The study of PEO coated zirconium doped aluminum composites

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Abstract. Powder aluminum composites without additives and doped with 0.2, 0.5, and 1 % Zr were obtained using the cold pressing and sintering in vacuum. The composites were investigated using scanning electron microscopy (SEM) and synchronous thermal analysis. It was found that with an increase in the zirconium content, the melting point of aluminum composites slightly rises. On the surfaces of aluminum composites samples oxide coatings with a thickness up to 50 μm were formed by plasma electrolytic oxidation (PEO). It was found that the coatings have a two-layer structure. The addition of 1 % Zr to the aluminum composite more than doubles decrease the incorporation of silicon from the electrolyte into the near-surface layer of the PEO coating.

1. Introduction
Powder aluminum composites are a promising structural material due to their low weight, high specific strength and low cost. Several methods to improve their strength properties have been developed (copper alloying, modification by nanoparticle additives, etc.) that allow to increase the tensile strength by up to 630 MPa [1–3]. However, the effective use of such materials in aviation and space technology requires an increase in their working temperature, wear resistance, and corrosion resistance. According to the data of [4], the addition of 0.1 % Zr increases the resistance to the high-temperature creep of aluminum. The addition of zirconium in aluminum leads to its significant hardening due to the formation of dispersed secondary precipitates of the metastable Al₃Zr phase [5].

One of the methods of aluminum composite materials wear resistance and corrosion resistance increasing is the formation of protective oxide coatings on their surface by plasma electrolytic oxidation (PEO) [6–8]. PEO is an electrochemical process using the energy of electrical microdischarges functioning on the surface of the processed material. It allows to obtain oxide coatings with high wear resistance, corrosion resistance, heat resistance, etc.

Alloying additives in aluminum composites, for example copper, substantially influence the PEO process and the properties of the formed coatings [9–10]. In this work aluminum composites without additives and zirconium doped were obtained, PEO coatings were formed on their surface and their characteristics were investigated.

2. Experimental setup and characterization techniques
Samples of aluminum composites without additives (Al) and those alloyed with zirconium (Al + 0.2, 0.5 and 1 % Zr) were obtained by the method of powder metallurgy (cold pressing and sintering in
vacuum). The aluminum powder with an average particle size of 4 μm was used as a matrix. The aluminum and zirconium powders were mixed in a planetary mill for 2 hours in hexane. Sintering was carried out in vacuum at a temperature of 650 °C for 180 min.

PEO coatings were formed in silicate-alkaline electrolyte containing 2 g/l of potassium hydroxide and 9 g/l of sodium silicate. PEO treatment was carried out under the AC electrical mode at equal values of anode and cathode currents and total current density of 10 A/dm². The duration of the PEO process was 60 minutes for zirconium doped composites and 90 minutes for pure aluminum composite. Samples of uncoated composites were studied using a Zeiss Evo scanning electron microscope (SEM) and synchronous thermal analysis (NETZSCH STA449F 1 Jupiter) in the temperature range from 30 to 750 °C at a rate of 10 °/min in an inert atmosphere (argon). PEO coated composites were investigated using SEM, X-ray microanalysis, X-ray diffractometer (Empyrean PANalytical, CuKα radiation) and scratch tester (Revetest Xpress +, CSM Instruments SA). Scratch tests were performed by a diamond indenter with a linearly increasing load from 1 to 120 N at a loading rate of 50 N/min. The scratch length was 6 mm.

3. Results and discussion

Figure 1 shows the dependences of the anodic voltage \( (U_a) \) on the duration of the PEO process at the initial stages. After 100 seconds of PEO process they almost coincide. With the increasing of the zirconium content in the composite to 0.5–1 % the voltage rise slowed at the initial stage of the PEO process, which was associated with the formation of the barrier oxide layer. It can be assumed that the presence of zirconium in the composites due to Zr high electrical resistance and lower thermal conductivity slowed down the rate of PEO coating formation.

The study of zirconium doped aluminum composite without PEO coatings was performed with the aid of synchronous thermal analysis in the mode of heating-cooling-heating. Figure 2 shows the diagrams of differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis.

Heating of the samples showed that up to 600 °C there are no changes in the DSC curve. In the temperature range 641–679 °C an endothermic process was observed on the DSC curve associated with the melting of the composite. Melting occurred in two stages. The beginning and maximum temperatures of two peaks in DSC curve and the melting heat of aluminum composites during first and second heating are given in table 1. With an increase in the zirconium content the melting point of aluminum composites slightly increases. Besides during the first heating, the two-stage melting process is less expressed than during the second heating. This may be due to the primary Al₃Zr crystals formation accompanied by a decrease in the amount of zirconium dissolved in aluminum in the process of composites cooling at a rate of 10 °/min. Solid solution decomposition with formation
of secondary Al₃Zr phases begins at 350–400 °C [4, 5]. This is also confirmed by decrease in the melting point of the composites upon reheating by an average of 1 °C. At cooling on the DSC curve the exothermic complex peak associated with the composites crystallization is observed that indicates a two-stage process. The crystallization start temperatures are 656 °C for Al + 0.2 % Zr composite and 657 °C for Al + 0.5 % Zr and Al + 1 % Zr composites.

![Figure 2](image.png)

**Figure 2.** Diagrams of differential scanning calorimetry (DSC) (1 – heating, 2 – cooling, 3 – heating) and thermogravimetric (TG) analysis (4 – heating, 5 – cooling, 6 – heating) for the aluminum composite Al + 0.2 % Zr.

| Zr content (%) | Beginning (°C) | First heat Max (°C) | Melting heat (J/g) | Beginning (°C) | Second heat Max (°C) | Melting heat (J/g) |
|----------------|----------------|---------------------|--------------------|----------------|---------------------|--------------------|
| 0.2            | 641            | 648                 | 669                | 250            | 648                 | 669                |
| 0.5            | 643            | 649                 | 671                | 335            | 642                 | 649                |
| 1              | 644            | –                   | 669                | 318            | 643                 | 646                |

Table 1. The beginning and maximum temperatures of two peaks in DSC curve and the melting heat of aluminum composites during first and second heating.

In figure 3 the microstructure of Al + 1% Zr aluminum composite surface is shown. The average grain size of aluminum composites is about 6 μm. Primary Al₃Zr crystals in the form of needles were not noticed in an aluminum matrix, which indicates the dissolution of zirconium in aluminum.

PEO coatings is characterized by the predominance of a crater-like structure with pores in the center of craters up to 10 μm in size (Figure 3(b)). The pores density on coating surface is approximately 3·10⁹ pores/m². Elongated areas of the globular structure are noticeable between the crater-like regions (Figure 3(c)). These areas comprise compounds of the electrolyte elements as was shown by X-ray microanalysis and in [9–10].
The coatings thickness on composites Al + 0.2, 0.5 and 1 % Zr after 60 min PEO treatment was 20–25 μm. The thickness of PEO coatings on pure aluminum composite after 90 min treatment was ~50 μm. The cross-section analysis of PEO coating structure on the composite Al + 0.5 % Zr revealed two main layers: inner and outer layers (Figure 3(d)). The outer layer thickness of is ~15 μm. Its structure is characterized by separate through crater channels remained in the coating after the end of the microdischarges’ burning. The inner layer thickness is about 10 μm and it characterizes by a polycrystalline structure.

![Figure 3. The SEM images of the Al + 1 % Zr composite microstructure (a), PEO coating on it (b), (c), the cross-section coating structure on Al + 0.5% Zr composite (d).](image)

X-ray microanalysis of the PEO coating near-surface layer on aluminum composite without Zr additives showed the presence of following elements: Al (25 at. %), O (60 at. %), Si (15 at. %), Na (0.5 at. %), K (1 at. %). The same layer of PEO coating on the aluminum composite doped with 1% Zr contains: Al (26 at. %), O (65 at. %), Si (7 at. %), Na (0.5 at. %), K (1 at. %), Zr (up to 0.2 at. %). It can be seen that the addition of 1 % Zr to the aluminum composite more than doubles decreased the incorporation of silicon from the electrolyte into the near-surface layer of the PEO coating.

The scratch test results for the PEO coating with a thickness of 50 μm on aluminum composite without Zr additives are shown in figure 4. Comparison of the change graphs of indenter penetration depth of \( R_d \), friction coefficient \( \mu \) and acoustic emission signal with increasing of the load from 1 to 120 N along the scratch length with the SEM image of the scratch showed that the critical load of the coating destruction is 70 N. It can be assumed that the beginning and end of the PEO coating outer layer destruction correspond to small local minimums on the change graph of penetration depth and critical loads of 5 and ~20 N. With an increase in the penetration depth of the indenter, the friction coefficient first decreases at outer layer – inner layer transition and then increases to approximately constant value (0.4), which corresponds to friction with the composite material.

X-ray phase analysis of the coatings formed for 60 min of PEO showed the presence of \( \gamma \)-Al\(_2\)O\(_3\) in the coatings on zirconium doped composites. For the pure Al composite high temperature phase – corundum \( \alpha \)-Al\(_2\)O\(_3\) also appeared in the coatings after 90 min of PEO. This can be related to an increasing of the local temperature in the microdischarges areas and also heat retention for a longer time due to worsening of the heat sink to the metal base and electrolyte because of the higher oxide layer thickness.
4. Conclusions
Powder aluminum composites without additives and doped with 0.2, 0.5, and 1 % Zr were obtained using the cold pressing and sintering in vacuum. It was found that with an increase in the zirconium content, the melting point of aluminum composites slightly rises. On the surfaces of aluminum composites samples oxide coatings with a thickness up to 50 μm were formed by plasma electrolytic oxidation. The addition of 1 % Zr to the aluminum composite more than doubles decrease the incorporation of silicon from the electrolyte into the near-surface layer of the PEO coating. With an increase in the duration of the PEO treatment from 60 to 90 min, the high-temperature corundum α-Al₂O₃ also appear in addition to γ-Al₂O₃ in the coatings on aluminum composites. The destruction critical load of PEO coating with a thickness of 50 μm is about 70 N.

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