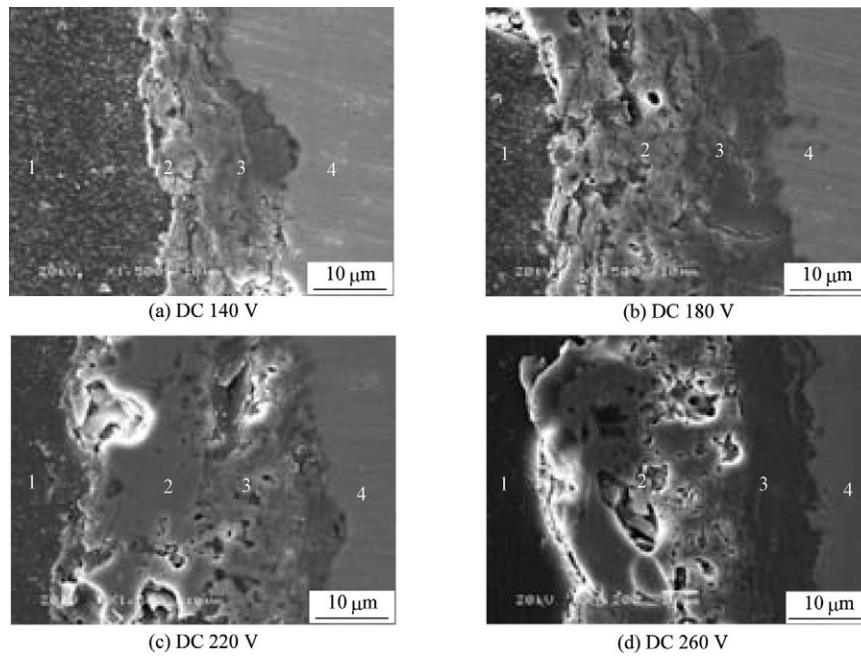
Fig.2　XRD patterns of ceramic layers prepared with different DC values.

(a) DC 140 V

(b) DC 180 V

(c) DC 220 V

(d) DC 260 V

1–Resin; 2–Outer layer; 3–Internal layer; 4–Substrate

Fig.3　Cross-sectional SEM micrographs of layers prepared with different DC values.

between inner and outer layers. With the lower DC values, a dense layer initiates first with fewer porosities, and as the DC value and layer thickness increase, the outer portion of the layer begins to form and grow with more porosities while the inner portion maintains nearly the same. This is because while higher voltage makes the inner layer undergo oxidization, it makes larger discharging channel break down the inner layer.

It is also clear that when DC value increases, the oxide layer undergoes three forming stages (see Fig.4), which are characterized by the variation of average layer thickness. In the first stage (DC 140-180 V), as the applied DC increases, the thickness shows a sharp rise; then in the range of DC 200-240 V, it remains rather stable at a medium level; and in the final stage (DC 260-280 V), it rises sharp to about 70 μm. In the first stage, the freshly formed ceramic layer, called barrier layer, is easy to break down by increased voltage, thereby producing numerous crater-like channels. At the same time, the amount of ejected alumina increases simultaneously, as a result, the layer thickness increases linearly in this stage. When the layer becomes thick enough, the plasma punch-through effect reaches a balance. Once the DC value increases up to 260 V, the thickness passes through another critical point and reaches a new balance between higher-voltage and thicker-layer.

The distribution of chemical elements across the layer was studied by EDS (see Fig.5). It is obvious that silicate and chlorine of the electrolyte have taken part in the PEO process. It can be seen that Si tends to be localized mainly in the outer portion of layer while Cl

in the inner portion. Several previous studies paid attention to the incorporation of electrolyte species with the anodic substance in both the conventional anodic oxidation[9] and PEO treatment[10], which also implies that the incorporated electrolyte products are immobile, inward-migrating or outward-migrating across the layer in the electric field.
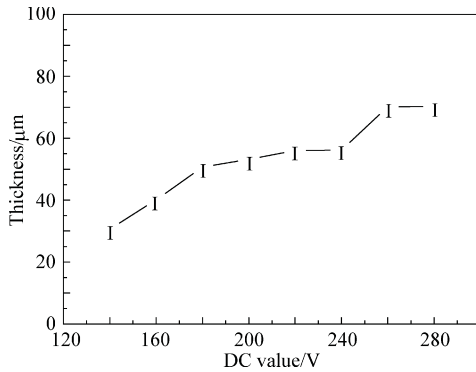

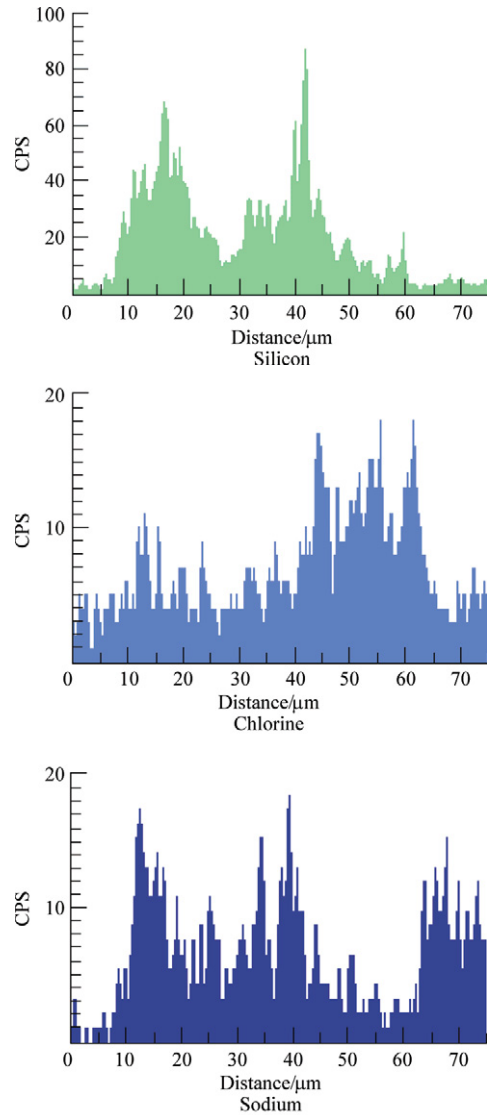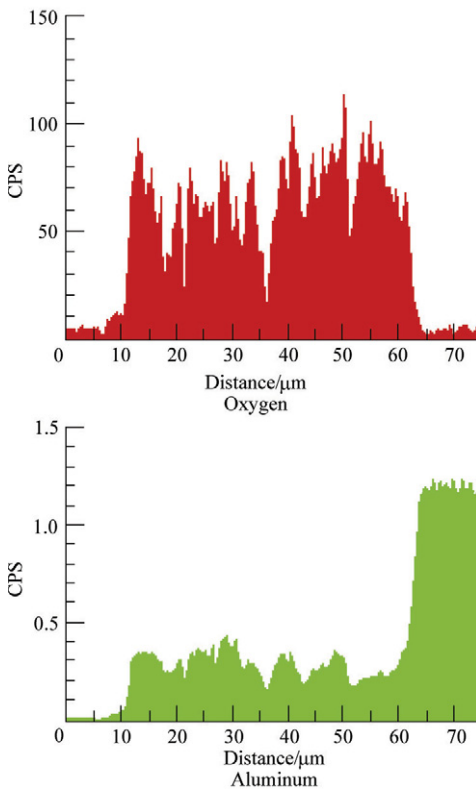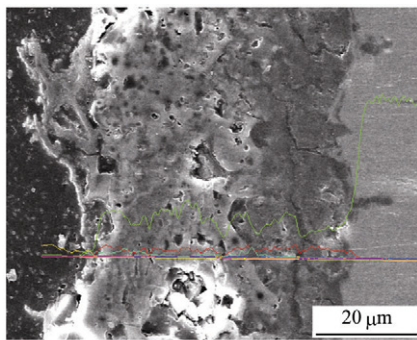Fig.4   Thickness curve of layers prepared with different DC values.

Fig.5   EDS line scanning of PEO layer prepared with DC 220 V and AC 200 V.

In PEO processes, the alumina turns out throughout the layers because of the migration of Al^{3+} and O^{2-} ions through the layer assisted by the high electric field. At the same time, the following reaction may probably occur: $SiO_3^{2-} + 2H^+ \rightarrow SiO_2 + H_2O$. With the DC increasing, SiO_2 would fuse with Al_2O_3 at high temperature in the range of 2×10^3-3×10^3 °C[6] thus forming mullite phase on the layer surface as follows: α-$Al_2O_3 + nSiO_2 \rightarrow Al_2O_3 \cdot n\,SiO_2$ (refer to XRD patterns in Fig.2). Therefore, Si-element mostly precipitates immobile in the outer layer. Cl-ions may also form the inner layer with soft $NaAlCl_4$ or $AlCl_3$ compounds. This inner layer may operate as a buffer possessive of good shock absorptivity.

It can be concluded that the immobile Si-element and inwards-migrating Cl-element result in the two-layer structure in the PEO layer. Fig.6 illustrates the micro-hardness of both layers including hard outer layer and soft inner layer as a function of DC values. Surely, the datum 93 HV itself is enough to evidence the PEO

treatment capable of strengthening the surface of 6061 Al-alloy. With DC and mount of α-Al$_2$O$_3$ increasing, the microhardness of inner layer also increases at a slow rate. The microhardness of outer layer increases sharply during the first stage, and as the ratio between α-Al$_2$O$_3$ and mullite gradually comes to strike a balance, the growth of microhardness begins to slow down and finally reaches upward of 1 900 HV.
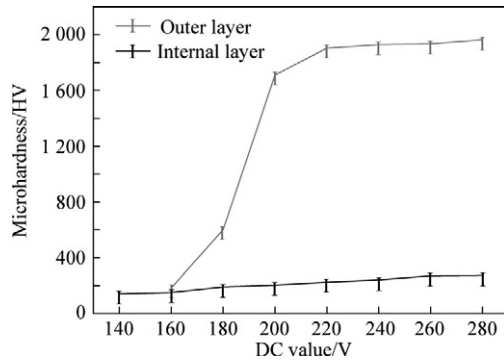

Fig.6　Curves showing microhardness of two layers vs DC values.

4. Conclusions

The PEO process has been carried out on the 6061 Al-alloy substrate in an alkaline-silicon-chlorine electrolyte for 5 min with combination of different DC values and constant amplitude of 200 V AC. It produces a surface layer of two-layer structure characteristic of crater-like appearance. The immobile Si-element and inward-migrating Cl-element contribute to hard Si-rich outer porous layer and soft Cl-rich inner dense layer. As DC value increases, meta-stable γ-Al$_2$O$_3$ forms on the surface first; then transforms into stable α-Al$_2$O$_3$, and finally mullite. The change of soft Al$_2$O$_3$ phase to hard one is affected by applied variable DC voltage, which is considered as the key factor to dominate surface morphology, structure and mechanical properties of the PEO-treated oxide layers.

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Biography:

Kai Wang　Born in 1981 and majoring in material science and technology, he received B.S. and M.S. degrees from Hefei University of Technology in 2003 and 2006 respectively. Now as a doctoral candidate, he is studying in Changwon National University in Korea.
E-mail: hfutwk927@gmail.com