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INFLUENCE OF THE CATHODIC PULSE ON THE FORMATION AND MORPHOLOGY OF OXIDE COATINGS ON ALUMINIUM PRODUCED BY PLASMA ELECTROLYTIC OXIDATION

WPŁYW IMPULSU KATODOWEGO NA TWORZENIE I MORFOLOGIĘ WARSTW TLENKOWYCH NA ALUMINIUM OTRZYMYWANYCH NA DRODZE PLAZMOWEGO UTLENIANIA ELEKTROLITYCZNEGO

Plasma electrolytic oxidation (PEO) is an effective method to obtain hard ceramic coatings on Al, Mg and Ti alloys. Micro-discharges occurring on the electrode surface during process promote the creation of crystalline oxides phases which improve mechanical properties of the coating. By using alternate current (AC) at some current conditions the process can be conducted in 'soft' spark regime. This allows producing thicker layers, increasing growth rate and uniformity of layer, decreasing amount of pores and defects. These facts proof the importance of cathodic pulse in the PEO mechanism; however its role is not well defined. In this work, influence of anodic to cathodic current density ratio on kinetics of coating growth, its morphology and composition were investigated. The PEO process of pure was conducted in potassium hydroxide with sodium metasilicate addition. The different anodic to cathodic average currents densities ratios of pulses were applied. The phase composition of coatings was determined by XRD analysis. Morphology of obtained oxide layers was investigated by SEM observations.

Keywords: Plasma electrolytic oxidation, PEO, Alumina coatings, Aluminium oxide

Plazmowe utlenianie elektrolityczne (PEO) jest efektywną metodą otrzymywania twardych, ceramicznych powłok głównie na stopach Al, Mg oraz Ti. Mikro-wyładowania występujące na powierzchni elektrody podczas procesu promują tworzenie się krystalicznych faz tlenkowych, które polepszają właściwości mechaniczne powłok. Stosując prąd zmienny, możliwe jest wprowadzenie procesu w tryb tzw. 'miękkiego' iskrzenia przy pewnych parametrach prądowych. Pozwala to otrzymywać grubsze powłoki, zwiększyć szybkość narastania i równomierność warstwy oraz zmniejszyć ilość porów i defektów. Świadczy to o dużym wpływie impulsu katodowego na mechanizm narastania warstwy w procesie PEO, jednak jego rola nie została jeszcze dobrze poznana. W niniejszej pracy badany był wpływ stosunku anodowej gęstości prądowej do katodowej na kinetykę wzrostu warstwy oraz jej morfologię i skład. PEO przeprowadzano w roztworze wodorotlenku potasu z dodatkiem metakrzemianu sodowego. Podkładką było czyste aluminium. Stosowane były przebiegi o różnym stosunku średniej gęstości prądowej anodowej do katodowej. Skład fazowy warstw został określony na drodze analizy dyfrakcji promieni rentgenowskich. Morfologia warstw tlenkowych była badana na drodze obserwacji pod skaningowym mikroskopie elektronowym.

1. Introduction

Plasma electrolytic oxidation (PEO) is a method used to produce relatively thick (up to hundreds of micrometres) oxide ceramic coatings on metals, mainly: Al, Mg and Ti and their alloys. Such of layers have good mechanical properties, corrosion and thermal resistances [1-3]. Very good mechanical properties (high microhardness and wear resistance) are regarded to the presence of the crystalline structure of the oxide layer. In case of aluminium mainly α-alumina and γ-alumina are detected in the oxide layer. Coatings formed by PEO have various applications, especially where high wear resistance is desired.

The mechanism of coatings formation during PEO can be divided into three stages that occur simultaneously [4]. First, it is an electrochemical formation of oxide on the metal-oxide interface, thus the electrolyte have to migrate through oxide layer towards substrate. Second stage is a chemical dissolution of oxide to gel form on the oxide-electrolyte interface. Third one is associated with high voltage that is enough to dielectric breakdown of the oxide layer. These breakdowns occur as short-living micro-discharges uniformly distributed on the whole surface of the anode. They cause formation of discharge channels, from which molten aluminium is ejected. Ejected aluminium is immediately oxidized, hydrolysed and precipitated on the anode surface. Additionally, due to high temperature inside the discharge channel and relatively low thermal conductance of the oxide phase transitions from amorphous Al_2O_3 and hydrolysed form to crystalline phase can occur [5].

There are a few affecting on the final properties of the oxide coatings. These are: substrate material, composition and

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temperature of the electrolyte, current conditions [1]. PEO process can be conducted using direct current (DC) or alternate current (AC) power supplies. DC conditions are the simplest to realization but have significant limitations (low thickness and uniformity of coatings). AC conditions allow to overcome these disadvantages, and thicker oxide layers with no serious defects, caused by preferential occurrence of arcs [1,6]. Recently, AC sources with controllable magnitude and duration of pulses are used to control PEO process in more flexible way [7].

The 'soft' sparking is the phenomena, which occurs under AC conditions when cathodic current is higher than anodic [8]. The 'soft' sparking appears in some advance of process and is characterized by a different appearance of the micro-discharges, decrease in anodic voltage and reduced acoustic emission [9,10]. During 'soft' sparking transition considerable change in emission of optical spectrum is observed. In initial stages there are intensive emission peaks from bound-bound electron transitions between atomic levels, while after establishing the 'soft' sparking emission spectrum is continuous [11]. This continuous part corresponds to bound-free and free-free electron transitions [12].

The coatings consist of three sub-layers: amorphous barrier layer at the metal-oxide interface, intermediate dense layer with relatively low porosity and outer loose layer [1]. The transition to 'soft' sparking is possible when the coating reaches certain thickness [13]. Slonova et al. [9] suggest that the amorphous phases are "seeds that trigger" phase transition to γ and α-alumina.

Jaspard-Mécuson et al. [10] compared two different anodic to cathodic charge ratios (1.57 and 0.89). In both cases process run similarly up to 40th minute and after this time the change of micro-discharges appearance was observed for the 0.89 currents ratio. It resulted in the decrease of optical emission and higher growth rate of the layer. They also noticed higher uniformity of the coating morphology and smaller discharge channels when the cathodic charge exceeded anodic one.

Various excess of cathodic over anodic current during anodizing the Al-Cu-Mg alloy samples was investigated [9]. Higher asymmetry of currents resulted in a decrease of total limiting thickness but simultaneously an increase of the thickness ratio of intermediate sub-layer to the total thickness was found. Authors observed higher percentages of crystalline phases content in intermediate and outer layers for higher current asymmetry.

The role of the cathodic pulse in the layer formation was investigated by Sah et al. [14]. It was concluded that cathodic breakdowns can randomise sites of anodic breakdowns by forming nanoporous layer which is high resistive than neighbouring areas and prevents the occurrence of the anodic breakdown in the same place.

The literature review shows that the influence of the cathodic currents on the mechanism of the coating formation and its phase composition is considerable but not clear enough. The anodic to cathodic currents ratio have an effect on the temperature of the micro-discharges as well as chemical and electrochemical processes during PEO [9]. Thus, the aim of this study was to investigate the effect of cathodic current on the kinetics of coating formation as well as structure and composition of the oxide layers on aluminium.

2. Experimental

Samples of the size 10mm×30mm×1.5mm made of 1050A aluminium were used as a substrate. Before experiments samples were prepared in following stages: degreasing in acetone, etching in 0.25 mol·dm^{-3} NaOH solution, brightening in 7 mol·dm^{-3} HNO$_3$ solution, rinsing in deionised water. Aluminium samples were oxidized in the alkaline-silicate electrolyte with composition of: 0.04 mol· dm^{-3} KOH, 0.08 mol·dm^{-3} Na$_2$SiO$_3$. The 4 dm^3 electrolytic cell made of stainless steel was acted as counter electrode. The bath was agitated by a mechanical stirrer and its temperature was controlled by cooling system in the range of 23-26˙C.
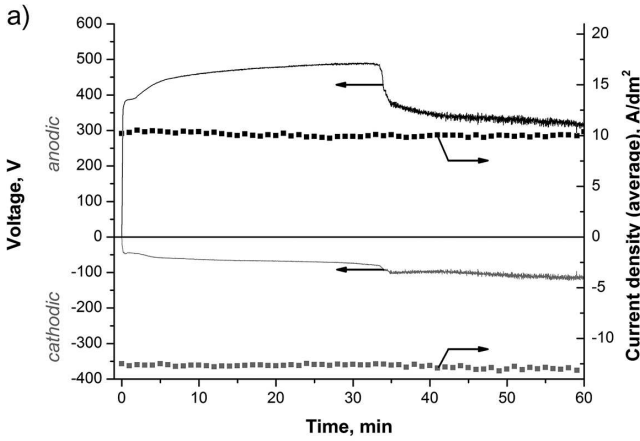
PEO process was carried out using ambipolar current. Two power supply units controlled anodic and cathodic currents, separately. The switch was fixed at 100 Hz with 0.5 ms dead-time between pulses. Average anodic current density of 10 A·dm^{-2} was constant for all experiments. Anodic to cathodic average currents ratio was changed in range from 1 to 0.7 with 0.1 step, therefore cathodic average current densities were 10, 11.1, 12.5, 14.3 A·dm^{-2}. Voltage and current waveforms were recorded by digital oscilloscope connected to PC with the LabVIEW software.

Thickness of obtained oxide layers was measured by the eddy currents method. Each sample was measured twenty times in different places on the surface and the average thickness of the coating was calculated. Microstructure was observed on SEM (Hitachi SU-70). Phase composition was determined by XRD analysis (Rigaku MiniFlex).

3. Results and discussion

The plot (Fig. 1 a) presents changes of voltage and average current density during the process at 0.8 ratio. The average current density is maintained at the same level. The voltage in the first stage of process increases immediately and kept up on almost same levels in case of anodic and cathodic parts. After about 34 minutes rapid decrease of anodic voltage and slight increase on cathodic voltage was observed. From this moment the process went in 'soft' sparking. Micro-discharges changed their colour from yellowish to white. They lasted shorter and sweep the whole surface of the electrode uniformly and fast. The gas evolution (mainly oxygen [4]) on the anode surface lowered significantly. Moreover, quite high acoustic emission before "soft" sparking then reduces almost to zero.

The real waveforms of current and voltage of one cycle from experiment are presented in Fig. 1 b. In the first period of anodic pulse high current peak appeared. Then it decreased rapidly and kept up on the same level to maintain average current set. The dead-time between pulses was followed by the cathodic pulse where the cathodic current increased asymptotically.
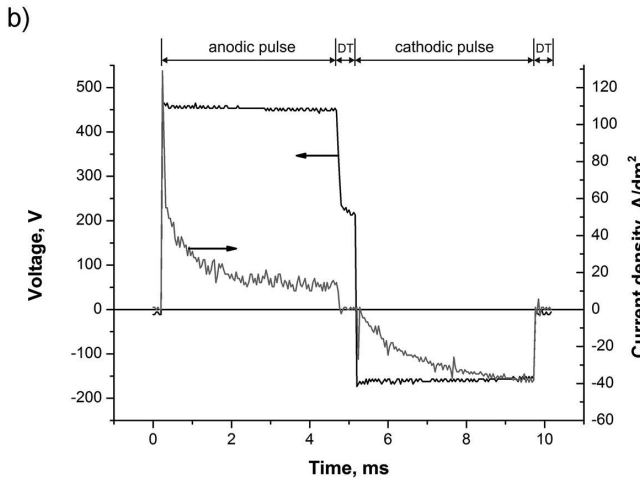
Fig. 1. Changes in voltage and current density during the whole process (a), during one cycle (b) (R=0.8)

Fig. 2 shows changes of voltage during the PEO process at different anodic to cathodic current densities ratios. In the initial period, the voltage changes are almost identical for all ratios; only very slight differences in the cathodic voltage are seen. For 0.7 and 0.8 ratios the 'soft' sparking was observed after 27 and 34 minutes respectively. At the lower ratio shorter time was needed to transition into 'soft' sparking and the more significant decrease in the anodic voltage was observed.
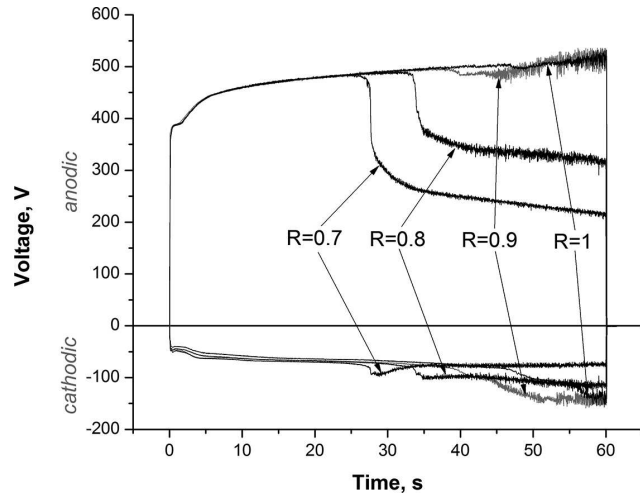

Fig. 2. Anodic and cathodic voltages at different anodic to cathodic average current density ratio. ($J_{A\,avg}$ =10 A·dm^{-2})

The higher cathodic current caused lower anodic voltage drop, thus the layer became less resistive for the flow of the anodic current. For the ratios 0.9 and 1 no characteristic decrease in voltage was noticed. However, small drop of the anodic voltage was visible at about 39 and 47 minutes, respectively. From these times higher fluctuations in the voltages were seen. The transition to 'soft' sparking was also observed, but only partially due to the occurrence of bigger discharges besides 'softer' ones. These big arcs were responsible for the voltage fluctuations in subsequent periods and led to formation of defects in the oxide layer. Therefore, above the current ratio of 0.9, the anodic current was too high (in respect to the cathodic one) to establish stable 'soft' sparking regime.
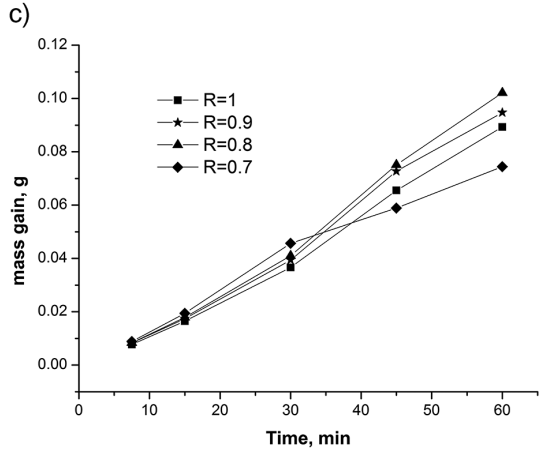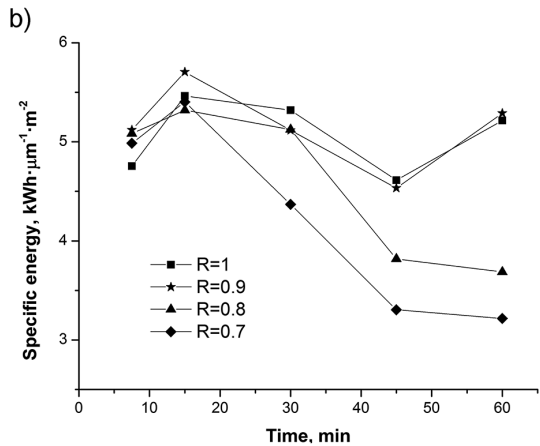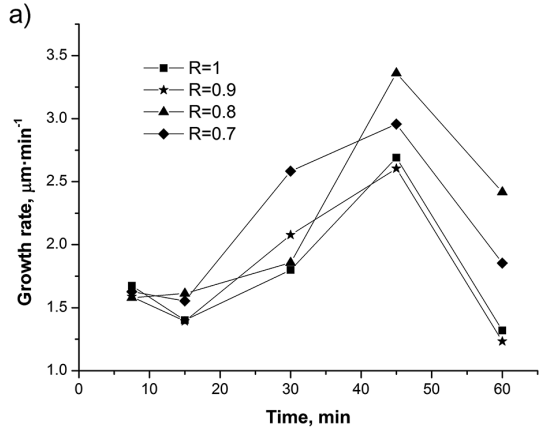

Fig. 3. The growth rate of layer (a), the energy consumption (b) and the mass changes (c) at different anodic to cathodic average current density ratio ($J_{A\,avg}$ =10 A·dm^{-2})

Growth rate of oxide layers increased with process time and had maximum at 45 min (Fig. 3 a). For R=0.8 we can observe the highest growth rate in 'soft' sparking stage. The thickness recalculated to total power consumptions is shown in Fig. 3 b. It can be seen that lower current ratio corresponds to lower specific energy. In cases of R=0.8 and R=0.7, where the stable 'soft' sparking was observed, the lower energy consumptions in the 'soft' sparking stage than before the transition was visible. So it is clear that the soft sparking provides higher process yield. Thus the following relationship could be concluded: the increase of the cathodic current contribution causes the increase of process effectiveness. However, for the R=0.7 non-uniform, area especially in lower part of the electrode was observed. The plot in Fig. 3.c, where but mass change was taken into account, confirmed this. This means that there is some range of current ratios for which stable 'soft' sparking can be maintained resulting in the formation of uniform coatings.

In case of samples for which processing time was too short to achieve 'soft' sparking transition, two types of areas on the surface could be distinguished: lighter and darker. The lighter areas had higher thickness and roughness and could be considered as porous outer layer. The darker areas were unaffected by 'soft' sparking [14]. The coverage of the anode by lighter areas increased with process time. Thus the 'soft' sparking can occur partially on some part of electrode and its transition is possible, when the whole surface of the electrode is covered by outer layer. Therefore the outer layer may play crucial role in 'soft' sparking regime establishing.

The SEM micrographs (Fig. 4) show characteristic porous microstructure of the PEO coatings. For R=1 and R=0.9 so-called pancakes that are solidified alumina, large discharge channels and cracks can be observed. In case of R=0.8 and R=0.7 many round shaped precipitates and no cracks on the surface are visible.
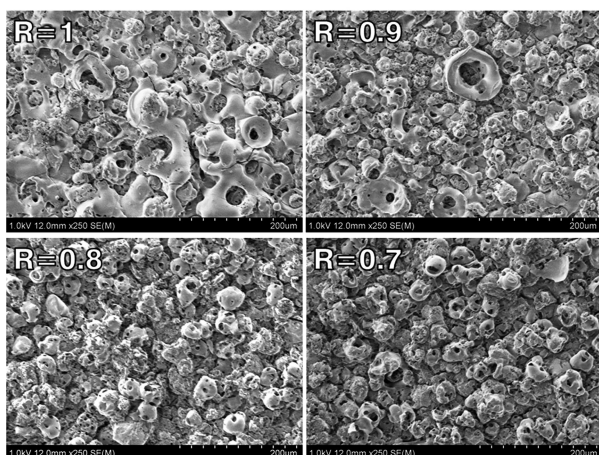

Fig. 4. SEM images of top surface of the oxide layers obtained after 60 min at different anodic to cathodic average current density ratio ($J_{A\,avg}$ =10 A·dm^{-2})

The X-ray diffraction analysis of the layers shows higher content of α-alumina and mullite (3Al$_2$O$_3$·2.1SiO$_2$) phases in higher current ratio (Fig. 5). On the other hand, at the lower ratio the higher γ-alumina phase content was found. Moreover, in cases of lower ratio, higher broad peak on the patterns can be observed. It corresponds to higher content of amorphous phases in oxide coatings.
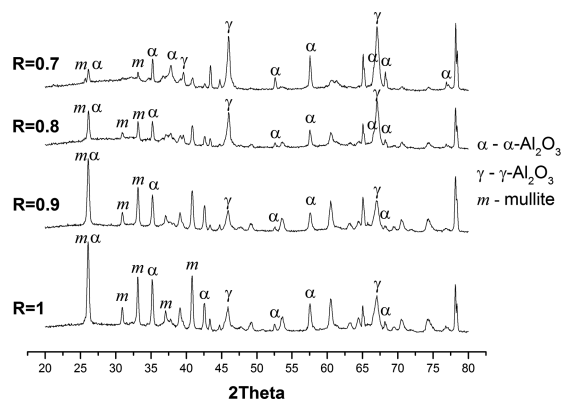

Fig. 5. X-ray diffraction patterns of oxide layers obtained after 60 min at different anodic to cathodic average current density ratios ($J_{A\,avg}$ =10 A·dm^{-2})

Result presented in this work describes coatings on samples as obtained, without any special treatment after PEO process instead of rinsing in distilled water. It is well known that these kinds of layers are composed of three main parts: loose porous outer layer, dense intermediate layer and thin barrier layer [1]. Because of low mechanical properties of the outer part of the layer it is crucial to analyse inner sublayer which is mainly responsible for high mechanical properties. Therefore more profound investigations are required to verify this phenomenon.

4. Conclusions

1. The 'soft' sparking provides higher growth rate of coatings and gives more cost effective process. Layers have no cracks, but contain less percentage of the crystalline phases. During 'soft' sparking, the higher cathodic currents cause that the layer is less resistive for the flow of the anodic currents.

2. The anodic to cathodic average current densities ratio of 0.8 give the best results (the highest growth rate, uniform layer with no large defects). At higher ratios (R=1–0.9) 'soft' sparking occurred partially and large discharges lead to large defects of oxide layer. In case of lower ratio (R=0.7) non-uniform layer is produced. Thus there is some quite narrow range of current ratio for stable 'soft' sparking.

3. Layers obtained at lower ratios have smaller discharge channels, no cracks, higher content of γ-alumina, mullite and amorphous phase compared with higher content of α-alumina at higher ratios.

4. To establish stable 'soft' sparking, whole surface of the electrode must be covered by outer layer. This demonstrates the great importance of outer, loose part of layer on mechanism of coating formation during 'soft' sparking.

REFERENCES

[1] A. Y e r o k h i n, X. N i e, A. L e y l a n d, A. M a t t h e w s, S.J. D o w e y, Surf. Coat. Tech. **122**, 73 (1999).

[2] L. Krishna, A. Purnima, G. Sundararajan, Wear **261**, 1095 (2006).

[3] M. Aliofkhazraei, A.S. Rouhaghdam, Fabrication of Nanostructures by Plasma Electrolysis, Weinheim 2010.

[4] L. Snizhko, A.L. Yerokhin, A. Pilkington, N. Gurevina, D.O. Misnyankin, A. Leyland, A. Matthews, Electrochim. Acta **49**, 2085 (2004).

[5] C.S. Dunleavy, I.O. Golosnoy, J.A. Curran, T.W. Clyne, Surf. Coat. Tech. **203**, 3410 (2009).

[6] S. Xin, L. Song, R. Zhao, X. Hu, Thin Solid Films **515**, 326 (2006).

[7] M. Chen, Y. Ma, Y. Hao, Front. Mech. Eng. China **5**, 98 (2009).

[8] A.S. Shatrov, V.I. Samsonov, Patent US 2003/0188972 A1.

[9] A.I. Slonova, O.P. Terleeva, Prot. Met. **44**, 65 (2011).

[10] F. Jaspard-Mecuson, T. Czerwiec, G. Henrion, T. Belmonte, L. Dujardin, A. Viola, J. Beauvir, Surf. Coat. Tech. **201**, 8677 (2007).

[11] R. Arrabal, E. Matykina, T. Hashimoto, P. Skeldon, G.E. Thompson, Surf. Coat. Tech. **203**, 2207 (2009).

[12] M.D. Klapkiv, H.M. Nykyforchyn, V.M. Posuvailo, Mater. Sci. **30**, 333 (1994).

[13] E. Matykina, R. Arrabal, P. Skeldon, G.E. Thompson, P. Belenguer, Surf. Coat. Tech. **205**, 1668 (2010).

[14] S.P. Sah, E. Tsuji, Y. Aoki, H. Habazaki, Corros. Sci. **55**, 90 (2012).