The influence of SiO\textsubscript{2} nanoparticles addition into electrolyte on the thermal conductivity of oxide layer formed on eutectic aluminum-silicon alloy by PEO

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Abstract. Oxide layers formed by plasma electrolytic oxidation with SiO\textsubscript{2} nanoparticles addition into electrolyte on eutectic aluminum-silicon alloy were investigated by scanning electronic microscopy (SEM), energy dispersive X-ray microanalysis (EDXMA) and X-ray diffraction (XRD) analysis. The thermal conductivity of oxide layers was measured by constant heat flow method. Obtained values of the thermal conductivity of oxide layers are significantly smaller than the values of oxide layer components as bulk materials. Decreasing of thermal conductivity of oxide layer in ratio of two is observed if SiO\textsubscript{2} nanoparticles are added into electrolyte. It is shown that the sedimentation of nanoparticles into oxide layer and decreasing of crystalline sizes are the reasons of decreasing of thermal conductivity.

The extension of the use of aluminum alloys often needs the strengthening and thermal protection of their surface. One of the developing technologies for surface treatment of aluminum is plasma electrolytic oxidation (PEO) [1] that allows getting wear and corrosion resistant coating on aluminum alloys. But very few researches devoted to thermal properties of oxide layers formed by PEO are known [2].

It is known that the structure and strength of oxide layers formed into electrolytes with nanoparticles additions can be improved [3] in particular in case of SiO\textsubscript{2} nanoparticles at the PEO of aluminum-silicon alloys [4]. The thermal insulation properties of oxide layers are important in this case because of thermal-stressed details made of aluminum-silicon alloys (e.g. pistons of internal combustion engines).

The aim of this research is the analysis of the influence of SiO\textsubscript{2} nanoparticles addition into electrolyte on the thermal conductivity of the oxide layer formed by PEO on the eutectic A04130 aluminum-silicon alloy.

Oxide layers were formed by PEO on the samples of A04130 aluminum-silicon alloy with 60×20×6 mm\textsuperscript{3} sizes (chemical composition weight %: 12.2 % Si; 0.2 % Fe; 0.3 % Mn; 0.12 % Ti; 0.05 % Cu; 0.25 % Mg, 0.25 % Zn; balance – Al). The heat treatment by T6(8) [5] and polishing (Ra 2...2.5) of these samples were done out before PEO.

PEO was carried out by AC current source with 33 ± 1 A/dm\textsuperscript{2} constant current density and 50 Hz frequency during 240 minutes. The anode/cathode current ratio was 1 ± 0.05 and kept constant. The
water solution of sodium hydroxide \(\text{NaOH} \) (3 g/l), sodium pyrophosphate \(\text{Na}_4\text{P}_2\text{O}_7\cdot 10\text{H}_2\text{O} \) (10 g/l) and sodium liquid glass \(\text{Na}_2\text{O}(	ext{SiO}_2)_n \) (10 g/l) is the basic electrolyte. The roentgenomorphic [6] \(\text{SiO}_2 \) nanoparticles (n-SiO\(_2\)) with average particle size 25 nm were added into electrolyte in 3 g/l concentration.

The average thickness was measured by eddy current gauge and ascertained by SEM on the cross sections. The structure and element composition of oxide layers were also observed on the cross sections. Quantity analysis of element composition was carried out as it is described in [7]. Scanning electronic microscope Carl Zeiss Sigma with energy-dispersive X-ray spectroscopy unit by EDAX TEAM EDX was used for these researches.

XRD analysis of oxide layers was carried out with Shimadzu Maxima XRD-7000 diffractometer with filtered \(\text{CuK}_\alpha \) radiation at Bragg-Brentano geometry at radiation power 2 kW. Scanning speed step was 0.1°·min\(^{-1}\) with recording step of 0.02° by 2\(\Theta\) angle. Shimadzu PDF2 database was used for identification of crystalline phases. Jana 2006 software was used for profile analysis of diffraction patterns. Crystallite sizes were obtained by Scherrer equation.

Thermal conductivity (\(\lambda\)) of oxide layers was measured by steady state method of constant heat flow [8] in 50–150 °C temperature range. The experimental setup and method are described in details in [9]. Thermal conductivity of each oxide layer was determined for the whole layer and for the polished sample. Around 30 % of oxide layer thickness was detached by grinding at outer side. It roughly corresponds to outer porous part of oxide layer (figure 1).

![Figure 1. Macrostructure of oxide layer formed in basic electrolyte (a); macrostructure of oxide layer formed in electrolyte with n-SiO\(_2\) (b).](image)

The values of thickness and thermal conductivity (at 100 °C) are shown in the table 1. The use of n-SiO\(_2\) as the addition into electrolyte leads to increase of thickness (figure 1) and decrease of thermal conductivity of oxide layer approximately in ratio of two (table 1). It is noticeable that thermal conductivity of basic oxide layer does not change after polishing but \(\lambda\) of oxide layer formed in electrolyte with n-SiO\(_2\) increases after polishing twice and becomes equal to thermal conductivity of oxide layer formed into basic electrolyte. Moreover, calculated thermal conductivity of detached part of oxide layer formed with n-SiO\(_2\) is much smaller than \(\lambda\) of basic oxide layer (table 1).

| Electrolyte | Basic | With n-SiO\(_2\) |
|-------------|-------|------------------|
| Thickness, \(\mu\text{m}\) | \(\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) | Thickness, \(\mu\text{m}\) | \(\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) |
| Oxide layer | | | |
| Whole | 93 ± 23 | 1.7 ± 0.37 | 143 ± 29 | 0.86 ± 0.15 |
| Polished | 63 ± 11 | 1.85 ± 0.4 | 95 ± 20 | 1.9 ± 0.43 |
| Detached part of oxide layer\(^b\) | 30 ± 25 | 2.27 ± 1.4 | 48 ± 35 | 0.41 ± 0.24 |

\(^a\) uncertainties are calculated with Students distribution at coverage probability 0.9.

\(^b\) calculated by method described in [8].

The distribution of elements into oxide layers is common to previous work [7] and it changes due to n-SiO\(_2\) addition into electrolyte (figure 2), namely the concentration of silicon in the outer part of
oxide layer is higher in ratio of 1.5 for the sample formed in the electrolyte with n-SiO$_2$ (figure 2(a) and table 2). The concentration of aluminum in the outer part of oxide layer is around 1.4 times smaller in this case. The oxygen distribution is uniform like in [7] and does not depend on the presence of SiO$_2$ nanoparticles into electrolyte i.e. the replacement of aluminum by silicon is observed. It could be explained due to sedimentation of silica nanoparticles into oxide layer.

Oxide layers formed in both electrolytes mainly consist of mullite, gamma-alumina (γ-Al$_2$O$_3$) and corundum (α-Al$_2$O$_3$) (figure 3). Addition of n-SiO$_2$ into electrolyte leads to increase of background signal ($S_{bg}$) in 2θ-angle range of 17–33° and decrease the intensity of peaks on the XRD-pattern (figure 3). It shows the increase of amorphous components content into oxide layer and the reduction of structure element size of the oxide layer. So the average crystallite size obtained by Scherrer equation is 32.3 ± 3.9 nm for the oxide layer formed into basic electrolyte and it is 21.4 ± 3.5 nm for oxide layer formed into electrolyte with n-SiO$_2$ i.e. crystallite size is reduced by one third. Taking into consideration increase of silicone concentration (figure 2(a) and table 2) into the oxide layer formed in the electrolyte with n-SiO$_2$ addition, it is possible that the sedimentation of amorphous silica nanoparticles into the oxide layer is the reason of amorphization of oxide layer.

The obtained values of thermal conductivity of oxide layer formed in basic electrolyte are in good agreement with known results [2, 9]. Significant difference of measured thermal conductivity of oxide layer and thermal conductivity of its main components (alumina and silica in bulk condition [10]) can be explained due to significant influence of porosity, crystallite sizes and amorphous phases on the thermal conductivity as it is noticed in [2].

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**Table 2.** Concentration of elements into oxide layers weight %\(^a\).

| Electrolyte       | Basic          | With n-SiO\(_2\) |
|-------------------|----------------|------------------|
|                   | Inner part of oxide layer | Outer part of oxide layer | Inner part of oxide layer | Outer part of oxide layer |
| O                 | 49 ± 1         | 48 ± 2           | 46 ± 2         | 46 ± 1.5       |
| Al                | 45 ± 5         | 33 ± 3           | 45 ± 5         | 23 ± 6         |
| Si                | 4.7 ± 3.5      | 13.6 ± 2.8       | 6.1 ± 3        | 21 ± 4.6       |

\(^a\)uncertainties are calculated with Students distribution at coverage probability 0.9.

Oxide layer formed into electrolyte with n-SiO\(_2\) contains significant part of amorphous phases (figure 3) and silicon (table 2). So it can be assumed that the main reasons of decrease of thermal conductivity of oxide layer formed into electrolyte with n-SiO\(_2\) are sedimentation of roentgenomorphomorphic silica nanoparticles having very low thermal conductivity [11]. It is proved by low thermal conductivity of detached outer silicon enriched zone and significant increase of thermal conductivity after polishing of oxide layer.

**Figure 3.** XRD-patterns of oxide layers formed into basic electrolyte (base) and into electrolyte with silica nanoparticles (n-SiO\(_2\)).

Thus, it was obtained experimentally that addition of SiO\(_2\) nanoparticles into electrolyte leads to decrease of thermal conductivity of oxide layer in ratio of two only on account of decreasing of thermal conductivity of outer zone of oxide layer. The main reason of that is the sedimentation of silica nanoparticles into oxide layer. Besides this, smaller crystallite sizes of oxide layer formed into electrolyte with n-SiO\(_2\) lead to lower thermal conductivity too [2]. The obtained results show that
thermal insulation properties of oxide layers formed by PEO on aluminum-silicon alloys can be improved.

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