



# Stereometry specification of anodised and PVD coated surface of aluminium alloy

J. Konieczny <sup>a,\*</sup>, K. Labisz <sup>a</sup>, J. Wiczorek <sup>b</sup>, L.A. Dobrzański <sup>a</sup>

<sup>a</sup> Division of Materials Processing Technology, Management and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

<sup>b</sup> Department of Alloys and Composite Materials Technology, Silesian University of Technology, ul. Krasińskiego 8, 40-019 Katowice, Poland

\* Corresponding author: E-mail address: jaroslaw.konieczny@polsl.pl

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## ABSTRACT

**Purpose:** The aim of the work is to present the influence of casting method and anodic treatment parameters on properties, thickness and structure of an anodic layer with (PVD) physical vapour deposition method achieved TiN layer formed on aluminum casting alloys.

**Design/methodology/approach:** Investigations were carried out on the laser profile measurement gauge MicroProf from company FRT, abrasive wear test was made with using ABR-8251 equipment delivered by TCD Teknologii ApS and microstructure investigations were made with using a light microscope equipped with an electronic camera configured with a computer on two casting aluminum alloys which both were founding by pressure die casting and gravity casting.

**Findings:** The researches included analyze of the influence of geometry, roughness and abrasive wear resistant of anodic layer obtained on aluminum casts. The studied PVD coating deposited by cathodic arc evaporation method demonstrates high hardness, adhesion and wear resistance.

**Research limitations/implications:** Contributes to research on anodic and PVD layer for aluminum casting alloys.

**Practical implications:** Conducted investigations lay out the areas of later researches, especially in the direction of the possible, next optimization anodization process of aluminum casting alloys, e.g. in the range of raising resistance on corrosion.

**Originality/value:** The range of possible applications increases staidly for example for materials used on working building constructions, elements in electronics and construction parts in air and motorization industry in the aggressive environment.

**Keywords:** Metallic alloys; Mechanical properties; Metallography; Computational material science; Surface treatment

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## PROPERTIES

## 1. Introduction

Today's investigations connected to materials engineering progress made it possible to solve the problems with development of metallic materials, satisfactorily increasing of strength both of structural and tool materials. A continuous growth of use of alloys aluminum in different branches in the wide comprehended industry is observed technology development of production of aluminum, its alloys and composites with aluminum matrix was state in last years in many scientific centers on all world [1-5]. A considerable influence on the products' durability is exerted by properties of a surface layer [6,7].

Such a great interest in surface layer technologies is dictated among other things by the fact that every year the world economy bears tremendous losses reaching milliards dollars, attributable to the product damage due to surface layer degradation.

As shown on Figure 1, the anodic layer growth process involves four steps:

- barrier layer development;
- growth of small inhomogenities;
- continuously grow of pores;
- stabilization of the interpore distances.

One among the technologies that is characterised by great development dynamics, as regards both carried on theoretical research work and specific practical applications e.g. in industry, is surface layer technology, in particular the manufacturing of such surface layers, which protect material against corrosive action of environment and improve its mechanical properties.

A porous and conducting layer forms from the basic layer, which is dissolved by electrolyte. A porous size obtained on aluminium in  $H_2SO_4$  electrolyte is about 20 nm. The basic layer is simultaneously restored by formation of aluminium oxide that proceeds with the same speed as it transforms into the surface layer. In this way the basic layer maintains its thickness at almost constant voltage [8,9].

Anodic oxide layers which are connected fixedly with the aluminum substrate are resistant on corrosion. The corrosion resistance can be reduced by the pores and pits in layer or the presence of harmful alloy-forming elements and admixtures, particularly the copper or by impurities [10]. The intermetallic copper aluminum phase dissolves during anodizing, which causes a hardness and thickness decrease of coat, and the enlargement the porosity [11].

The anodic layers have a protective – decorative function applying on the aluminum electronic elements, articles of home farm, part of instruments, the gardens – pieces of furniture, the touristic equipment and sport, the motor accessories and elements of aluminum woodwork [12,13]. The oxides layers are produced on aluminum foil placed as electrode. Hard anodic layers [14,15] can be applied in air and motor industry.

During the forming process of the aluminum oxide layer a small increase of mass and volume occurs. Dissolving of oxides layer is possible only in basic solutions or acid about larger pH than 8.8 or lower than 4.0 [16].

The alumina layer (Fig. 1) is composed of (a) a very thin and free of pores dielectric basic layer – the so-called „barrier layer”, (b) than a growth of small inhomogenities occurs (Figs. 2 and 3), (c) next the underlying porous surface layer occurs, (d) with the

stabilization of the interpore distances. Thickness of the basic layer depends on the voltage [V] applied during anodizing.

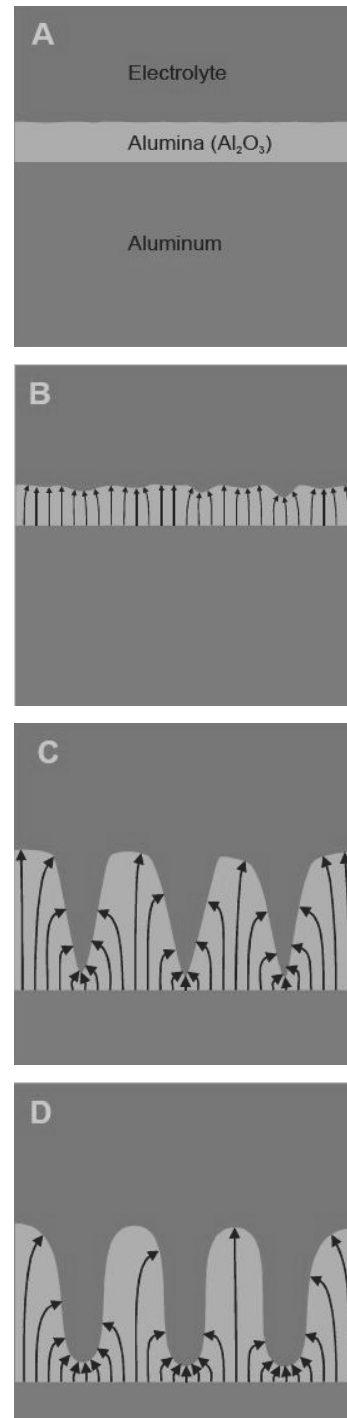


Fig. 1. Stages in the development of the alumina surface layer, a) barrier layer development, b) growth of small inhomogenities, c) continuously grow of pores, d) stabilization of the interpore distances (JPK Instruments AG, 2003)

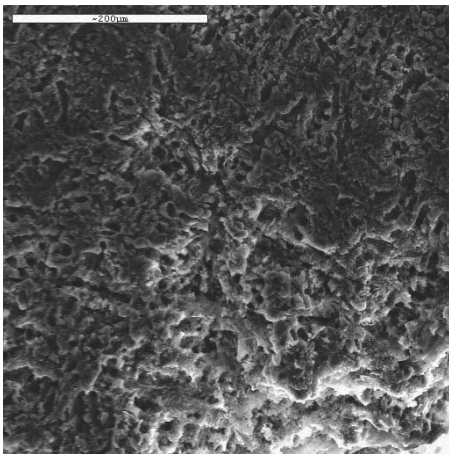


Fig. 2. Oxides layer Al<sub>2</sub>O<sub>3</sub> creation on EN AC-ALSi12(b)+2% Mg, SEM

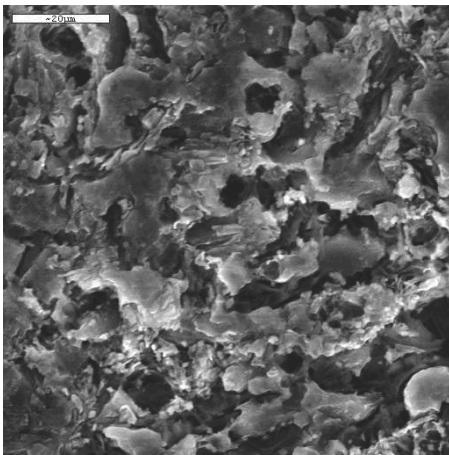


Fig. 3. Inhomogeneity of oxides layer Al<sub>2</sub>O<sub>3</sub> creation on EN AC-ALSi12(b)+2% Mg, SEM

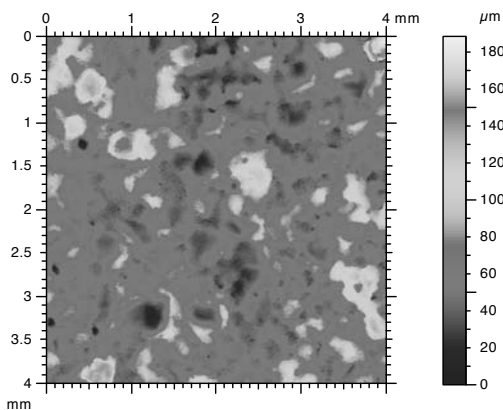


Fig. 4. Isomeric surface image in 2D view (shown as colour intensity scale)

During anodic treatment one can obtain the oxide layer, which is characterized by the structure presented on Fig. 4. and Fig. 5. as an isomeric surface image in 2D view, on which basis an numerical micrograph can be achieved as presented in Fig. 5.

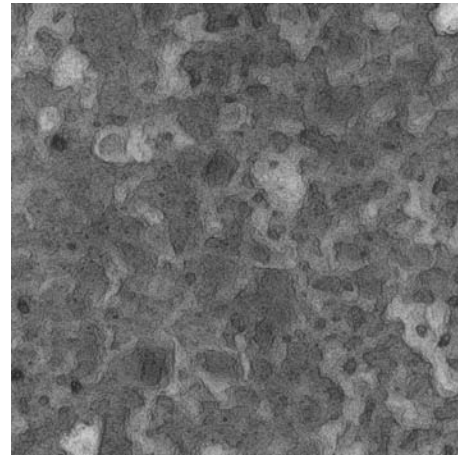
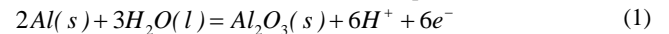


Fig. 5. Numerical micrograph of the investigated sample area

The oxide grows at the anode electrode in electrochemically anodized aluminum in accordance with equation:



and hydrogen evolves at the cathode:



Six main alumina oxide forms are mostly discussed (Table 1). Anodic Al<sub>2</sub>O<sub>3</sub> was mostly reported as a form of X-ray amorphous solid. Several authors demonstrated for the barrier layer, the presence of nanocrystallites of γ'-Al<sub>2</sub>O<sub>3</sub> with sizes of 2-10 nm. Intermediate form between amorphous and γ-crystalline Al<sub>2</sub>O<sub>3</sub> is considered γ'-Al<sub>2</sub>O<sub>3</sub>. Shimizu [19] suggested that aluminum oxides may consist of nanocrystallites, hydrated alumina, anions, and water molecules [20].

Table 1.

Alumina oxide forms

Name	Crystalline form	Crystal system	Density (g/cm <sup>3</sup> )
Corundum	α-Al <sub>2</sub> O <sub>3</sub>	hexagonal	3.97
Boehmite	α-Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	ortho-rhombic	3.44
Gibbsite	α-Al <sub>2</sub> O <sub>3</sub> ·(H <sub>2</sub> O) <sub>3</sub>	monoclinic	2.42
Diaspore	β-Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	ortho-rhombic	3.4
Bayerite	β-Al <sub>2</sub> O <sub>3</sub> ·(H <sub>2</sub> O) <sub>3</sub>	monoclinic	2.53
Gamma alumina	γ-Al <sub>2</sub> O <sub>3</sub>	—	—

The layer growth depends on anodized material, its chemical composition and structure as well as on preliminary surface treatment and anodic treatment conditions, such like:

- type of used current,
- current density,
- electrolyte composition,
- electrolyte concentration,
- temperature.

The purpose of this elaboration is testing the structure and thickness of the layers formed during anodic treatment on aluminium casting alloys adopted casting method onto the formed anodic layer.

## 2. Material and methods

The analysis of geometry of surface was based on data acquired with measurement of selected fragments of casts, executed on laser profile measurement gauge MicroProf of the FRT company. Measurements were executed for 8 samples divided on two groups.

First of them was the starting material, in state directly after casting without any processing of surface. Material made up second group after apply an oxide layer by galvanic method.

Investigations were carried out on EN AC-ALSi12(b) alloy. As casting method for this alloy two methods were used: high pressure and sand casting. The chemical composition of the alloy is showed in Table 2.

- Two elements were anodized:
- EN AC-ALSi12(b) high pressure cast alloy,
  - EN AC-ALSi12(b) sand cast alloy.

Table 2. Concentration of alloying elements in EN AC-ALSi12(b)

Alloy	Elements concentration, % (mass)						
	Si	Mn	Fe	Zn	Mg	Cu	Al
ALSi12(b)	12.5	0.5	0.6	0.1	0.05	0.05	Rest

Preliminary investigations with 3% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 4% H<sub>3</sub>PO<sub>4</sub>, 4% H<sub>2</sub>SO<sub>4</sub>, 3%CrO<sub>3</sub> electrolytes allow to determine the influence onto homogeneity of pores in the oxides layer at the same conditions, the samples of EN AC-ALSi12(b) alloy were put under anodic treatment in the presence of the electrolytes. For anodizing the 4% H<sub>2</sub>SO<sub>4</sub> was chose. Anodizing parameters are shown in Table 3.

Table 3. Anodizing parameters

Parameter	Value
Electrolyte	H <sub>2</sub> SO <sub>4</sub> with a concentration 295-315 g/l
Temperature	-4 - 2°C
Pulsating current	2 A/dm <sup>2</sup> during 0.25 s 1 A/dm <sup>2</sup> during 0.1 s
Concentration of aluminum ions	6 - 9 g/l

Table 4. Deposition parameters of the coatings

Coating	Substrate bias voltage [V]	Arc current source [A]	Pressure [Pa]
TiN	-100	80	2.0

The coating deposition process was made in a device based on the cathodic arc evaporation method in an Ar and N<sub>2</sub> atmosphere. Cathodes containing pure metal (Ti) were used for deposition of the coatings. The base pressure was 5×10<sup>-4</sup> Pa, the deposition

temperature was approximately 350°C. The deposition conditions are summarized in Table 4.

Microstructure photographs were made with using a light microscope (BX60M type made by OLYMPUS) with the magnitude of 500, 1000 times). The microscope was equipped with an electronic camera (DPI0 model, made by OLYMPUS) configured with a computer. It was applied the „analySIS” programme for recording and processing the photographs.

Abrasive wear test was made with using ABR-8251 equipment delivered by TCD Teknologii ApS. The tests were conducted according to the specification and requirements of the standard ISO 8251. It was applied the load of 4.9 N, at a slip velocity of 40 cycles/min for the test purposes. The test surface area amounts to 12 x 30 mm. The grindability tests was performed at temperature of 23°C, humidity of 63%. The test was repeated 5 times.

## 3. Results and discussion

The alloy used for investigation was cast by two methods: pressure and gravitational cast, therefore several factors as well:

- parameters of casting (pressure, to sand form),
  - attendance of layers,
- could have influence on the surface geometry formation.

Comparing the two- and three- dimensional surfaces figures (Fig. 6) can be clearly state a different roughness distribution was found. This result can be found both for covered samples layer with oxide and materials in initial state.

The surface shape geometry is clearly depending on the casting method applied. The surface images of the casts a very similar, regardless the anodizing method is used or not (Fig. 7).

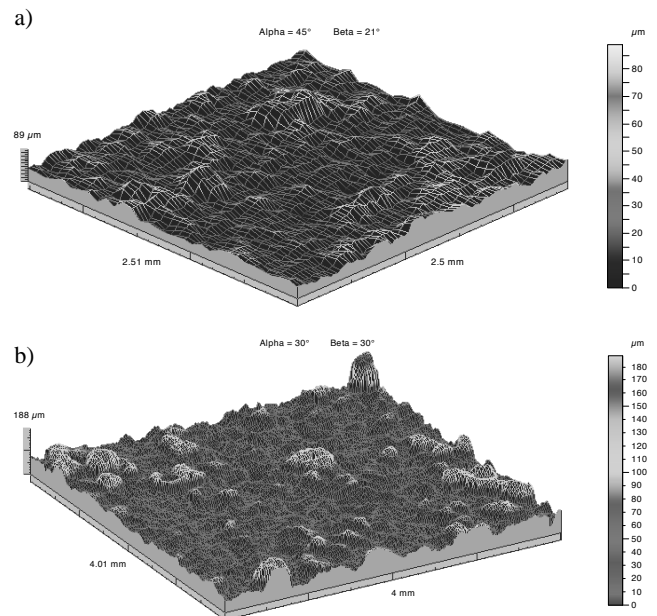


Fig. 6. The geometrical shape of fragment of studied surface, topography of 3D surface, sand cast EN AC-ALSi12(b) alloy a); anodized and TiN coated sand cast EN AC-ALSi12(b) alloy b)

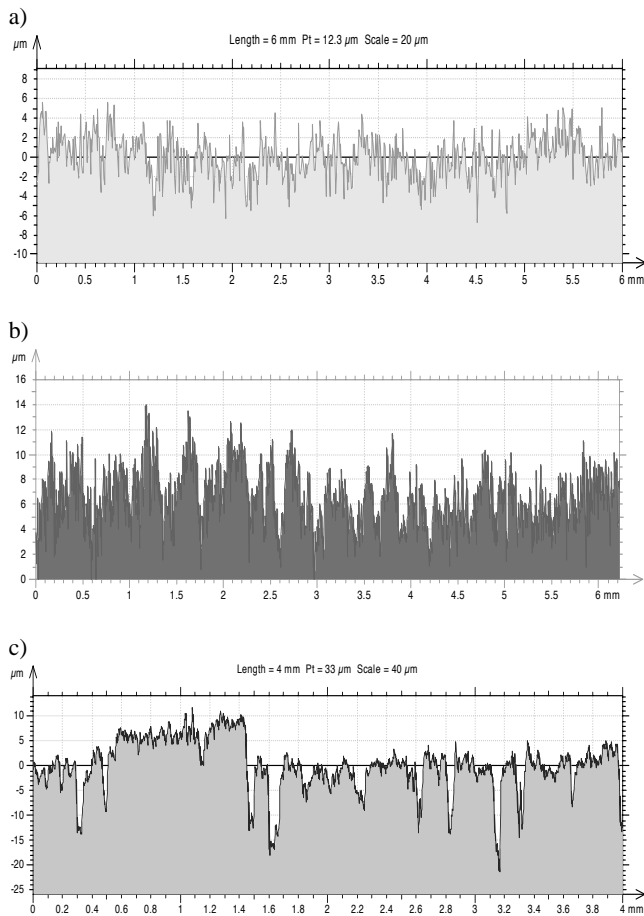


Fig. 7. Profiles 2D cut out from studied surface in plane N-S, EN AC-AlSi12(b) high pressure cast alloy; a) before anodization, b) after anodization; c) anodized and TiN coated sand cast EN AC-AlSi12(b) alloy

The roughness values achieves the maximum by 80  $\mu\text{m}$ . Using the 3D images, it was possible to observe “islands” with regularly spread character of altitudes on surfaces. Comparing the geometrical shape of studied anodic layer can be found that it is a representation of substrate surface shape. The surface configuration keeps characteristic features even after applying of anodic layer. With other words the applying of anodic layer does not affect the geometry profile of surface. The surface analysis of the anodized sample with PVD TiN coating compares that the sample with sample PVD TiN coating has the same characteristic features as the only anodized sample.

This “acclivity” has a high of circa 5  $\mu\text{m}$ . Its formation should be considered with any damage of the cast form (scratching or impurity). Taking into consideration that “acclivity” is forming on to the sample covered of oxide layer, its existence can be connected with discontinuity or local deformation of layer. To confirm this presumption any microscope investigations should be performed which will be helpful for unequivocally genesis of this “acclivity”.

Comparing of the results of obtained investigations for samples before and after applying the anodizing layer and with PVD TiN layer on anodized sample, it can be seen that applying layer hasn’t any influence on geometrical characteristics of the surface.

For high pressure cast material, the maximum roughness value of surface does not exceed 15  $\mu\text{m}$  (Fig. 8). The roughness distribution on the whole analyzed surface is identical without of any anomalies. But for high pressure cast material with PVD TiN layer the maximum roughness value of surface increases to 65  $\mu\text{m}$ . And bigger difference between the maximum and minimum value can be state, the difference is about 50  $\mu\text{m}$ . It is significantly smaller compared to the PVD coated sand cast material. Also a big roughness difference occurs on the investigated surface and is not homogenous distributed on it.

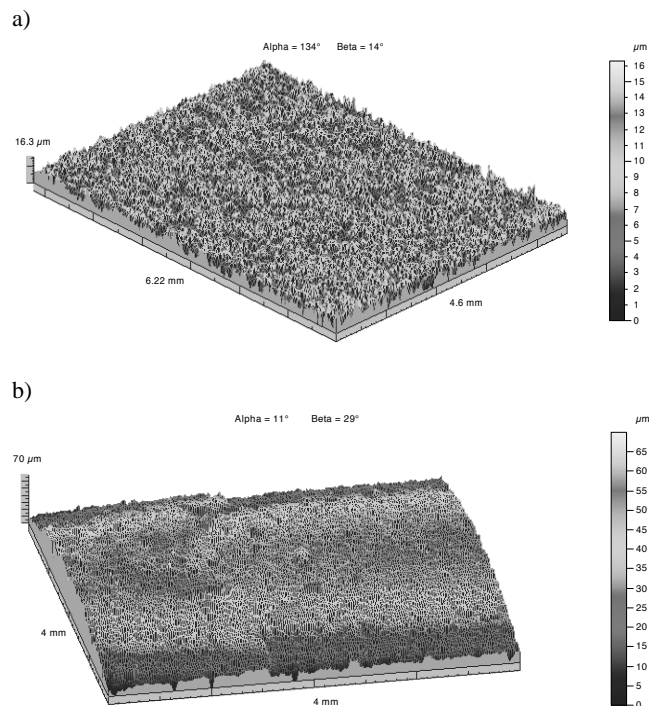


Fig. 8. Three-dimensional topography of surface, high pressure cast alloys; a) EN AC-AlSi12(b), b) anodized and TiN coated sand cast EN AC-AlSi12(b) alloy

In case of sand cast material the roughness distribution observed on 3D images after applying of the anodized layer and anodized + PVD TiN laers doesn’t not change. The distribution for each set (unanodized – anodized – anodized + PVD TiN sample) is identical, keeping all characteristic features, such as “islands” type of roughness formed during casting process. The presence of layer does not change such features like picks distribution (Figs. 7 and 8) or the preferred orientation (Figs. 9 and 10).

The anodic layer and anodized + PVD TiN layer hasn’t any influence on roughness value of the surface – for casts sand 60 to 70  $\mu\text{m}$  and with PVD TiN layer 130 to 140  $\mu\text{m}$ .

On the other side in case of high pressure cast material, where the roughness and anodic surface shape is similar to substrate surface material (before anodizing), but after PVD TiN coating the surface character changes essentially. For casts high pressure sample the roughness value of the surface is max 15  $\mu\text{m}$ , but the roughness value of the surface with PVD TiN layer increase to 65  $\mu\text{m}$ .

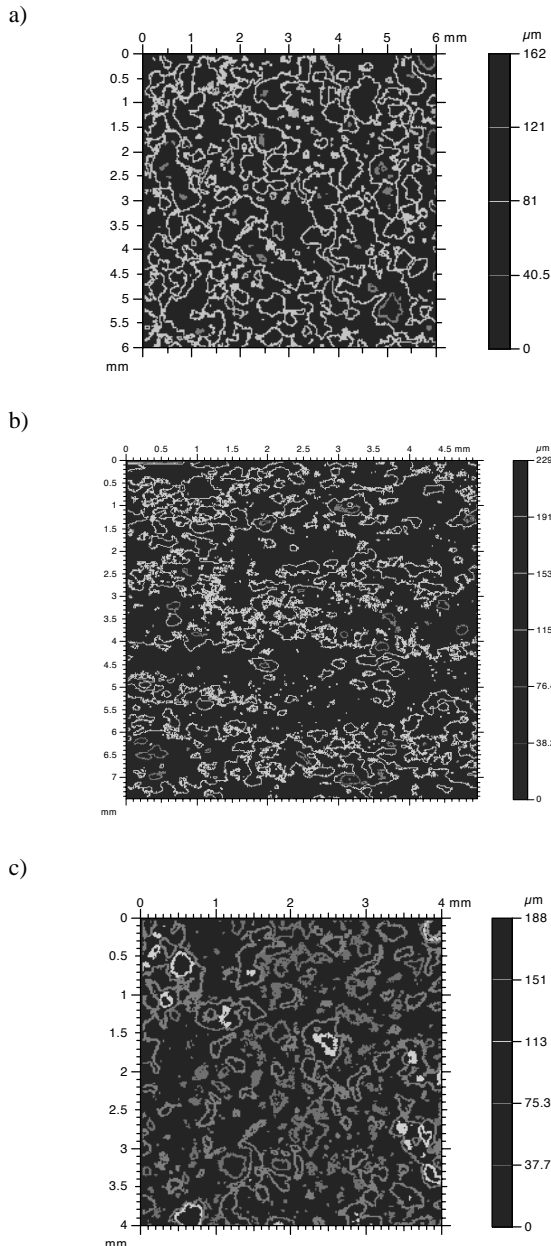


Fig. 9. The distribution of tops on surface of sample from EN AC-ALSi12(b) sand cast alloy a) before anodization; b) after anodization; c) anodized and TiN coated sand cast EN AC-ALSi12(b) alloy

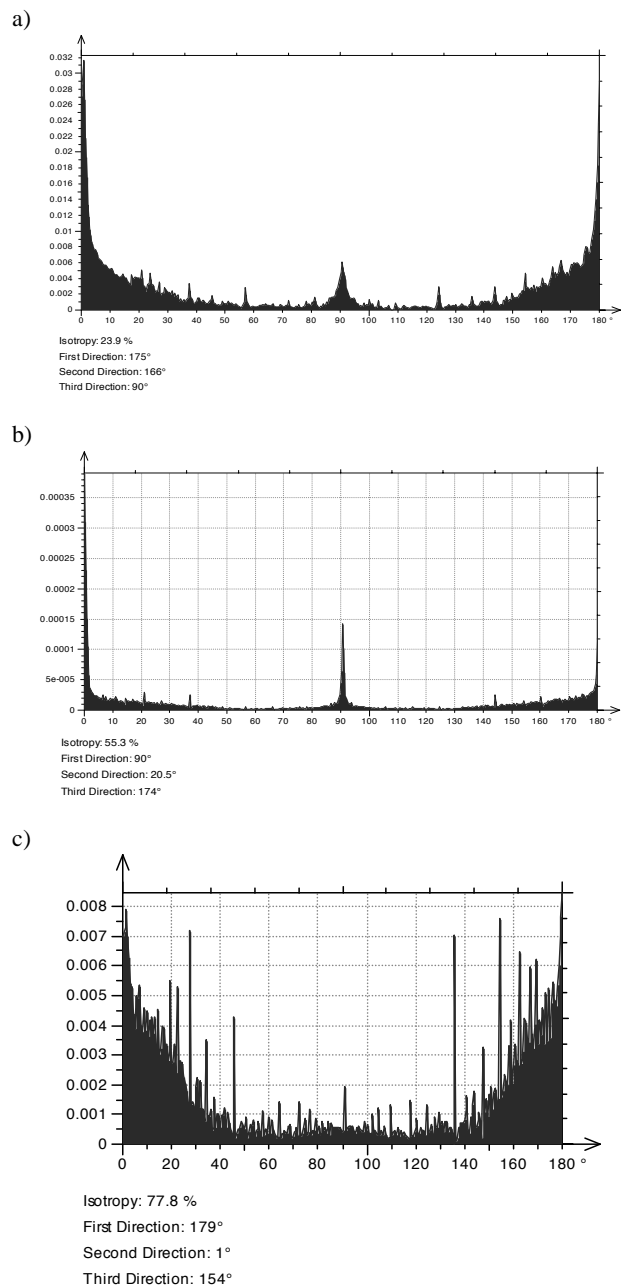


Fig. 10. The texture of surface (the schedule of characteristic directions) from EN AC-ALSi12(b) a) sand cast alloy; b) high pressure alloy; c) anodized and TiN coated sand cast EN AC-ALSi12(b) sand cast alloy

Based on the metallographic examinations made on the light microscope (Figs. 11-16) it was stated that the anodic layer produced on pressure die castings and sand mould castings for both alloys does not reveal any discontinuity, which prevents from formation of pitting and the precipitated silicon (in the form of needles) contained therein influences on gain in abrasive resistance.

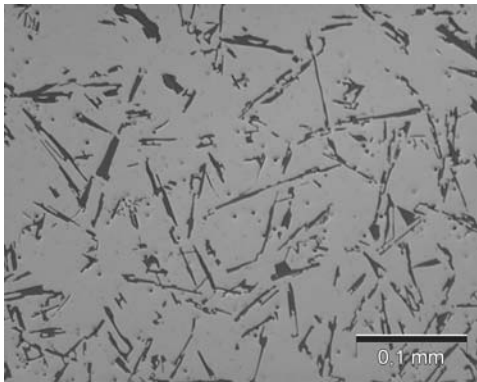


Fig. 11. structure of the EN AC-ALSi12(b) alloy, sand cast alloy, light microscope

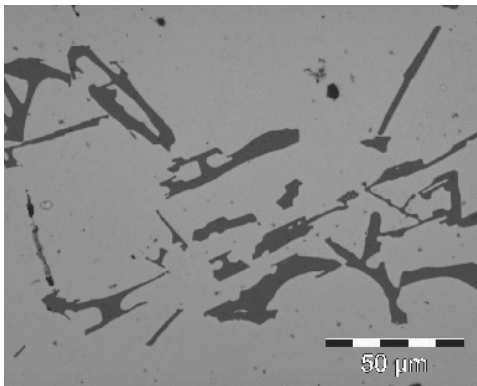


Fig. 12. structure of the EN AC-ALSi12(b) alloy, sand cast alloy, light microscope

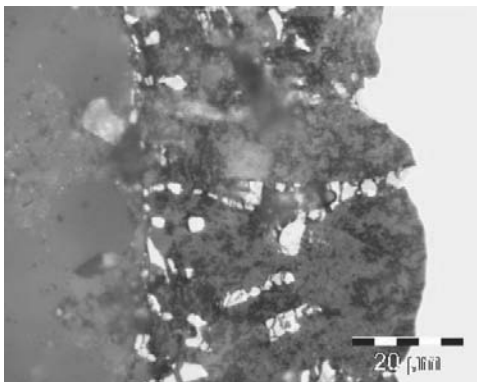


Fig. 13. Oxide cross-sections of anodic layer generated on the EN AC-ALSi12(b) alloy, sand cast alloy, light microscope

As a result of the abrasive wear test it was stated, that anodic treatment increases abrasive wear resistance. The best wear resistance was achieved for high thickness of anodic layer (about 48 μm). A partial removal of the coat was observed for all casts produced in a pressure casting die, where thickness of the coat is lower (about 10 μm). The samples made of EN AC-ALSi12(b)

alloy present greater loss in weight, which is caused by the fact that the testing place is located close to the electrode attachment (the layer in this place is probably thinner).

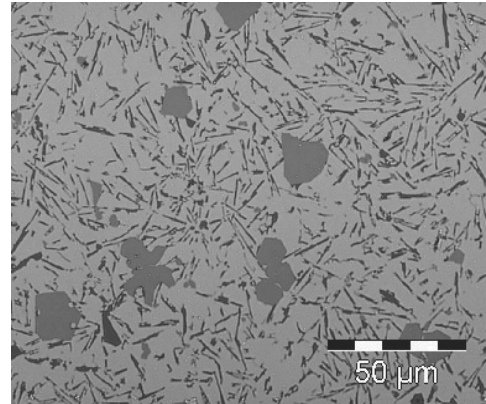


Fig. 14. Structure of the EN AC-ALSi12(b) alloy, high pressure cast alloy, light microscope

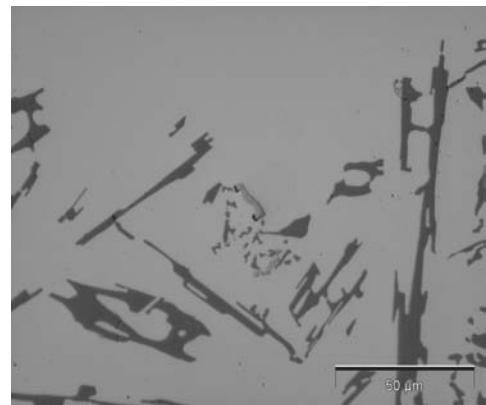


Fig. 15. Structure of the EN AC-ALSi12(b) alloy, high pressure cast alloy, light microscope

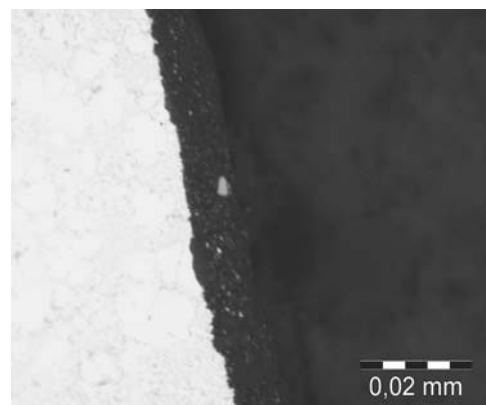


Fig. 16. Oxide cross-sections of anodic layer generated on the EN AC-ALSi12(b) alloy, high pressure cast alloy, light microscope

The results presented in Table 5 indicate that anodised samples made of the EN AC- $\text{AlSi12(b)}$  alloy, cast are characterised by the weight loss decreases from 30 to 47%.

Table 5.  
Mass loss in mg registered during wear test

alloy	Cast method			
	Sand cast		High pressure cast	
	unanodized	anodized	unanodized	anodized
EN AC- $\text{AlSi12(b)}$	14.0	10.2	18.7	10.0

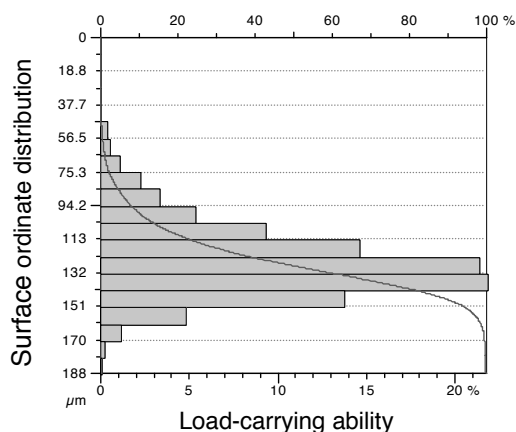


Fig. 17. Load-carrying ability curve (surface ordinate distribution)

## 4. Conclusions

The analysis involved geometry investigations of anodic layer surface proved the technology of casting for studied group of materials determining the quality of surface on the basis of its geometrical features. Similar results were obtained in [16].

The applying of an oxide layer reproduces the primary geometry of surface, shaped in casting process. The only attendance of applied kind of coat has not influence on characteristic features of surface.

Finally it can be stated that the additionally PVD coating on the anodised basis layer improves the friction coefficient value and therefore decreases the surface roughness (Fig. 17). This makes such technique more reliable for practical application, moreover also hardness increase will be achieved compared to the only anodised aluminium alloy samples.

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