



Stereometry specification and properties of anodization surface of casting aluminium alloys

J. Konieczny ^{a,*}, K. Labisz ^a, J. Wiczorek ^b, L.A. Dobrzański ^a

^a 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

^b 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

Received 08.05.2008; published in revised form 01.09.2008

ABSTRACT

Purpose: The aim of the work is presents the influence of casting method and anodic treatment parameters on properties, thickness and structure of an anodic layer formed on aluminium 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 aluminium alloys which both were founding by pressure die casting and gravity casting.

Findings: The researches included analyze of the influence of chemical composition, geometry, roughness and abrasive wear resistant of anodic layer obtained on aluminium casts.

Research limitations/implications: Contributes to research on anodic layer for aluminium 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 aluminium casting alloys, e.g. in the range of raising resistance on corrosion.

Originality/value: The range of possible applications increases for example as materials 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**

MATERIALS

1. Introduction

A progress in Materials Engineering made it possible to solve the problems connected with metallic materials strength satisfactorily as regards both structural and tool materials. In the continuous growth of use of alloys aluminium in different branches the wide comprehended

industry as well as development of technology of production of aluminium and its alloys and composites with aluminium matrix was observed in last years in many scientific centres on all world [1-5]. A considerable influence on the products' durability is exerted by properties of a surface layer.

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.

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.

The anodic layers have a protective – decorative function applying on the aluminium 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 aluminium woodwork [6, 7]. The oxides layers are produced on aluminium foil designed on electrode in condenser too. Hard anodic layers [8, 9] can be applied in air and motor industry.

Anodic oxide layers which are connected fixedly with the aluminium 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 phase of copper with aluminium dissolve during anodizing, which causes lowering the hardness and thickness of coats, and the enlargement the porosity [11].

The gain in thickness of the anodic layer in relation to the thickness of the formed oxide film amounts about to 0.001 μm per 1V. 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 [13]. 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 [14, 15].

During the forming process the aluminium oxide occurring the small increase of mass element as well as his volume. The layer of oxides is fixedly with substrate very strongly. Dissolving of oxides layer is possible only in basic solutions or acid about larger pH than 8.8 relatively lower than 4.0 [16-18].

During anodic treatment one can obtain the oxide layer, which is characterized by the structure presented on Fig. 1. The said layer is composed of a very thin and free of pores (a) dielectric basic layer – the so-called „barrier layer” (c) as well as of the underlying porous surface layer (b). Thickness of the basic layer depends on the voltage [V] applied during anodizing.

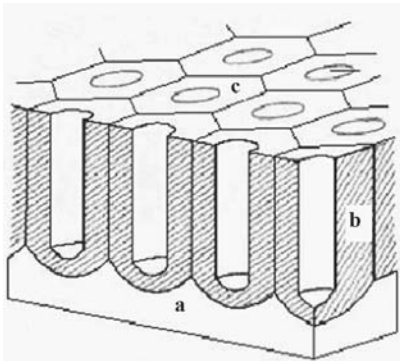


Fig. 1. Scheme of hexagonal, columnar structure of cells of anodic surface layer: a) barrier layer, b) porous layer, c) pores [12]

For example on Figure 2 show oxide layer creation on aluminium alloy.

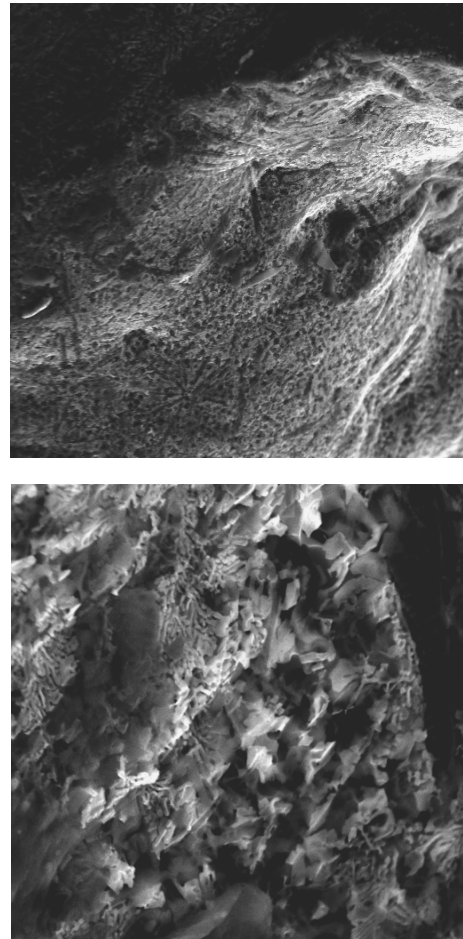
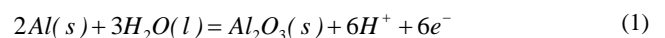


Fig. 2. Oxides layer Al_2O_3 creation on EN AC-ALSi12(b)+2% Mg, scanning microscope

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



and hydrogen evolves at the cathode:



Six main alumina oxide forms are mostly discussed (Table 1). Anodic Al_2O_3 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_2O_3 with sizes of 2-10 nm. Intermediate form between amorphous and γ -crystalline Al_2O_3 is considered γ' - Al_2O_3 . Shimizu [19] suggested that aluminium 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 ³)
Corundum	α -Al ₂ O ₃	hexagonal	3.97
Boehmite	α -Al ₂ O ₃ ·H ₂ O	ortho-rhombic	3.44
Gibbsite	α -Al ₂ O ₃ ·(H ₂ O) ₃	monoclinic	2.42
Diaspore	β -Al ₂ O ₃ ·H ₂ O	ortho-rhombic	3.4
Bayerite	β -Al ₂ O ₃ ·(H ₂ O) ₃	monoclinic	2.53
Gamma alumina	γ -Al ₂ O ₃	–	–

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) as well as EN AC-ALSi9Cu3(Fe) alloys. For both EN AC-ALSi12(b) as well as EN AC-ALSi9Cu3(Fe) alloys, high pressure and sand casting was used. The chemical composition of these alloys is showed in Table 2.

Four elements were anodized:

- EN AC-ALSi12(b) high pressure cast alloy,
- EN AC-ALSi12(b) sand cast alloy,
- EN AC-ALSi9Cu3(Fe) high pressure cast alloy,
- EN AC-ALSi9Cu3(Fe) sand cast alloy.

To determine the influence of a kind of electrolyte 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 following electrolytes: 3% H₂C₂O₄, 4% H₃PO₄, 4% H₂SO₄, 3% CrO₃ (Table 3).

Table 2.
Concentration of alloying elements in EN AC-ALSi12(b) and EN AC-ALSi9Cu3(Fe) alloys

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
ALSi9Cu3(Fe)	9.5	0.5	0.9	0.5	1.5	3.0	Rest

Table 3.
Anodizing parameters

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

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 alloys used for investigation with similar chemical composition were cast by two methods: pressure and gravitational cast, therefore several factors as well:

- chemical composition of alloys,
- parameters of casting (pressure, to sand form),
- attendance of layer,

could have influence on the surface geometry formation.

Comparing the two- and three- dimensional surfaces figures (Figs. 3 and 4) as well roughness distribution can be clearly state that investigated samples any chemical composition influence on surface forming 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. 5).

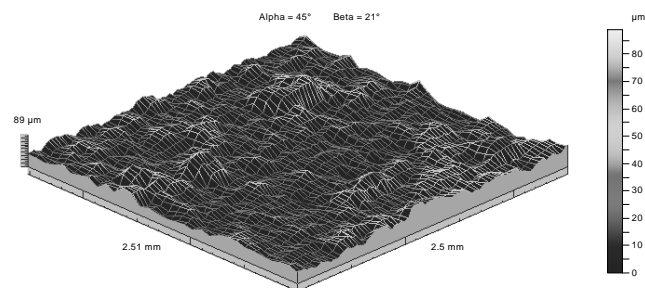


Fig. 3. The geometrical shape of fragment of studied surface, topography of 3D surface, sand cast EN AC-ALSi12(b) alloy

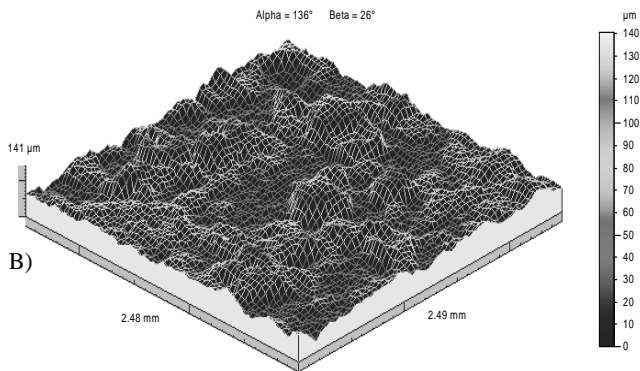


Fig. 4. The geometrical shape of fragment of studied surface, topography of 3D surface, sand cast EN AC-AlSi9Cu3(Fe) alloy

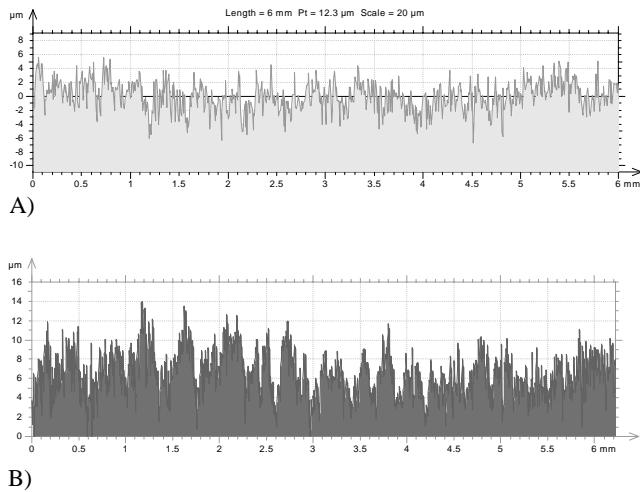


Fig. 5. Profiles 2D cut out from studied surface in plane N - S, EN AC-AlSi12(b) high pressure cast alloy; A) before anodization, B) after anodization

The roughness values achieves the maximum by 80 μm . 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.

For high pressure cast materials, the maximum roughness value of surface does not exceed 15 μm (Fig. 6). The roughness distribution on the whole analyzed surface is identical without of any anomalies. On the EN AC-AlSi 9Cu3(Fe) alloy surface there was observed an “acclivity” going across the investigated surface.

This “acclivity” has a high of circa 5 μm . 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 witch will be helpful for unequivocally genesis of this “acclivity”.

Comparing of the results of obtained investigations for samples before and after applying the layer, it can be seen that applying layer hasn't any influence on geometrical characteristics of the surface. The roughness distribution observed on 3D images after applying of the layer doesn't not change. The distribution for each set (unanodized – anodized 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 (Fig. 9).

The anodic layer hasn't any influence on roughness value of the surface (for casts high pressure max 15 μm , for casts sand 60 to 70 μm).

Based on the metallographic examinations made on the light microscope showed on Figures 10-17 it can be concluded that:

- generally the microstructure of the anodized alloy hasn't any influence on the anodization process and on the properties and quality of the achieved anodic layer;
- 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.

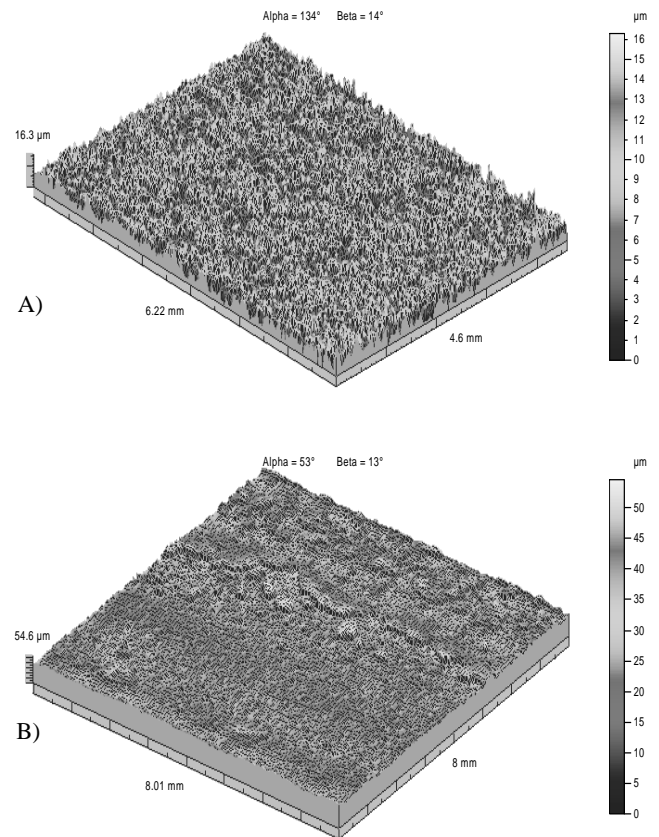


Fig. 6. Three-dimensional topography of surface, high pressure cast alloys; A) EN AC-AlSi12(b), B) EN AC-AlSi9Cu3(Fe)

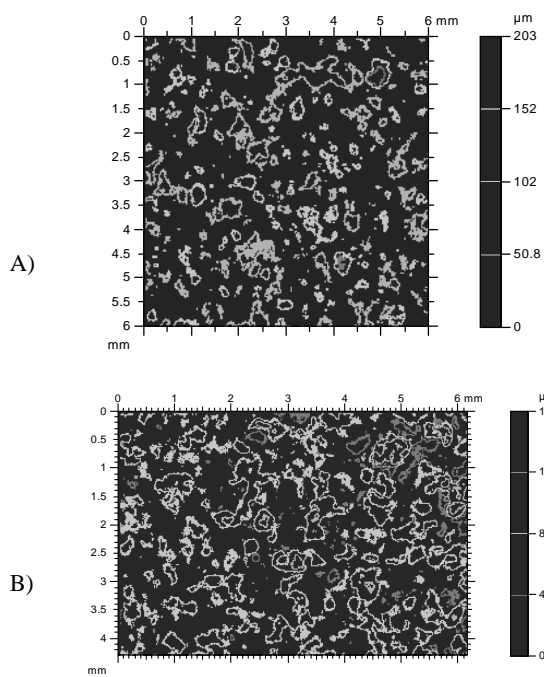


Fig. 7. The distribution of tops on surface of sample from EN AC-ALSi9Cu3(Fe) sand cast alloy A) before anodization, B) after anodization

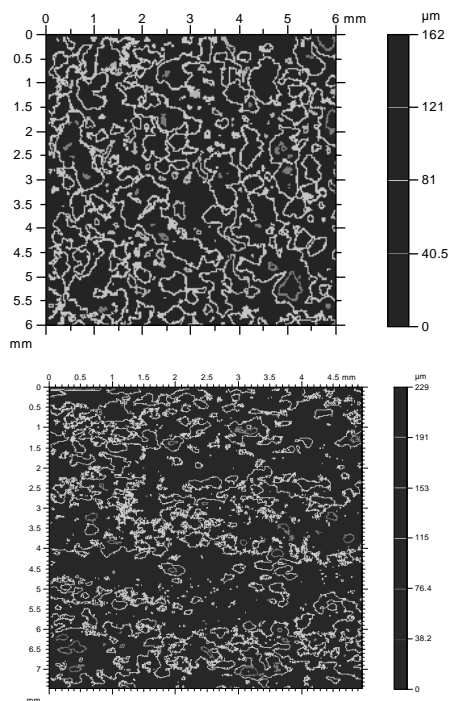
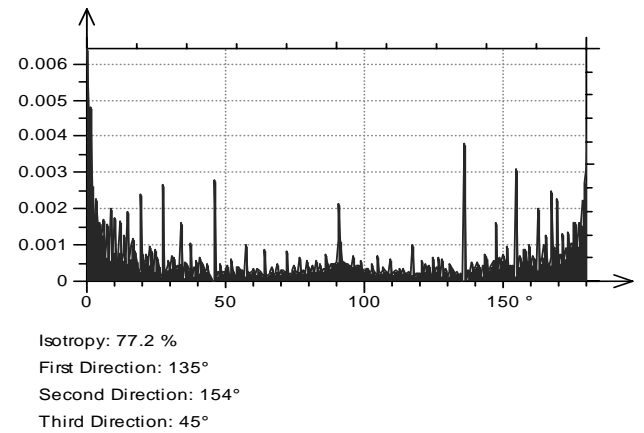
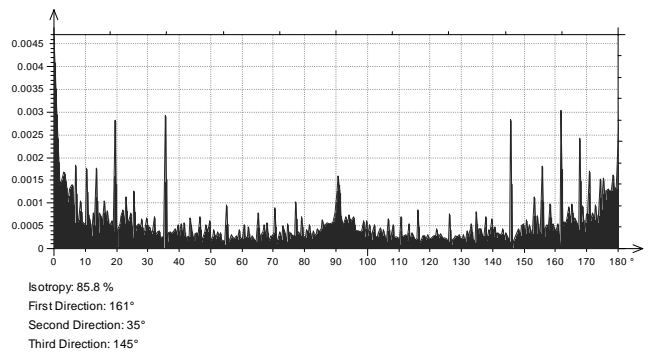


Fig. 8. The distribution of tops on surface of sample from EN AC-ALSi12(b) sand cast alloy A) before anodization, B) after anodization



A)



B)

Fig. 9. The texture of surface (the schedule of characteristic directions) from EN AC-ALSi9Cu3(Fe) sand cast alloy A) before anodization, B) after anodization

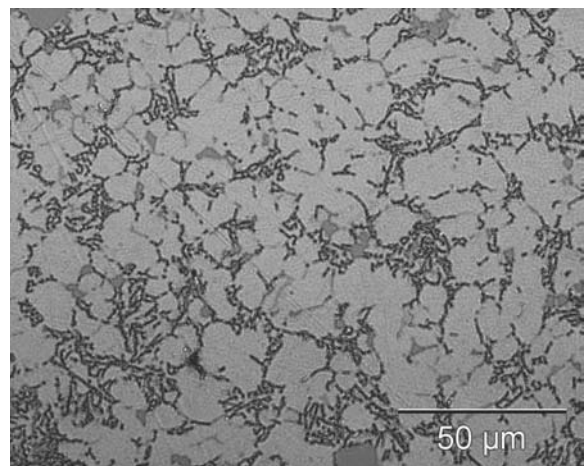


Fig. 10. Structure of the EN AC-ALSi9Cu3(Fe) aluminium alloy, high pressure cast alloy, light microscope

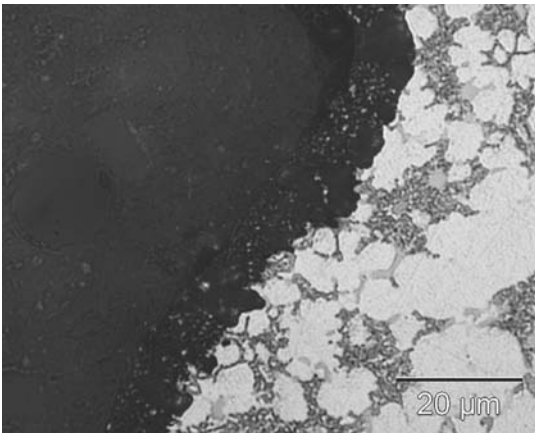


Fig. 11. Oxide cross-sections of anodic layer generated on the EN AC-AlSi9Cu3(Fe) alloy, high pressure cast alloy, light microscope

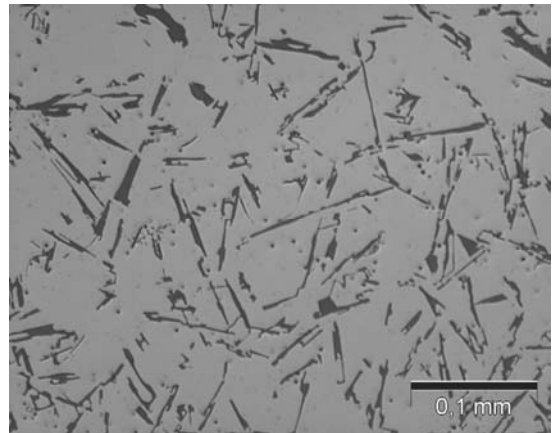


Fig. 14. structure of the EN AC-AlSi12(b) alloy, sand cast alloy, light microscope

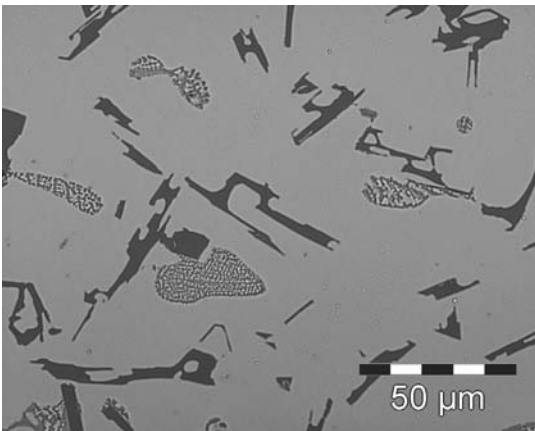


Fig. 12. Structure of the EN AC-AlSi9Cu3(Fe) alloy, sand cast alloy, light microscope

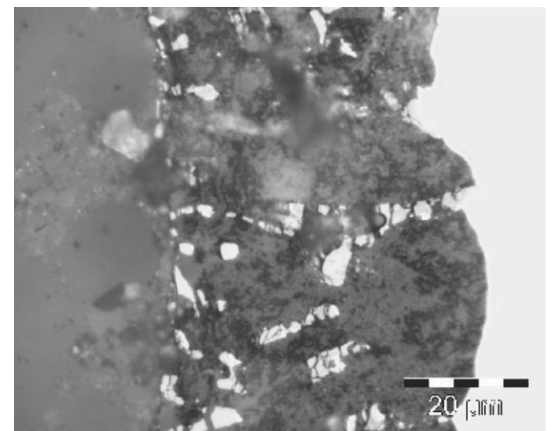


Fig. 15. Oxide cross-sections of anodic layer generated on the EN AC-AlSi12(b) alloy, sand cast alloy, light microscope

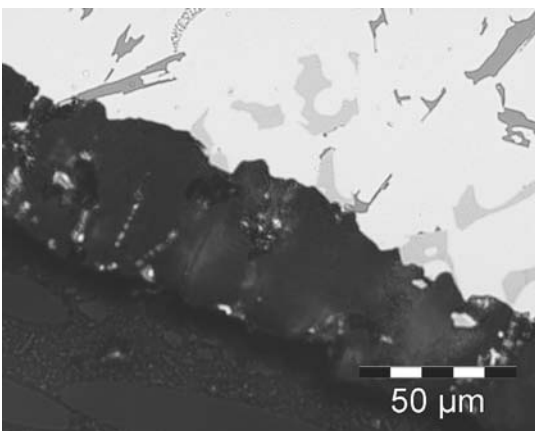


Fig. 13. Oxide cross-sections of anodic layer generated on the EN AC-AlSi9Cu3(Fe) alloy, sand cast alloy

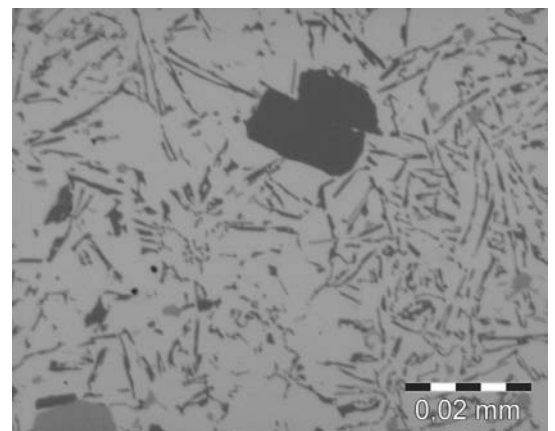


Fig. 16. Structure of the EN AC-AlSi12(b) alloy, high pressure cast alloy, light microscope



Fig. 17. Oxide cross-sections of anodic layer generated on the EN AC-ALSi12(b) alloy, high pressure 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).

Table 4.
Mass loss in mg registered during wear test

alloy	Cast method			
	Sand cast		High pressure cast	
	unanodized	anodized	unanodized	anodized
EN AC-ALSi12(b)	14.0	10.2	18.7	10.0
EN AC-ALSi9Cu3(Fe)	14.7	7.3	17.6	10.9

The results presented in Table 4 indicate that anodised samples made of the EN AC-ALSi9Cu3(Fe) alloy, cast into a sand mould, are characterised by a half lower loss in weight in comparison to the not anodised samples. In other cases the weight loss decreases from 30 to 47%.

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 [21].

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.

Acknowledgements

The authors are very grateful to dr. Anna Dolata-Grosz from Department of Metal Alloy and Composites of Technology of Silesian University of Technology for casting alloy.

References

- [1] T. Haga, H. Sakaguchi, H. Inui, H. Watari, S. Kumai, Aluminum alloy semisolid strip casting using an unequal diameter twin roll caster, *Journal of Achievements in Materials and Manufacturing Engineering* 14 (2006) 157-162.
- [2] J. Myalski, J. Wiczorek, A. Dolata-Grosz, Tribological properties of heterophase composites with an aluminum matrix, *Journal of Achievements in Materials and Manufacturing Engineering* 15 (2006) 53-55.
- [3] M.H. Robert, D. Delbin, Production of cellular A2011 alloy from semi-solid state, *Journal of Achievements in Materials and Manufacturing Engineering* 17 (2006) 137-140.
- [4] M. Wierzbńska, J. Sieniawski, Effect of morphology of eutectic silicon crystals on mechanical properties and cleavage fracture toughness of AlSi5Cu1 alloy, *Journal of Achievements in Materials and Manufacturing Engineering* 14 (2006) 31-36.
- [5] M. Kciuk, The structure, mechanical properties and corrosion resistance of aluminum AlMg1Si1 alloy, *Journal of Achievements in Materials and Manufacturing Engineering* 16 (2006) 51-56.
- [6] A.W. Brace, *The Technology of Anodizing Aluminium*, Third Edition, Interall Srl, Modena, 2000.
- [7] K.P. Han, J.L. Fang, Decorative-protective coatings on aluminium, *Surface and Coatings Technology* 88 (1996) 178-182.
- [8] H. Konno, K. Utaka, R. Furuichi, Two step of anodizing process of aluminium as a means of improving the chemical and physical properties of oxide films, *Corrosion Science* 38/12 (1996) 2247-2256.
- [9] M. Maejima, K. Saruwatari, M. Takaya, Friction behaviour of anodic oxide film on aluminum impregnated with molybdenum sulfide compounds, *Surface and Coatings Technology* 132 (2000) 105-110.
- [10] I. Vrublevsky, V. Parkoun, V. Sokol, J. Schreckenbach, Study of chemical dissolution of the barrier oxide layer of porous alumina films formed in oxalic acid using a re-anodizing technique, *Applied Surface Science* 236 (2004) 270-277.
- [11] J. Konieczny, L.A. Dobrzański, K. Labisz, J. Duszczuk, The influence of cast method and anodizing parameters on structure and layer thickness of aluminum alloys, *Journal of Materials Processing Technology* 157-158 (2004) 718-723.
- [12] G. Patermarakis, K. Moussoutzanis, N. Nikolopoulos, Investigation of the incorporation of electrolyte anions in porous anodic Al_2O_3 films by employing a suitable probe catalytic reaction, *Journal Solid State Electrochem* 3 (1999) 193-204.
- [13] C. Sunseri, C. Spadaro, S. Piazza, M. Volpe, F. Di Quarto, Porosity of anodic alumina membranes from electrochemical measurements, *Journal of Solid State Electrochem* 10 (2006) 416-421.

- [14] L.E. Fratila-Apachitei, J. Duszczyk, L. Katgerman, AlSi(Cu) anodic oxide layers formed in H₂SO₄ at low temperature using different current waveforms, *Surface and Coatings Technology* 165 (2003) 232-240.
- [15] S. Wernick, R. Pinner, *The surface treatment of aluminium and its alloys*, ASN International Finishing Publications Ltd., Tedington, 1986.
- [16] L.E. Tichelaar, F.D. Thompson, G.E. Terryn, H. Skeldon, J. Duszczyk, A transmission electron microscopy study of hard anodic oxide layers on AlSi(Cu) alloys, *Electrochimica Acta* 49/19 (2004) 3169-3177.
- [17] I. Vrublevsky, V. Parkoun, J. Schreckenbach, G. Marx, Effect of the current density on the volume expansion of the deposited thin films of aluminum during porous oxide formation, *Applied Surface Science* 220 (2003) 51-59.
- [18] I. Vrublevsky, V. Parkoun, V. Sokol, J. Schreckenbach, G. Marx, The study of the volume expansion of aluminum during porous oxide formation at galvanostatic regime, *Applied Surface Science* 222 (2004) 215-225.
- [19] L.E. Fratila-Apachitei, H. Terryn, P. Skeldon, G.E. Thompson, J. Duszczyk, L. Katgerman, Influence of substrate microstructure on the growth, of anodic oxide layers, *Electrochimica Acta* 49/7 (2004) 1127-1140.
- [20] M.C. Maris-Sida, G.H. Meier, F.S. Pettit, Some water vapor effects during the oxidation of alloys that are α -Al₂O₃ formers, *Metallurgical and Materials Transactions* 34A/11 (2003) 2609-2619.
- [21] L.E. Fratila-Apachitei, J. Duszczyk, L. Katgerman, Voltage transients and morphology of AlSi(Cu) anodic oxide layers formed in H₂SO₄ at low temperature, *Surface and Coatings Technology* 157/1 (2002) 80-94.