MICROSTRUCTURE OF Al_2O_3 ANODIC HARD COATINGS ON EN-AW5251 ALUMINIUM ALLOY OBTAINED BY PULSE METHOD

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Abstract

This paper presents the possibility of modifying the microstructure of anodic hard coatings on aluminium alloys by applying a pulsed method in the process of their electrochemical deposition. Anodic hard coatings were formed on an aluminium alloy intended for plastic working. The electrolytic process was conducted using the pulsed method with a rectangular current waveform in time, applying variable frequencies, current densities and duty cycles of the waveform. Examination of the microstructure of the anodic hard coatings was carried out by image analysis of the images obtained by means of SEM from fractures of the coatings. The obtained results indicate that the application of the pulse anodizing method results in the occurrence of local changes in the microstructure of the anodic hard coatings.

Keywords: Anodic hard coatings, aluminium alloy, pulse method, microstructure

1. INTRODUCTION

Al_2O_3 coatings obtained on aluminium and its alloys by means of electrochemical methods are characterized by a two-layer structure. They consist of a compact non-porous barrier layer which adheres to the substrate and has an insignificant thickness (typically from ca 10 to 100nm), and a porous layer growing over the barrier layer (**Figure 1**), with a columnar structure and thickness of a few hundred micrometres (depending on the manufacturing conditions) [1-4]. Due to its porous microstructure, the anodic hard coating produced on aluminium using electrochemical methods facilitates its use as a matrix for composite coatings [5-7].

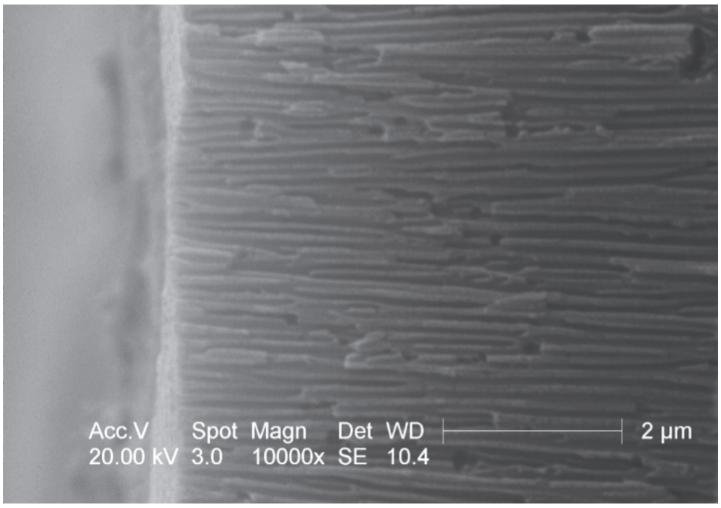

Figure 1 Microstructure of anodic oxide coatings on aluminium alloy EN-AW 5251

The columnar-fibrous structure of Al_2O_3 coatings is characteristic of amorphous coatings. The columnar structure is built of longitudinal fibres of Al_2O_3 (cells with a circular, hexagonal or triangular section) [6] distributed, in an idealized case, parallel to one another and perpendicular to the aluminium substrate. There are channels inside the fibres (longitudinal pores) which are filled with electrolyte during anodic oxidation. Exchange of ions and electric charges participating in the growth of the oxide coating takes place through the pores and the barrier layer. In practice, some fibres or groups of fibres are twisted or oriented non-parallel [2-4,8]. Also, the diameters of pores inside the microstructural cells tend to change, since the dissolving effect of the electrolyte on the Al_2O_3 coating produced in the electrochemical process causes a gradient change of the fibre wall thickness: from the substrate to the surface of the coating. The homogeneity and directionality of the columnar structure depend mainly on the chemical composition and structure of the substrate, as well as its condition before anodizing. The wall thickness of Al_2O_3 fibres and the number of cells in the microstructure depend on the temperature and chemical composition of the electrolyte, as well as on the time and current density of the electrochemical process [8-10]. This paper presents the possibility of modifying the microstructure of anodic hard coatings Al_2O_3 by applying a pulsed method in the process of their electrochemical deposition. The pulsed method (with a rectangular waveform) is most frequently applied during cathodic deposition of metallic coatings. This enables obtaining of coatings with enhanced structure homogeneity, lower surface porosity and roughness [11]. Similar effects are obtained when applying the pulsed method during anodic oxidation of aluminium [12-13], which is corroborated by the results of the authors' own studies.

2. EXPERIMENTAL DETAILS

Anodic hard coatings Al_2O_3 were formed on an aluminium alloy intended for plastic working, EN-AW5251. The electrolytic process was conducted using the pulsed method with a rectangular current waveform in time, applying variable frequencies, current densities and duty cycles of the waveform. The process of coating formation was carried out in an electrolyte composed of an aqueous solution of sulphuric, oxalic and phthalic acids, in time of 60 minutes and at electrolyte temperature of 303 K, while maintaining the average electric charge density of 108 A·s/m^2. **Table 1** presents a list of modifications introduced in the current waveform during pulse anodizing and **Figure 2** shows the designations of parameters of the applied current. Examination of the microstructure of the anodic hard coatings was carried out by image analysis of the images obtained by means of SEM (HITACHI microscope S-4700) from fractures of the coatings. The investigated surfaces were preliminarily sputtered with carbon and subjected to analyses in high-vacuum conditions.

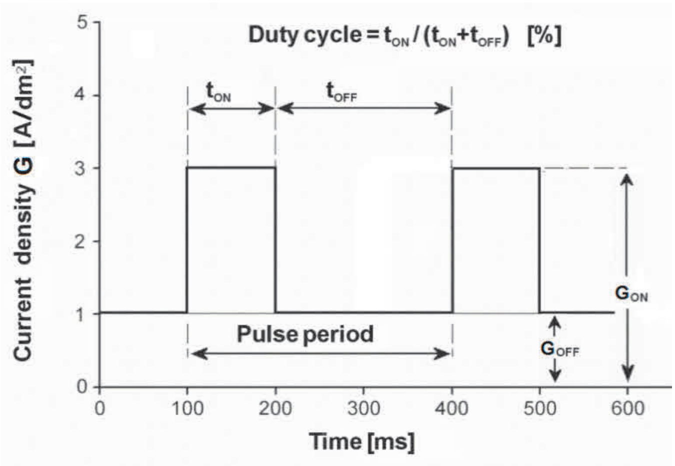

Figure 2 Designations of the parameters of the pulse current applied

Table 1 Applied modifications of pulse anodizing current

Sample	Current density G_{off} [A/dm^2]	Current density G_{on} [A/dm^2]	G_{on}/G_{off}	Duty cycle [%]	Pulse period [s]
Kr10	1.5	4.5	3	50	75
Kr4	1.5	4.5	3	50	100
Kr11	1.5	4.5	3	50	250
Kr3	1.5	4.5	3	50	500
Kr2	1.5	4.5	3	50	3600
Kr12	1.5	7.5	5	33	250
Kr13	1.0	5.0	5	50	250

3. EXPERIMENTAL DETAILS

The obtained results indicate that the application of the pulse anodizing method results in the occurrence of local changes in the microstructure of the anodic hard coatings Al_2O_3. The images in **Figures 3** and **4** present examples of fractures of coatings obtained using pulse anodizing with the ratio of currents: G_{on}/G_{off} = 3. It can be observed in **Figures 3a** and **3b** that the amount of Al_2O_3 fibres grows and the fibre wall thickness decreases as a result of a temporary reduction of the anodizing current density. The reduction of the current density also leads to a slower growth of the oxide coating. In consequence, the microstructure of coatings produced by the pulsed method shows the existence of alternate "zones": with fewer cells, thicker fibre walls and greater intensity of growth of the oxide coating, and "zones" characterized by more numerous Al_2O_3 fibres, smaller transverse dimensions of fibre walls and lower growth intensity of the coating.

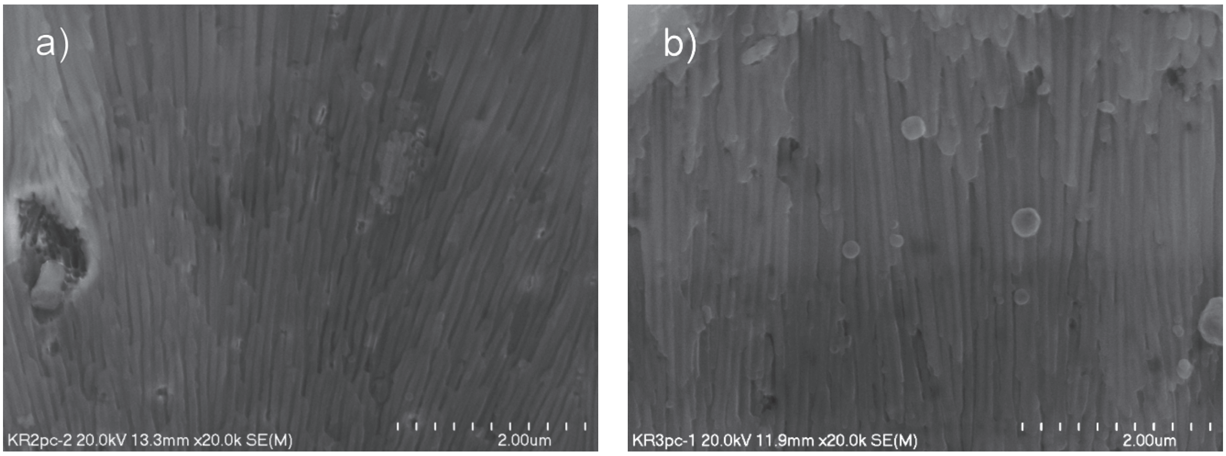

Figure 3 SEM image of fresh cross section of Al_2O_3 oxide coating fabricated using a pulse anodizing method; a) sample Kr2, b) sample Kr3; magnification 20000 x

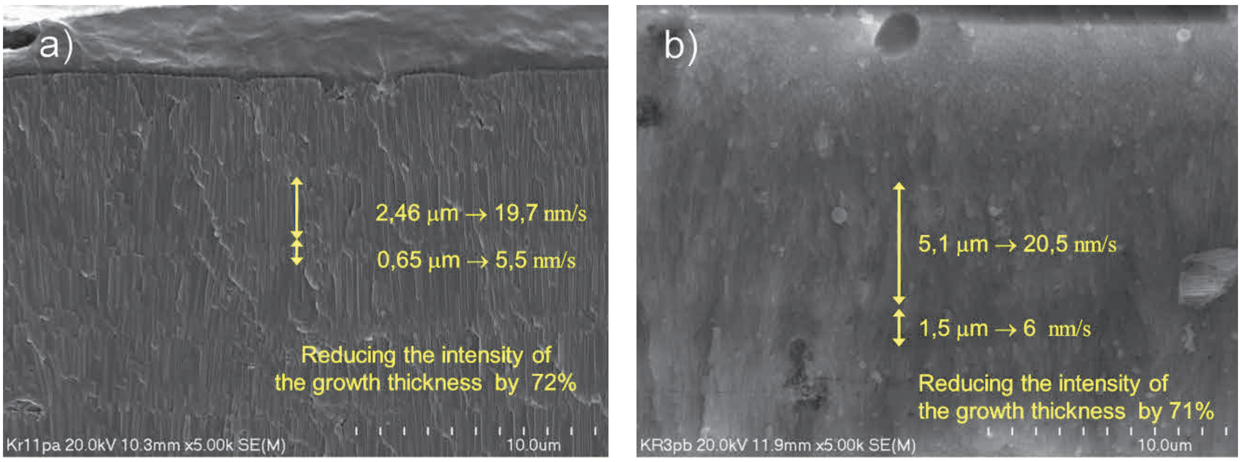

Figure 4 SEM image of fresh cross section of Al_2O_3 oxide coating fabricated using a pulse anodizing method; a) sample Kr 11, b) sample Kr3; magnification 5000 x

Figures 4a and **4b** show a magnification of the coatings, which allows the evaluation of the intensity of the oxide coating growth at low and high levels of current pulse. The results of image analysis for all the samples produced are presented in **Table 2**. The results in **Table 2** show that the use of G_{on}/G_{off} ratios of currents with a value of 3 during pulse anodizing leads to a local reduction by 32 % of transverse dimensions of the walls of Al_2O_3 cells, and to a reduction in the intensity of coatings' growth by 71.5 %. An increase in the ratio of the anodizing current density G_{on}/G_{off} to value 5 enhances local changes in the microstructure. At the same time, the frequency of current in the pulse anodizing process has a significant influence on the number of fibrous cells in the microstructure.

Table 2 The results of microstructure

Sample	Local reducing in the intensity of coatings' growth [%]		Local reducing of transverse dimensions of the walls of Al_2O_3 cells [%]		Local reducing in the number of Al_2O_3 cells [%]	
Kr10	Do not measurable		32	± 9.2	12	± 0.8
Kr4	71	± 0.6	29	± 8.3	14	± 0.6
Kr11	72	± 0.7	32	±13.2	17	± 0.5
Kr3	71	± 0.9	34	±10.5	28	± 0.6
Kr2	72	± 0.7	34	± 9.7	40	± 0.7
Kr12	80	± 1.0	51	±12.3	41	± 0.6
Kr13	86	± 1.1	43	±10.6	47	± 0.9

4. CONCLUSION

The work shows the possibility of modifying the microstructure of Al_2O_3 hard anodic coatings by applying the pulsating method with a rectangular current course in the process of electrochemical deposition. Local changes in the microstructure were obtained by applying variable frequencies, current densities and duty cycles of the waveform. It has been shown that an increase in the ratio of the anodizing current density G_{on}/G_{off} enhances local changes in the microstructure, while the change in the current frequency in the impulse anodizing process has a significant effect on the number of fibrous cells in the microstructure.

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