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INFLUENCE OF ELECTROLYTICAL OXIDISING OF SILUMINE SURFACES ON THE QUALITY OF BONDING WITH EPOXY RESIN

The article presents the preparation process of AC- AlSi12 aluminum alloy surface by application of anodic oxidation method. The method enables the formation of a porous oxide layer (Al_2O_3) which generates the substrate of durable adhesive bond with an epoxy resin. It also presents the influence of the form of silicon precipitates in the modified alloy upon anodizing process, uniform structure and thickness of the oxide layer as well as the topography of its surface which is expected to improve adhesion of the resin and silumin. The paper describes how the position of oxidized surface against the negative electrode influences the coating structure. The studied silumins are intended to form the material for casting of 3 dimensional objects whose parts will change the distribution of electric field strength that may cause non-uniform structure of the coating.

Keywords: skeleton cast, composite, oxidizing, surface development

1. Introduction

Construction of modern machinery, mainly technical means of transport, resulted in ever-increasing demand for materials exhibiting high relative strength (the ratio between ultimate strength and density), corrosion resistance and dynamic loads as well as good tribological properties. Conventional coated materials no longer meet these requirements. Therefore, composite materials have been developed [1-5] based on matrix alloy, ceramics and metal powders [6] which contain a reinforcing phase of various forms, such as fibers, particles, spheres, metal or ceramic foams [1-3] and nanowires or nanotubes [1, 6]. Metallic foams can be developed by metallurgical methods with the use of suitable blowing agents or gas blowing process generating bubbles [7-8]. An introduction of 10% of ceramic foam into AlCu5 alloy increases about four times the compression strength of this alloy [2]. They are not suitable as reinforcing material of composites with plastics matrix because they are too brittle.

Frameworks are better than foams since they are composed of several millimeters diameter connecting rods. Their increased heat capacity reduces the effects of thermal expansion differences [9-11]. The dimensions and arrangement of connecting rods develop the ability to design the shape and dimensions of the cells, allowing a number of properties variations to be obtained both within the strength and density. By selection of light metal alloys, such as aluminum and magnesium, the composite density can be modified.

Skeletal castings are produced by traditional casting methods [9, 10]. The combination of polymer matrix with aluminum frame should give high adhesion and ensure high strength properties. Therefore, reinforcement materials with high wettability and low surface tension in the liquid state should be used for the preparation of scaffold polymer

composites, which would result in a durable bond between components. Surface topography exerts a significant influence upon adhesion. Adhesive forces on the border between plastic and metal connecting rod depend on the shear strength of the bond and its surface area. Therefore, to achieve high forces at a given resin, the surface area should be developed at the interface. Efficient development of the casting surface area of aluminum and magnesium alloys can be implemented in a physical, chemical, and electrochemical way. The complex shape of skeletal castings and short distances between separate connecting rods hinder or even make impossible the use of physical methods. As already mentioned, aluminum and magnesium alloys can be used as the material for skeletons, therefore their surface can be increased by electrochemical oxidation method. The oxide coatings formed with this method are porous and have a large surface development which depends on the chemical composition of the oxidized alloy and oxidation parameters [1]. Chemical treatment of aluminum alloys before oxidation enables selective etching of chosen alloy components which additionally advance the development of casting skeleton surface. This article describes the impact of oxidation of silumin AC- AlSi12 upon the topography of the surface as well as upon the strength of resin/silumin bond.

2. Terms and course of the research

The study attempted at determining the effect of oxidation process upon the topography of the surface after oxidation as well as upon the strength of resin/silumin bond. The topography of the surface determines its development, and the increase of skeletal casting surface determines the manner in which the skeleton and the polymer that fills it are joined together. The more developed the surface, the better the adhesion of the resin

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to the metal casting. On the basis of previous findings [9] was selected AC- AlSi12 (Si-12.9, Cu-0.24, Mg-0.23, Mn-0.16, Ni-0.02, Fe-0.58 Zn-0.08, Ti + Zr-0.05%) alloy as a material suitable for frameworks. Castings made of this alloy absorb static and dynamic loads well, by partial plastic deformation and brittle fracture of connecting rods thus forming a spatial grid. An additional advantage of the selected material are very good casting properties which help obtain good quality the spatial structure featuring complex geometry with connecting rods of 5 mm diameter.

The tests were performed in five stages:

1. execution of test castings made of modified silumin;
2. electrolytic oxidation of castings;
3. profilometric tests of casting surface topography before and after oxidation,
4. microscopic examination of the surface after oxidation;
5. measurement of adhesion of resin to silumin.

2.1. Preparation of the samples

The test specimens were made by casting the skeletons from liquid silumin at a temperature of 670 °C into ceramic molds. Then the samples containing single elements and fragments with 6 connecting rods (5 mm in diameter) were cut out. After the ceramic molds were removed and the skeletons cleaned, individual connecting rods were cut from topped-up samples. The obtained square samples were subjected to oxidation. Additionally, skeletons fragments, with six connecting rods each and pointing in either direction, were oxidized. The purpose of spatial structures oxidation was to determine the effect of the position of connecting rods in relation to the cathode upon the topography of the surface after oxidation. Rectangles were used in the tests of surface topography with the application of contact less profilometer and thickness measurements.

2.2. Anodic oxidation of the samples

Oxidation of the samples was performed in such a way as to control of the impact of the position of skeletal casting in relation to the cathode upon structure of oxide coating. Therefore, the samples were placed in the galvanic bath in a controlled manner (Fig. 1) which made it possible to determine how the position of oxidized surface, in relation to the cathode, affects the surface topography and thickness of oxide coating. Square and cylindrical samples were used for the research. The position of the square sample directly conditions the growth of oxide coating upon the surface closest to the cathode (points 1-4, Figure 1(a)). The distribution of the force lines of the electromagnetic field around the electrodes is directly responsible for the above mentioned. Figure 1(a) also shows the cylindrical sample, which is a fragment of skeletal casting connecting rods. During the oxidation of individual samples, two lead electrodes arranged on opposite sides can be used. Then such arrangement might reduce variations in thickness of the oxide coatings. However, during oxidation of the spatial skeleton the introduction of electrodes between all connecting rods is not possible. The only possible alternative is the use of several electrodes, as shown in Figure 1(b).

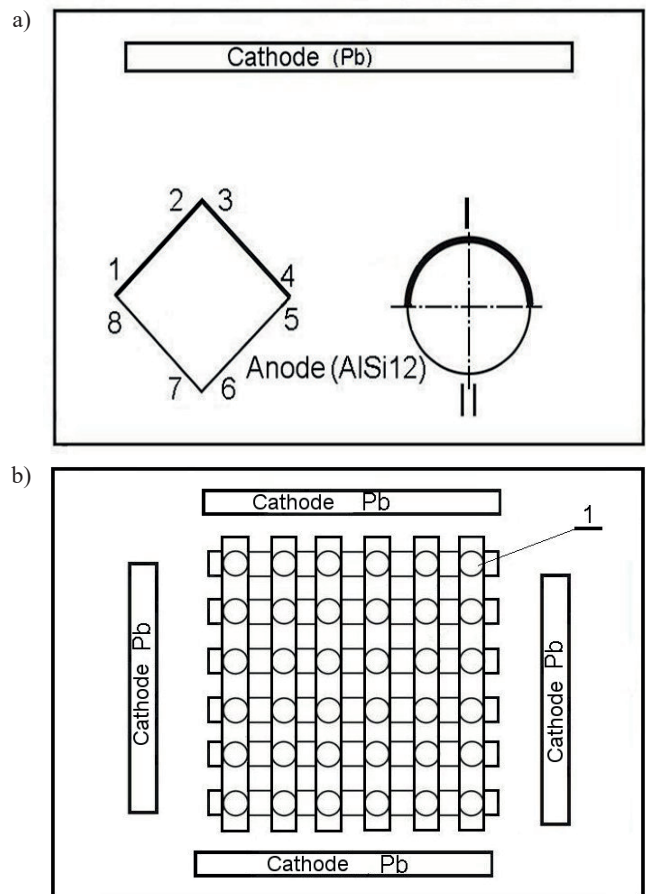


Fig. 1. Influence of skeleton's element position versus cathode on the structure of oxide coating: a) using one cathode, square and cylindrical connector rod; b) using four cathodes, 1 – cast skeleton being oxidized.

To study the effect of oxidation upon the surface topography three samples for each experiment were used. Anodizing was carried out according to the following scheme:

- etching in 10% aqueous KOH solution for 10 min at 20 °C to remove the natural oxide and residual impurities;
- sensitization with 15% aqueous HNO_3 solution for 10 min at 20 °C in order to remove heavy metals, the presence of which could cause discontinuities of oxide coating;
- anodizing with 15% aqueous H_2SO_4 solution for 1 h at an anode current density of 0.8 A/dm².

Oxidation conditions were selected based on previous studies of the authors [1, 11].

2.3. The study of oxide coating

In course of the study, the measurements of the coating thickness and surface roughness were performed. Thickness measurement, according to ISO 2360, was performed on the surface of the samples (Fig. 1(a)) in 8 selected points using the eddy currents meter (ISOSCOPE FMP10) with accuracy of 5%. During the measurement the measuring probe is placed on the sample surface which, in case of high roughness surfaces, may increase the measurement inaccuracy.

In order to determine the surface topography of oxide coatings the optical profilometer was used. The use of contact

less profilometer allowed to perform measurements without disturbing the geometric structure of the surface, such as silicon precipitates chipping or without deformation of the coating, which usually happens during measurements performed with contact method.

2.4. Test on resin adherence to silumin surface

Cylindrical samples were used to test the effect of oxidation upon the adhesion of resin to silumin as in case of the static tensile test with a sample length of 5d (Fig. 2(a)). Silumin samples were oxidized and topped-up with resin in a mold. In order to obtain the required properties of the resin, the cast combined with resin was left for 24 h at room temperature. The samples were then subjected to tensile test.

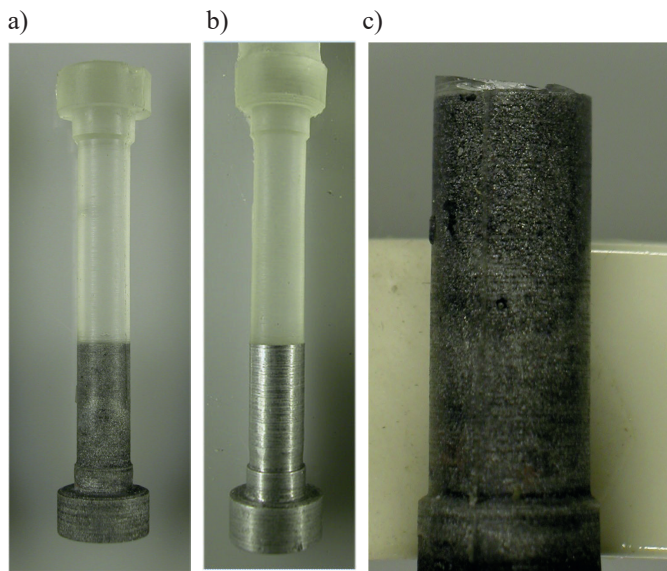


Fig. 2. Samples for measuring of adhesion forces between silumin and resin before investigation (a-oxidized, b-non oxidized) and silumin part after rupture with resin residuum at the top (c)

3. Test results

3.1. Microscopic studies

After oxidizing the samples were subjected to microscopic and profilometric examinations which aimed at determining their surface topography. Figure 3(a) shows the view of a polished silumin surface before oxidizing. In the matrix some small, oblong silicon precipitates (brighter highlights) can be observed. They shape the morphology of the oxide coating and affect the adhesion of the resin. Figure 3(b) presents the silumin surface after oxidizing. Brighter spots represent oxide coating, under which silicon precipitates are located. They conduct worse than aluminium the electric charge. Therefore, these spots are charged and “shine”. The shape and orientation of the brighter locations coincide with the shape and distribution of silicon precipitates. Oxide film formed on the silicon solution in aluminum (α) is gray (spaces between the bright coating above silicon precipitates).

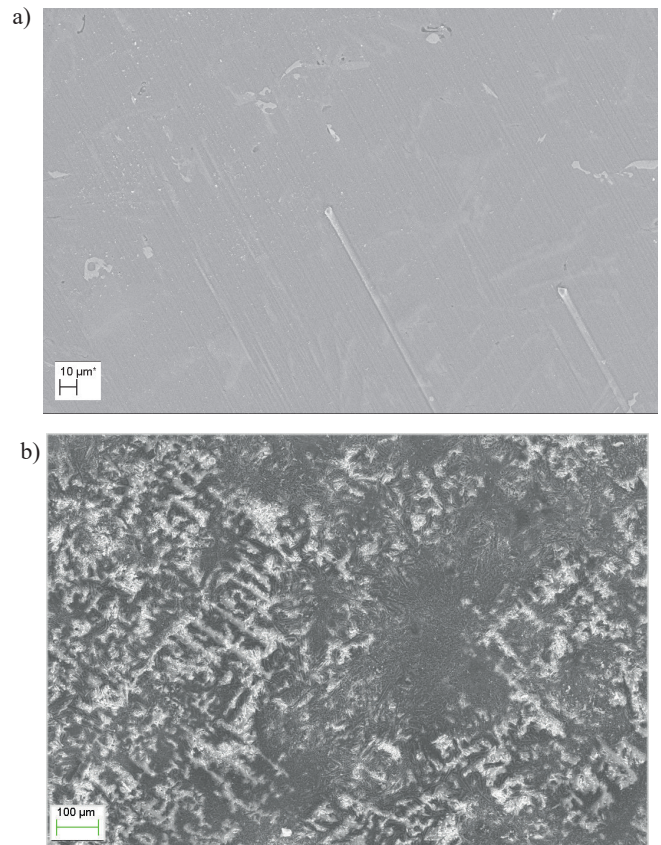


Fig. 3. Surface view of AC-AlSi12 alloy before (a) and after oxidizing (b)

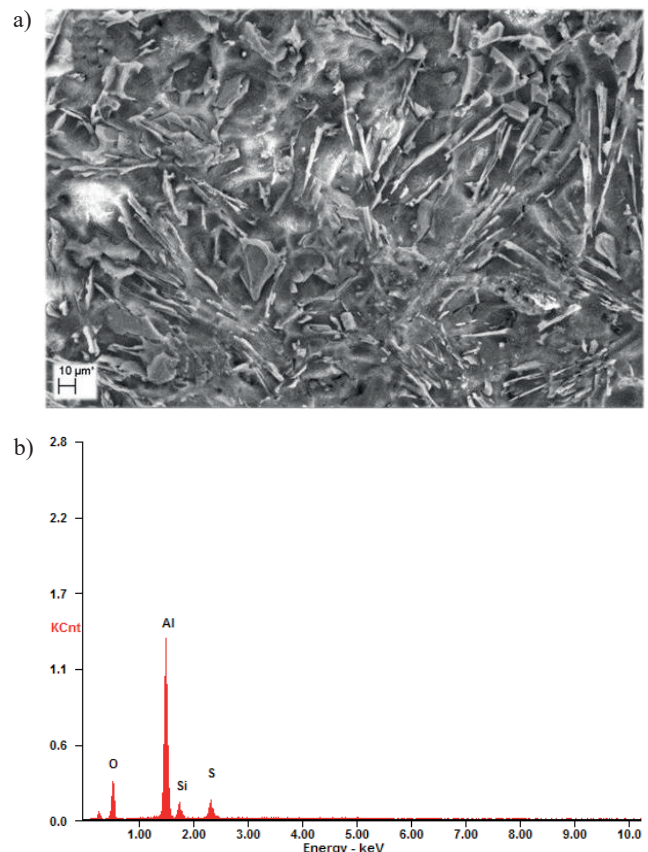


Fig. 4. Surface view of AC-AlSi12 alloy after oxidizing (a) and quantities of chosen elements at point 1 (b)

Figure 4 shows a magnified part of the oxide coating with qualitative analysis confirming the oxide formation in which the acid remains (of sulfur content) are left and silicon precipitates are included. The analysis results are listed in Table 1.

TABLE 1

Proportional content of elements from point analyze

Element	Wt%	At%
O	26,96	31,41
Al	40,22	27,78
Si	05,16	03,43
S	05,71	03,32

3.2. Measurement of coating thickness

The measurement results of oxide film thickness formed upon the oxidized samples at various points (according to the diagram in Figure 1) depending on the position with respect to the cathode are shown in Table 2.

TABLE 2

Thickness of the oxide coating on selected measuring points

Measuring point	1	2	3	4	5	6	7	8
Coating thickness, μm	18	20	21	19	21	26,5	20	27

3.3. Profilometric research

During the profilometric tests three 3D profiles have been recorded which help read roughness parameters listed in Table 3. Sample 3D profile of the silumin surface before oxidation is shown in Figure 5, while Figure 6(a) shows its oxidized version. 2D profiles in the longitudinal direction to the length of connecting rods are presented in Figures 5(c) and 6(c). Figures 5(b) and 6(b) show the fragments of 3D roughness profiles cut from Figs. 5(a) and 6(a) and magnified to show surface development. Profiles of Figures 5(a) and 6(a) seem to be smooth. It results from the fact that the scale of peaks height (in mm) is accepted automatically depending upon the measured field surface (1 mm x 1 mm). In Figures 5(b) and 6(b), the field is much smaller (0.29 mm x 0.23 mm), so the roughness is given in micrometers.

Silumin surface oxidation improves the adhesion forces of the resin but depends on the depth of the roughness valleys. The capacity of the valleys, as the resin depots is illustrated by the right part of the curve in the graph (Abbott curve) in Figure 7. Capacity of valleys in oxidized silumin surface is significantly greater than non-oxidized. Depth differences for non-oxidized silumin are 0.92 mm, and 1.38 mm for oxidized one. 2D profiles analysis (Figs. 5(c) and 6(c)) shows that the smaller roughness peaks disappeared. This results from both chemical (degreasing) and electrochemical treatment during oxidation.

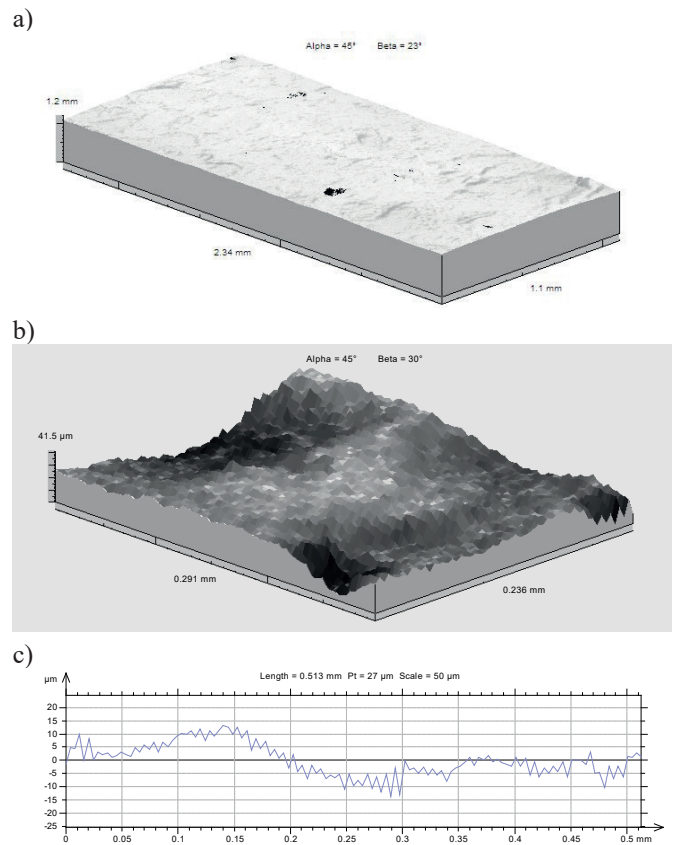


Fig. 5. Surface topography of the AlSi12 alloy before oxidizing (as casted): a- 3D roughness profile, b- 3D magnified part of fig. 5a, c- 2D along the sample

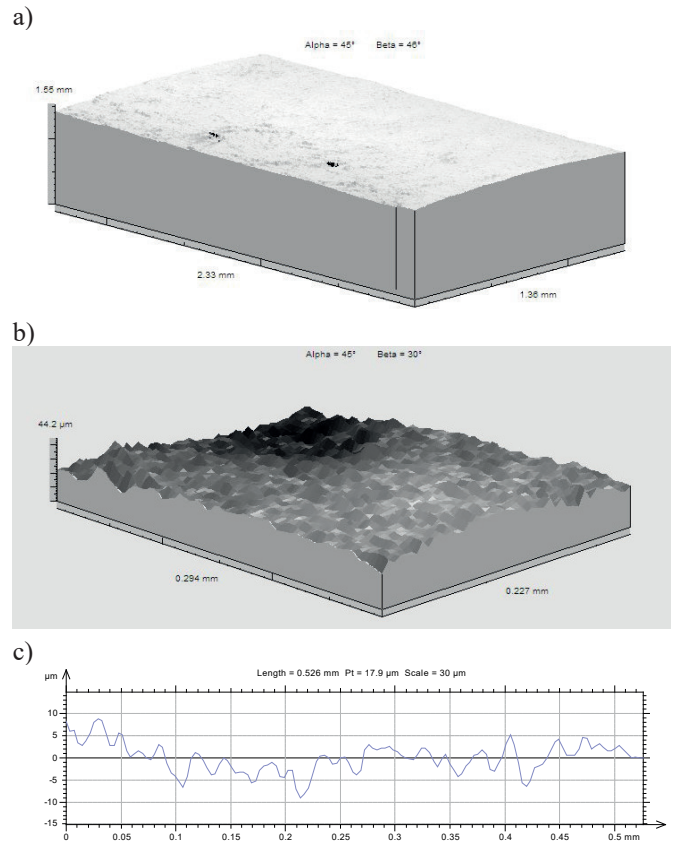


Fig. 6. Surface topography of AlSi12 alloy after oxidizing: a- 3D-roughness profile, b- 3D magnified part of Fig 3a, c- 2D- profile along the sample

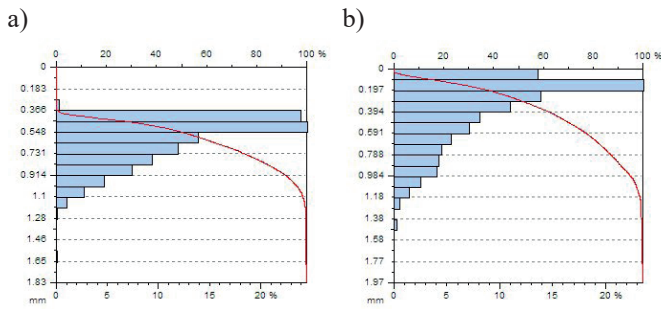


Fig. 7. Abbot-curve for surface of investigated alloy before (a) and after oxidizing (b)

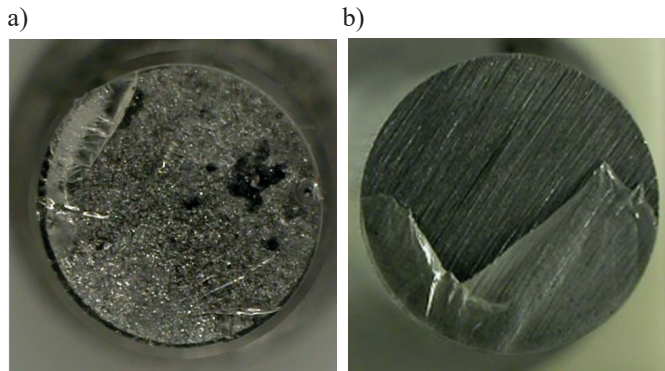


Fig. 8. Fracture of silumin sample after tensile test; a – oxidized with rest resin, b- non oxidized with delamination's place

3.4. Measurement of resin adhesion to oxidized silumin surfaces

To determine the resin adhesion to the silumin, adherence test was performed for samples made in accordance with the requirements of the static tensile testing (Fig. 2(a)). On the basis of the values of designated forces, at which the destruction of resin-silumin contact appeared, destruction stresses were determined. The value of strains (1.2-2.2 MPa) for samples with oxidized silumin was mainly connected with tensile strength of resin as the rupture took place inside the resin (Figs. 2 and 8). Strains for non-oxidized silumin resulted from adhesion on the border of resin-silumin, because destruction appeared on the border of resin-silumin. Therefore it is not possible to determine, without any doubts, the effect of oxidation on the value of the adhesion forces of resin to silumin. Carefully selected resin featuring higher tensile strength should be used instead. Studies have shown that the contact of the resin used and oxidized silumin was strong and provided better adherence than in case of non-oxidized silumin.

4. Discussion of the results

On the basis of the results of microscopic examination, it was found that the oxide film formed on the modified AC-AlSi12 alloy is continuous. The oxide film includes numerous minor silicon precipitates (Fig. 3(b)). This is confirmed by the results of qualitative analysis (Fig. 4(b)). As a result of the alloy modification, Si precipitates are fragmented. Therefore pure oxide is formed mainly in places with matrix (α solution

of silicon in aluminum). Aluminum oxide grow in 50% of its thickness into the oxidized material and 50% protrudes above the surface area before oxidation. In addition, the oxide layer grows in a direction parallel to the oxidized surface. This is the reason for partial covering of fine silicon precipitates with oxide. Si precipitates and coating fragments extend to 10 micrometers above the average line, which is confirmed by 2D roughness profiles (Fig. 6(c)). Such structure of the surface promotes adhesion of the resin to silumin.

The thickness of oxide coating on the sample walls is uniform, but in points 6 and 8 (Fig. 1) it is much greater (Table 2), which may indicate greater silicon precipitates protruding from oxide which increase the value of thickness measurement.

In the analysis of surface roughness profiles of the examined alloys after oxidation it was found that the electrolytic oxidation process consisting of chemical treatment (KOH etching, sensitization of HNO₃), and electrochemical oxidation has a significant effect on the alloy surface topography.

In the oxide are small craters formed (Fig. 5(a)) and smaller roughness peaks disappear (fewer peaks in Fig. 6(c) than in Fig. 5(c)). The curve course of surface share (Fig. 7) shows a large capacity of roughness valleys (the right part of the graph above Abbot-Firestone curve), which increases the adhesion of the resin to silumin.

By the obtained development of the surface through anodic oxidation of the silumins, the material which fills skeletal castings does not only form adhesive connection in a place where an oxide layer appears, but it is anchored upon exposed precipitates of Si phase which protrude above the surface of the oxide. The surface may also show areas, where the resin flows into the little craters created by removal of the silicon precipitates in course of chemical and electrochemical treatment.

TABLE 3
Chosen surface roughness parameters of investigated alloy before and after oxidizing

Material	Ra μm	Rmax μm	Rp μm	Rv μm
AlSi12	157	1834	614	1210
AlSi12 oxidized	246	1973	383	1590

Ra – average height of the roughness
Rmax – maximal height of roughness
Rp – height maximal of peaks
Rv – depth of maximal valleys

5. Summary

The study showed a significant effect of electrolytic oxidation of the AC-AlSi12 alloy upon the topography of its surface. The resulting oxide coating is a continuous structure and consists of thicker areas formed on the matrix of the alloy as well as of thinner areas formed in the vicinity of silicon precipitates. Also, the distance between oxidized surface and the cathode does not have a significant effect on the film thickness or its uniform structure, which proves the usefulness of electrolytic oxidation as a method of increasing the adhesion at the border connecting rod-resin in skeleton casts.

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