

Ceramic coatings on 6061 Al alloys by plasma electrolytic oxidation under different AC voltages

Kai Wang, Young Joo Kim, Yasunori Hayashi, Chan Gyu Lee and Bon Heun Koo*

School of Nano & Advanced Materials Engineering, Changwon National University, Changwon, Korea

Ceramic coatings have been produced on 6061 Al alloy substrates in a weak alkaline-silicon electrolyte under different AC voltage at 60 Hz combined with a 200 V DC voltage for 5 minutes by a plasma electrolytic oxidation process. The surface morphology, composition, structure and microhardness analysis of layers were carried out by an X-ray diffractometer, optical microscopy, scanning electron microscopy, an energy dispersive X-ray spectrometer and a microhardness tester. Analysis shows that a two-layer structure coating consist of different states of α -Al₂O₃, β -Al₂O₃ and γ -Al₂O₃, where Si concentrates in the hard outer layer, and Cl predominates in the soft internal layer. The influence of deposition AC voltages on the kinetics of coating formation, coating microhardness, the number and size of the discharging channels was investigated.

Key words: Plasma Electrolytic Oxidation, Ceramic Coating; Al Alloy, Weak Alkaline-Silicon Electrolyte, Voltages.

Introduction

Alumina coatings are very effective in developing wear resistance surfaces for Al alloys that also exhibit excellent corrosion protection. A number of deposition techniques such as arc-discharge plasma, gas-flame spray, vacuum deposition methods and high temperature glass enameling have been investigated to produce ceramic coatings on Al and its alloys. These techniques require a high substrate temperature to provide adequate coating adhesion under high contact loads. Plasma electrolytic oxidation (PEO) is a novel electro-chemical surface treatment process for generating oxide coatings on valuable metals such as Al, Mg, Ti and their alloys, which is characterized by a high temperature of 10^3 to 10^4 K and a high local pressure of 10^2 to 10^3 MPa in the discharge channels [1]. Earlier research showed that the coatings offered an attractive combination of wear resistance, corrosion resistance, mechanical strength, interfacial adhesion and thermal properties [2-4]. Some practical industrial applications of PEO coatings on machine parts manufactured from various materials have been discussed in Refs [5, 6].

However, the overall research emphasis remains centered on performance evaluation, characterization and the testing aspects of PEO coatings. Many of these earlier studies have not addressed the interrelationship between the kinetics of the PEO coating formation and the variation in the surface morphology and composition of ceramic coatings with reference to the treatment voltage and time. PEO is a multifactor-controlled physical-chemical process, and it is of great interest to analyze the evolution of the coatings

in the processes.

In the present study, the PEO method was carried out on 6061 Al alloy in a weak alkaline-silicon electrolyte to obtain ceramic coatings. The surface morphology, composition and microhardness of ceramic coatings treated with different AC voltages combined with a constant DC voltage were characterized.

Experimental

A 6061 Al alloy (composition 1% Mg, 0.65% Si, 0.3% Cu, 0.2% Cr, 0.15% Mn, 0.7% Fe, 0.15% Ti and Al balance) was used as the substrate. Columnar samples of 16 mm diameter 30 mm height size were fabricated. All the samples were subjected to polishing so as to obtain a uniform surface roughness of 0.1 ± 0.05 μ m. Prior to coating deposition, the samples were degreased and ultrasonically cleaned in an acetone medium and thoroughly dried, and then immersed in the electrolyte for PEO treatment. The electrolysis environment was an aqueous electrolyte containing NaOH, Na₂SiO₃ and NaCl at concentrations of 2 g/l, 8 g/l and 0.5 g/l respectively. A PEO coating unit designed and built by the authors has been employed in the present study, which mainly consists of a power supply unit, a bath container and a cooling system. The metallic samples immersed in the electrolyte were used as the anode and stainless steel was used as the counter electrode. Throughout the entire range of experimentation, the temperature of the electrolyte was maintained constant at approximately 25 ± 2 °C using a cooling system. The deposition was carried out for 5 minutes at different AC voltages at 60-Hz frequency (140-220 V) with the same constant 200 V DC power ($U_{DC}+U_{AC}$). The AC power was slowly increased to the required test level to maintain the current density at 2 A/cm². After deposition, the samples

*Corresponding author:
Tel : +82-55-213-3714
Fax: +82-55-262-6486
E-mail: bhkoo@changwon.ac.kr

were taken out of the electrolytic solution, thoroughly washed in cold running water, ultrasonically cleaned in an acetone medium and thoroughly dried.

The different phases present in the coating layers were investigated with Philips-X'Pert system X-ray diffractometer (XRD) ($\text{Cu K}\alpha$ radiation) and the scans were performed with 0.02° θ step size in the 2θ range of 30 – 90° . The microstructure of surfaces and cross sections of samples treated at different AC voltages were examined by a JSM 5610 scanning electron microscopy (SEM). The composition of the coatings was scanned by an Oxford energy dispersive X-ray spectrometer (EDS). The micro hardness of the coating layers in 10 different places was measured by a VLPK2000 Mitutoyo hardness test machine using 0.1 N load with a 30s dwell time, and then the average microhardness was calculated and reported.

Results and Discussion

A 200 V DC voltage was first established between the

Al alloy sample and the stainless steel counter electrode to raise the current to 2 A/cm^2 . Then an AC voltage was coupled with the DC power and gradually increased to the acquired level as to maintain the current at 2 A/cm^2 . A plasma was initiated to discharge on the surface of the Al alloy at AC 140 V. During the PEO process, a large amount of water vapor was generated by the exothermic PEO reaction.

Fig. 1 shows the surface features of the coated samples that were PEO treated at different AC voltages. The micrographs clearly indicate the presence of discharge channels appearing as dark circular spots, which maybe described as pancake-like microstructural features, distributed all over the surface of the coatings. It is also apparent that the number of such pancake-like discharge channels decreased with an increasing AC voltage while the discharge channel diameter clearly increased with an increased AC voltage.

It can be concluded from the X-ray analysis that $\alpha\text{-Al}_2\text{O}_3$, $\beta\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ are the main phases in the ceramic coatings at different AC voltages. The XRD results are

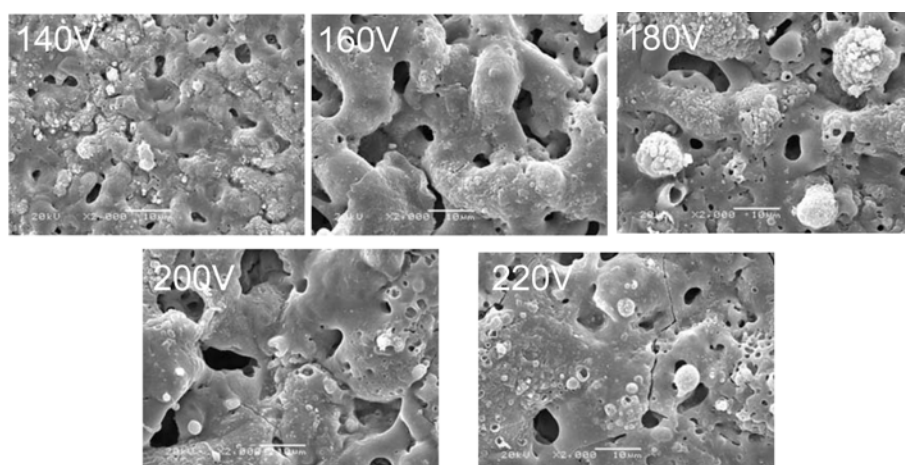


Fig. 1. SEM micrographs of the coating surfaces processed at different AC voltages.

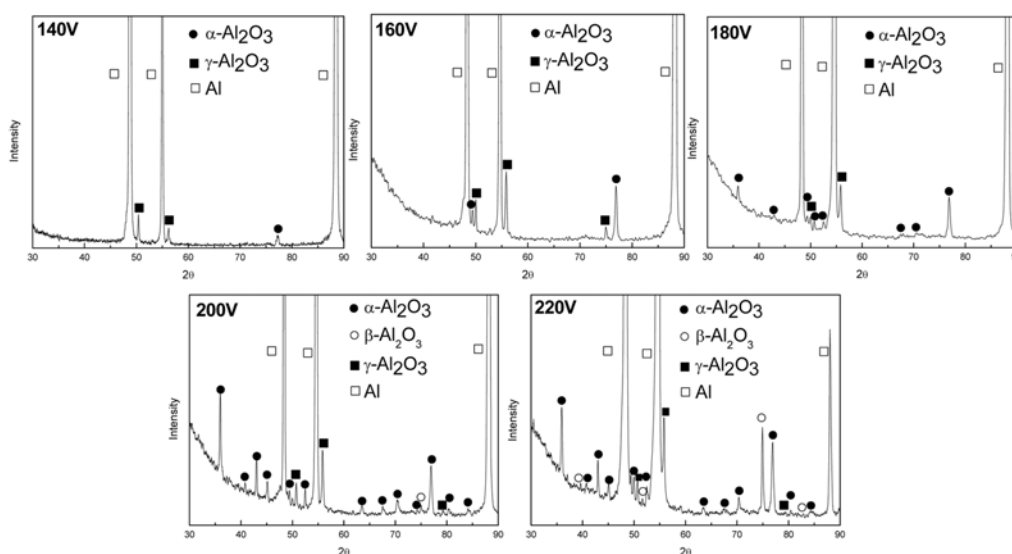


Fig. 2. XRD patterns for ceramic coatings processed at different AC voltages.

shown in Fig. 2. In addition, γ - Al_2O_3 phase dominates the surface during the low 140 V AC voltage treatment, while the amount of α - Al_2O_3 increases with an increase in the AC voltage. Trigonal α - Al_2O_3 is a stable alumina phase with a high melting point of 2050 °C, and γ - Al_2O_3 is a meta-stable phase which can transform into α - Al_2O_3 by heating to a temperature interval between 800 and 1200 °C [7, 8]. McPherson found that a high cooling rate favors the formation of α - Al_2O_3 during the solidification of alumina droplets in his study of the formation mechanism of the meta-stable alumina phase by the plasma spraying technique [9]. During the plasma electrolytic process, the molten alumina was injected into the electrolyte solution when plasma sparks were quenched, so the outer alumina contacting the electrolyte had a higher cooling rate, which

favoring the formation of α - Al_2O_3 on the outside. With an increase in the AC voltage, the temperature around the discharge channels can exceed 1000 °C, therefore, the γ - Al_2O_3 phase would transform into α - Al_2O_3 which is a stable alumina phase with high hardness [10]. When the temperature around the discharge channels of some local areas exceed 2050 °C by increasing the AC voltage, α - Al_2O_3 will then transform into the β - Al_2O_3 phase which will reduce the mechanical strength of the coatings.

Cross-sectional SEM micrographs of the coatings processed at AC 140 V, 160 V, 180 V, 200 V and 220 V are shown in Fig. 3. It is clear that the average thickness increases as the applied AC voltage increases in this initial stage (140–180 V). During the stage, the coatings

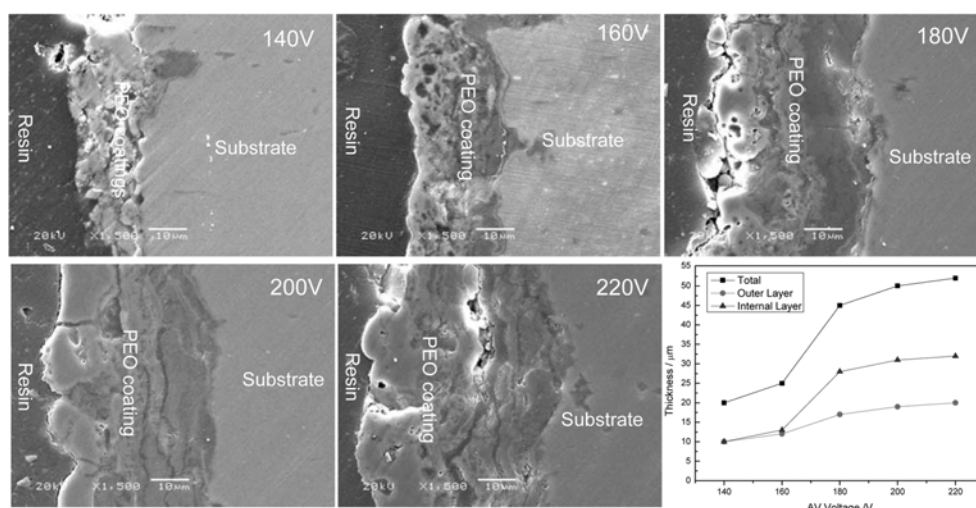


Fig. 3. Cross-section SEM micrographs of the coatings processed at different AC voltages.

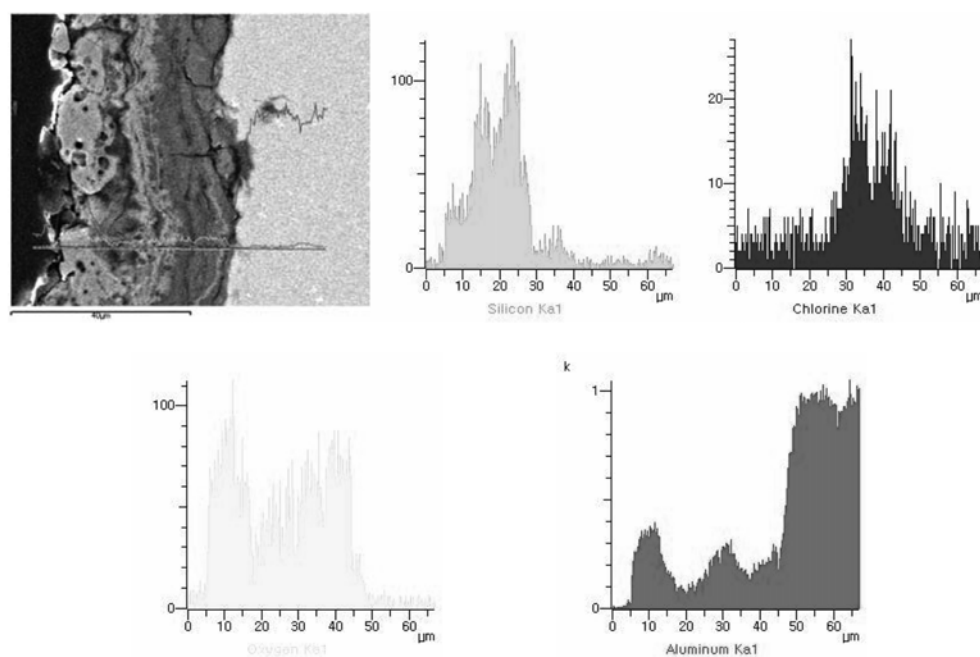


Fig. 4. EDS line scans of the PEO coatings processed at AC 200 V and DC 200 V for 5 minutes.

grow linearly and quickly. The duration of the linear regime decreases as the applied AC voltage reaches higher than 180 V. Similar growth kinetics for the formation of coatings were reported by other researchers [11, 12]. Indeed, according to these researchers, the coating growth results from molten aluminum that is oxidized when it flows out through the discharge channels. In this manner, alumina is formed, which contributes to the growth of coatings when it is ejected from the discharge channels and rapidly cooled down at the surface-electrolyte interfaces. So, the growth rate remains at a constant value as long as the discharge channels reach the metal surface, that is to say, as long as the coating formation is an interfacial-controlled process. Until the coatings grow sufficiently thick, they are hard to break down. Therefore, the growth rate decreases rapidly and comes to a limit. After the kinetics departs from a linear behavior, discharge phenomenon becomes yellow, larger and slower moving, which becomes the major feature of the process.

The distribution of chemical elements across the coatings is shown in Fig. 4. It is obvious that silicon and chlorine in the electrolyte participated in the PEO process. It can clearly be seen that there two layers generated on the surface, named the outer layer (the interfacial layer in contact with the electrolyte) and the internal layer (the interfacial layer in contact with the Al alloy substrate). Further EDS analysis revealed the presence of Al and O as the major constituents of coatings. Besides, Si and Cl introduced from both the substrate and electrolyte were also found in the layers, where Si tends to be located mainly in regions of the outer layer while Cl is distributed in the internal layer. So it may be predicated that during the PEO process Cl is more capable of penetrating into the coating/substrate interface. The phenomenon of the Si concentration tending to increase at the coating/electrolyte interface has been reported by Monfort et al. [12]. Several previous studies have paid attention to the incorporation of electrolyte species into the anodic substance in conventional anodic oxidation [14, 15]. In conventional anodic oxidation, the incorporated electrolyte species would be immobile, migrate-inward, or migrate-outward within the coating under the electric field. So it can be assumed that the PEO process in this paper may follow a similar mechanism as conventional anodization. An outward migrating element Si and a migrating-inward element Cl would create this PEO coating structure.

The microhardness profile of the two layers is shown in Fig. 5, which is characterized by the microhardness of outer layer begin much higher than that of the internal layer. Clearly the PEO process can strengthen the surface of an Al alloy with substrate microhardness of 93 Hv. A linear increase in microhardness of the outer layer occurred between 140 V to 200 V and a slight decrease occurred at 220 V. This growing trend is coincident with the transition of the γ - α - β Al_2O_3 phases. The maximum microhardness in the AC 200 V treatment can reach to 1200 Hv, compared with other reports of 900-2000 Hv [16], the experimental parameters can still be adjusted to achieve an even better

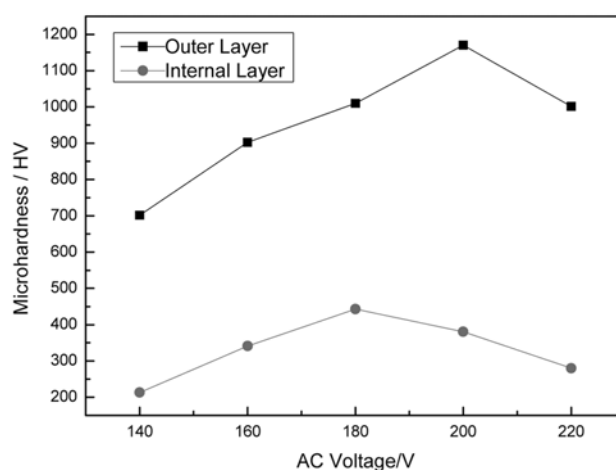


Fig. 5. Microhardness of the coating layers processed at different AC voltages.

performance. With an increase of the α - Al_2O_3 phase the average microhardness of the internal layer is about 300 Hv, which is a similar behavior to the outer layer, but its microhardness gradient is gentler. The internal layer plays a function as a transition layer. This may be caused by the incomplete oxidation of substrate materials, and Cl also contributes as a stabilizing agent. So it can be said that such a γ - α - β Al_2O_3 phase structure and Si/Cl element gradient is responsible for the observed hardness variation and coating layer departure across the coating layer.

Conclusions

The PEO process was carried out in a weak alkaline-silicon electrolyte on 6061 Al alloy substrate for 5 minutes at different AC voltages combined with a constant 200 V DC voltage. The surface morphology of PEO coatings is characterized by a pancake structure, the centre of each pancake representing the discharge channel surrounded by circular rings of rapidly solidified molten alumina. The diameter of pancake discharge channels increase linearly with an increase in the AC voltage, while the density of the discharge channels is the inverse. The PEO coating layer formed on the substrate surface is divided into two layers. The microhardness of the Si-rich outer layer is much higher than of the Cl-rich internal layer. Both layers grow with an increase of the AC voltage, but the growth rate will slow down above AC 180 V. As the AC voltage increases, metal-stable γ - Al_2O_3 will form on the surface first, and then transform into stable α - Al_2O_3 , and finally with a high voltage it will transform to β - Al_2O_3 . The transformations of different Al_2O_3 phases must be the root cause of the variations of surface morphologies and mechanical properties at different AC voltages.

Acknowledgement

This work was supported by the Korea Research Foundation Grant (KRF-2004-005-D00096).

References

1. G.P. Wirtz, S.D. Brown and W.M. Kriven, *Mater. Manuf. Process.* 6 (1991) 87-115.
2. W. Xue, C. Wang, Z. Deng, R. Chen, Y. Lai, T. Zhang and J. Phys.: *Condens. Matter.* 14 (2002) 10947-10952.
3. J.A. Curran and T.W. Clyne, *Surf. Coat. Technol.* 199 (2005) 168-176.
4. Y. Wang, T. Lei, B. Jiang and L. Guo, *Appl. Surf. Sci.* 233 (2004) 258-267.
5. W.Ch. Gu, G.H. Lv and H.Chen, etc, *Mater. Sci. Eng. A* 447 (2007) 158-162.
6. A.L. Yeronkhin, X. Nie, A. Leyland, A. Matthews, S.J. Dowey, *Surf. Coat. Technol.* 122 (1999) 73-93.
7. T.B. Wei, F.Y. Yan, J. Tian, *J. Alloys Compd.* 389 (2005) 169-176.
8. H.H. Wu, Z.S. Jin, B.Y. Long, F.R. Yu and X.Y. Lu, *Chin. Phys. Lett.* 20 (2003) 1815-1818.
9. R. McPherson, *J. Mater. Sci.* 8 (1973) 851-858.
10. T.B. Van, S.D. Brown and G.P. Wirtz, *Am. Ceram. Soc. Bull.* 56 (1977) 563-566.
11. W. Xue, Z. Deng, R. Chen and T. Zhang, *Thin Solid Films* 372 (2000) 114-117.
12. G. Sundararajan and L. Rama Krishna, *Surf. Coat. Technol.* 167 (2003) 269-277.
13. F. Monfort, A. Berkani, E. Matykina, P. Skeldon, G.E. Thompson, H. Habazaki and K. Shimizu, *J. Electrochem. Soc.* 152 (2005) C382-C387.
14. P. Skeldon, K. Shimizu, G.E. Thompson and G.C. Wood, *Philos. Mag. B* 72 (1995) 391-400.
15. G.C. Wood, P. Skeldon, E. Thompson and K. Shimizu, *J. Electrochem. Soc.* 143 (1996) 74-76.
16. R.C. Barik, J.A. Wharton, R.J.K. Wood, K.R. Stokes and R.L. Jones, *Sur. Coat. Tech.* 199 (2005) 158-167.