



Anodising of aluminium matrix MMC composites

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ABSTRACT

Purpose: This elaboration presents the influence of casting method and anodic treatment parameters on thickness and structure of an anodic layer formed on aluminium alloys. As test materials it was employed the aluminium alloys AlSi12 and AlSi9Cu3, supplied by the Dutch company MIFA b.v., in which casting process and anodic treatment of samples were carried out also. It was presented herein grindability test results and metallographic examination, as well. Hardness of non-anodised alloys with those ones subjected to anodising process were compared.

Design/methodology/approach: The investigations were performed using light and electron microscopy for the microstructure determination. By mind of the transmission electron microscopy, especially selected area diffraction method appliance it was possible to determine the phases occurred in the alloy in the as cast state. The morphology and size of the layer was also possible to determine.

Findings: Concerning the anodising conditions for surface hardening the influence was studied. The structure of the surface laser tray changes in a way, that there is a different thickness of the produced layer.

Research limitations/implications: The aluminium samples were examined metallographically using optical microscope with different image techniques as well as light microscope.

Practical implications: Improving the anodisation technology with appliance of different anodising conditions. Some other investigation should be performed in the future, but the knowledge found in this research concerning the proper process parameters for each type of alloy shows an interesting investigation direction.

Originality/value: The combination of metallographic investigation for cast aluminium alloys - including electron microscope investigation - and anodising parameters makes the investigation very attractive for automobile, aviation industry, and others where aluminium alloys plays an important role.

Keywords: Anodising; Surface treatment; Aluminium alloys

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Anodising of aluminium is one of the most popular techniques, using for forming of porous structure. The appliance

of aluminium after anodising depends mainly on the properties of oxide layers occurred during this process. 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 [1,2].

Anodised profiles are practically does not require maintenance, unless the surface is not clean. The profiles surface can be easily washed with water with a neutral detergent or white spirit. The ability of a coating to protect against corrosion, discoloration and abrasion increases with its thickness [3-7]. Hard aluminium coatings are applied in aircraft and automotive industry [8,9].

For the first time on an industrial scale anodizing process was performed in 1923 in the UK, in order to increase the corrosion resistance of duralumin by Bengough'a and Stuart. Soon Gower and O'Brien in 1927, patented anodizing in sulphuric acid [10]. Technological process of anodizing in many cases it is very fast and has a stochastic nature [11].

It was found that at the beginning of the anodic oxidation of aluminium there is formed relatively thin and very hard barrier layer having a thickness of 0.01 - 0.1 microns, which is dominated by amorphous, anhydrous aluminium oxide. During anodizing on the surface there increases the porous coating, where through the electrolyte penetrates the coating. Due to the flow in an electric field of Al^{3+} (of metal) ions, and O_2 -ions (of the solution) there is formed the aluminium oxide coating. The outer layer is a strongly hydrated oxide layer, while the inner film is less hydrated [12-14].

The pores in the oxide coating of the hexagonal-shaped cells have a regular size of tubes extending from the barrier layer to the surface (Fig. 1). The pore size determines to a large extent the quality of the coating and depends only on the type of electrolyte [15,16]. The thickness of the barrier layer and the thickness of the pore layer depends mainly on the anode voltage [4,17]. The maximum coating thickness is obtained for the given conditions process, when the growth rate equals the dissolution rate of [18].

For the reason to seal (fill out) an oxide coating there is applied a treatment technology, consisting of heating of the anodized aluminium in distilled water at 96-98°C corresponding to the time during the anodizing. This results in filling the pores, due to the formation of Al_2O_3 hydrates and sealing the coating [19].

In addition to the electrical current parameters and the chemical composition of the electrolyte also alloying additives have an influence on of the anode layer formation of the anodized material.

If magnesium is solute in solid solution, it does not affect the appearance of oxide coatings, since the refractive index of the magnesium oxide is close to the value of Al_2O_3 . However, at higher contents of Mg (5%) the oxide coating can be bleary [9].

Alloys without Mn content are suitable for anodizing, the oxide coating is clear and transparent to the content of 1% Si, even if the structure exhibits a large heterogeneity. When the Si contents higher than 3%, the coatings are more and more grey

coloured, which is used to achieve diverse grey shades ($AlSi_5$). On further increasing the Si content, there are obtained dark, black or purple coatings [9].

Coloring of oxide coatings is performed during the anodizing process (one step process) or in a subsequent operation after a clear coating with appropriate porosity is obtained (two-stage process) [20, 21].

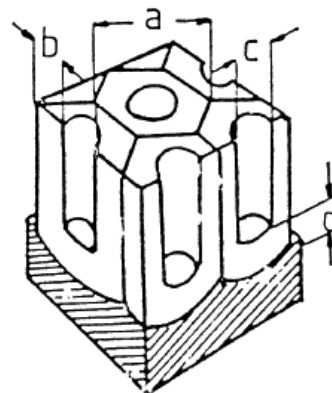


Fig. 1. Scheme of hexagonal, columnar structure of cells of anodic surface layer: (a) barrier layer; (b) porous layer; (c) pores [12]

In the industry, both civilian and military there are used light metal alloys, differing in mechanical properties and corrosion resistance. Each of technical aluminum alloys require modifying of the surface treatment methods and the optimization of chemical processes (electrochemical) for production of the protective coatings [22, 23].

Based on the morphology analysis of the surface there can be found, that it is possible to obtain layers with more or less developed porosity. It depends mainly on the electrolytic process parameters:

- Current density (process speed),
- Temperature of the electrolyte (granularity),
- Process duration.

Despite the assumptions and model presentation of the layer with regular pores, it can be found that on some figures the fibres of the aluminium oxide layer, or even their groups are bent and directed at different angles. This phenomenon may be due to the presence of impurities in the metal substrate.

During the anodizing process, additions are coming from the oxide film, causing a deviation from the columnar structure [24], as shown in Fig. 2. In the case of the investigated material the phenomenon described above is possible to occur.

Table 1.
Chemical composition of the $AlSi12$ and $AlSi9Cu3$ alloys

Alloy	Concentration of the elements %						
	Si	Mg	Cu	Mn	Fe	Zn	Al
$AlSi12$	12.5	0.05	0.05	0.5	0.6	0.1	Rest
$AlSi9Cu3$	9.5	1.5	3.0	0.5	0.9	0.5	Rest

Table 2.
Anodising parameters

Parameter	Value
Electrolyte	H ₂ SO ₄ with a concentration of 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 the aluminium ions	6-9 g/l

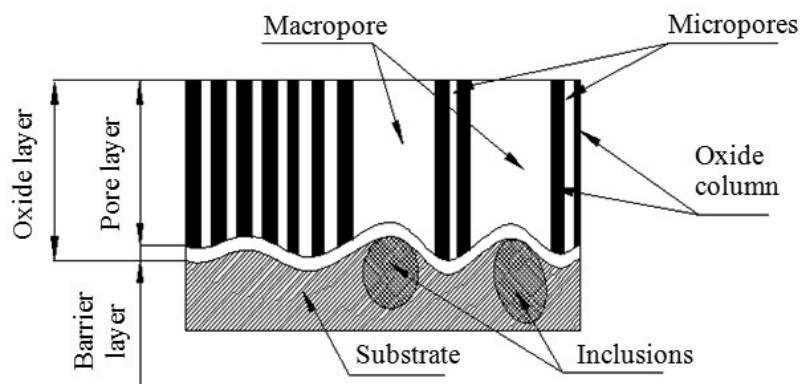


Fig. 2. Model of growing of the macro pores, causing deviations in the oxide layer, due to the influence of the additions in the metal matrix [22]

2. Material for investigations

Investigations were performed on AlSi12 and AlSi9Cu3 alloys samples. Casting and anodizing processes were carried out in the Dutch company MIFA. Both alloy AlSi12 and AlSi9Cu3 were cast using die casting and sand casting. The chemical composition of the alloys are given in Table 1

Technological parameters of the anodising process were presented in Table 2.

For evaluation of the electrolyte influence on the homogeneity of the pores in the oxide layer by identical anodising parameters there were investigated AlSi12 alloy samples in electrolytes like: 3% H₂C₂O₄, 4% H₃PO₄, 4% H₂SO₄, 3%CrO₃.

Wear test was performed using a ABR-8251 device supplied by TCD Teknologij ApS. The tests were carried out in accordance with the specifications and requirements of the standard ISO 8251. To applied test load was 4.9 N, sliding speed of 40 cycles / min. The test area was chosen as: 12 x 30 mm.

Metallographic investigations were carried out on the light microscope OLYMPUS of the BX60M type equipped with a camera Olympus DP10. Recording and processing of images was

made on a PC using the program analySIS supplied by OLYMPUS.

The investigations were performed on samples of aluminum alloys with the chemical composition presented in Table 3, as well as on samples from the composite material characterized in Table 4.

The aluminium alloy samples were subjected to the anodizing process in a sulphuric acid electrolyte containing H₂SO₄. The conditions and parameters of the electrolytic process are presented in Table 5, the anodisation process was carried out in a glass vessel where the anode was connected to the sample and cathode was applied in form of titanium sheet, a rectifier of the PDL t220type was used supplied by TESLA.

Analysis of surface geometry was based on data obtained from the measurement of selected areas of the castings, performed on a laser profilometer MicroProf supplied by the FRT company. Measurements were carried out for eight samples divided into two groups. The first is the initial material, in as cast state immediately after casting without any surface treatment. The second group was the material after the production of the oxide layer using the galvanic method. The investigations involve two types of aluminum alloys AlSi12 and AlSi9Cu3. Each alloy was cast by two methods: pressure cast and sand cast.

Table 3.
Designation, chemical composition [35]

Alloy designation	Chemical composition, [%at]									
	Si	Fe	Cu	Mn	Mg	Ni	Zn	Ti	Pb	Al.
EN-ACAlSi12 +2%Mg	10.5-13.5	≥ 0.65	≥ 0.15	≥ 0.55	≥ 0.1	≥ 0.1	≥ 0.15	≥ 0.2	≥ 0.1	rest

Table 4.

Type of composite matrix , designation and granularity

Type of composite	Designation	Matrix	Granularity
Composite without degassing	EN-AC AlSi12+2%Mg	10% Al ₂ O ₃ ,	100µm
		10% C glasslike (amorphous)	100µm
Composite after degassing	EN-AC AlSi12+2%Mg	10% Al ₂ O ₃ ,	100µm
		10% C glasslike (amorphous)	100µm

Table 5.

Parameters of the anodizing process in sulphuric acid solution

Parameters	Value
Electrolyte composition	H ₂ SO ₄ 300- $\frac{g}{dm^3}$
Temperature	18°-22°C
Anodic current density	$1-2-\frac{A}{dm^2}$
Current voltage	17- 22 V
Time	7 h
Kathode	Titan
Clams	Aluminium
Vessel material	glass

3. Investigation results

3.1. Wear resistance test results

As a result of the performed wear test, it was found that anodisation reduces wear resistance. The best wear resistance was achieved when the thickness of the anode layer is high (approximately 48 µm). Partial removing of the coating was observed for all high pressure casts, where the coating thickness is lowers (about 10 µm). AlSi12 alloy samples show increased

weight loss which is caused by the fact that the test area is close to the electrode mounting (the layer is at this point is probably thinner).

Analysing the test results presented on Fig. 3, there can be found that for the sand cast AlSi9Cu3 alloy the anodized samples have about half the mass loss compared to the non-anodised sample. In other cases there is registered a reduction in weight loss of 30 to 47%.

On the basis of the thickness measurements of the anodized layer, as shown on Fig. 4 it was found that for both alloys the thickness of the anodized layer formed is higher in the case of the sand cast material, and lower for high pressure cast material measured under the same anodizing parameters.

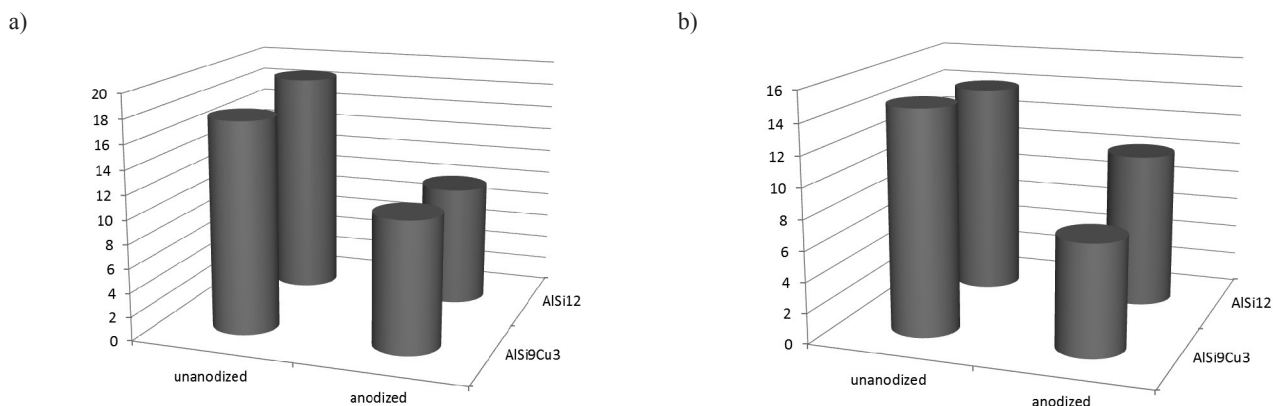


Fig. 3. Comparison of wear resistance of sand cast alloys (a) and high pressure cast alloys (b)

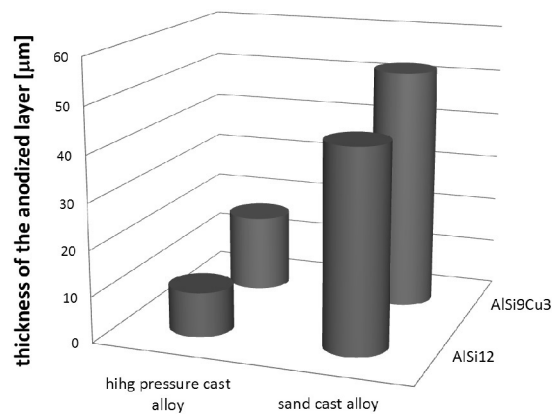


Fig. 4. Comparison of the thickness of the anodic layer formed on the alloy AlSi12 (sand casting and pressure) and AlSi9Cu3 (sand casting and pressure)

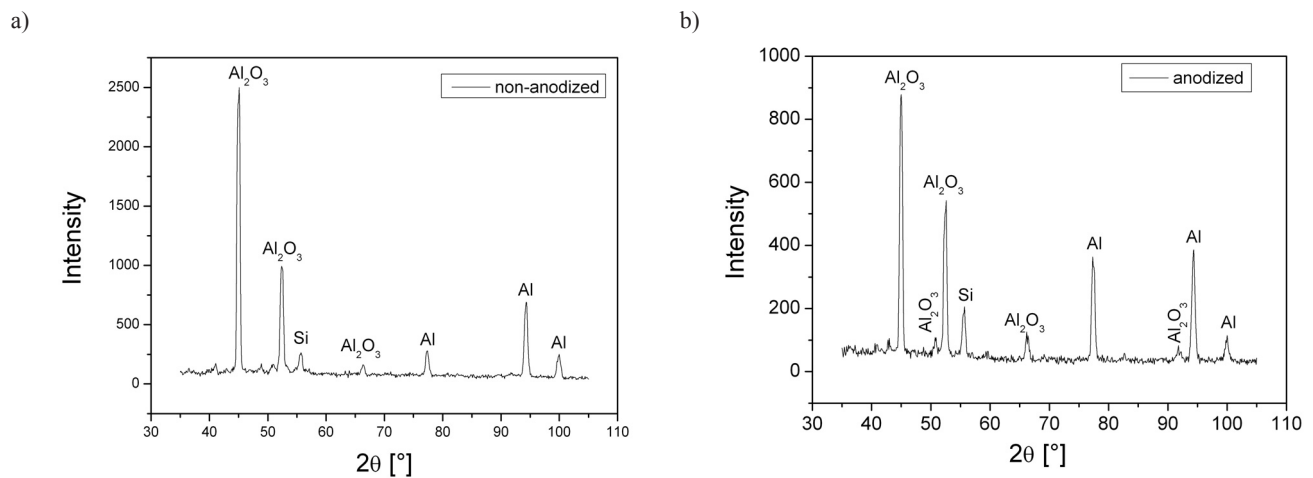


Fig. 5. X-Ray diffraction for the composite materials made on the basis of EN AC-AlSi12 (Al_2O_3 -C) non-anodised a) and anodised b)

Table 6.
Results of X-Ray diffraction analysis

Composite EN AC-AlSi12 (Al_2O_3 -C)							
Non-anodised				anodised			
2θ [°] calculated	2θ [°] tabulated	phase	plain	2θ [°] calculated	2θ [°] tabulated	phase	plain
45.03	45.56	Al_2O_3 (R3c)	111	44.89	44.98	Al (Fm3m)	111
52.44	52.205	Al_2O_3	033	50.75	51.33	Al_2O_3 (R3c)	113
55.70	55.53	Si (Fd3m)	220	52.63	52.205	Al_2O_3	033
66.38	66.112	Al_2O_3	1 3 4	55.71	55.53	Si (Fd3m)	220
77.26	77.37	Al (Fm3m)	220	66.22	66.22	Si (Fd3m)	311
94.26	94.207	Al (Fm3m)	331	66.43	66.112	Al_2O_3	1 3 4
99.95	99.84	Al (Fm3m)	222	77.26	77.37	Al (Fm3m)	220
				91.76	91.77	Si (Fd3m)	331
				92.21	92.375	Al_2O_3 (R3c)	1010
				94.41	94.207	Al (Fm3m)	331
				99.97	99.84	Al (Fm3m)	222

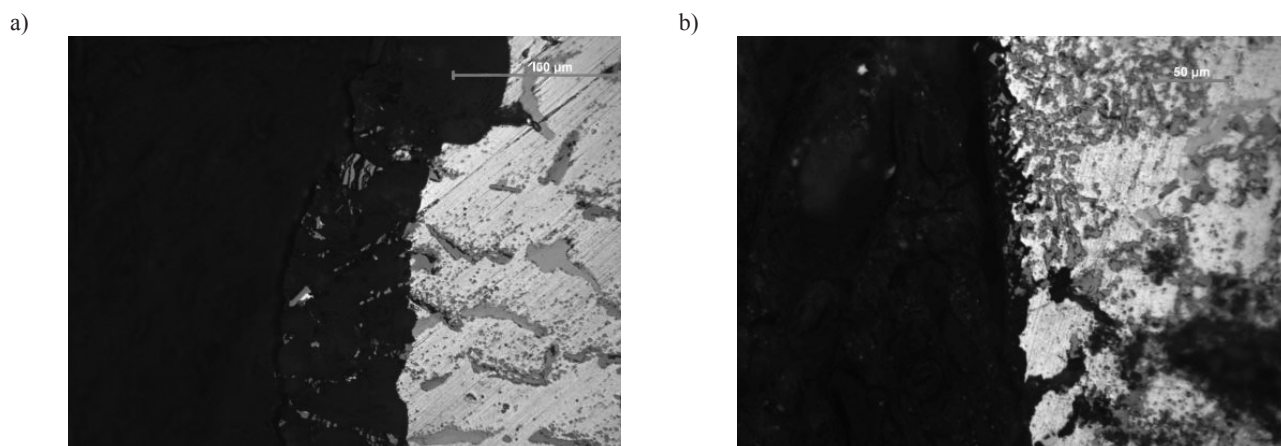


Fig. 6. Anodic layer produced on the composite EN-ACAlSi12 + 2%Mg + 10% Al_2O_3 + 10% C_s a) degassed, b) not degassed; light microscope

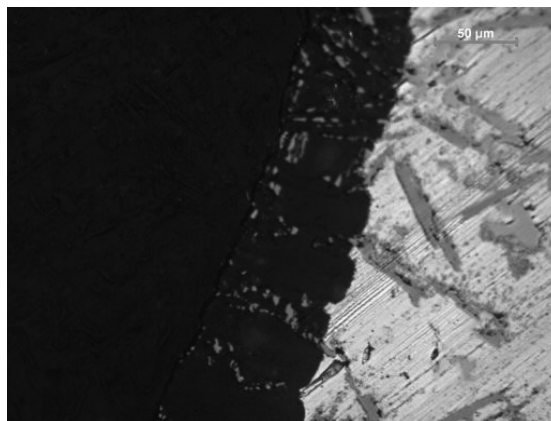


Fig. 7. Anodic layer produced on the alloy EN-AC AlSi12 + 2%Mg, light microscope

3.2. X-ray diffraction analysis results

For each of the investigated sample qualitative analysis X-ray diffraction was carried out (Fig. 5 and 8). Each phase, as a compound of the material, has its own characteristic picks, on the basis of which it can be identified. Phase analysis is based on the interpretation of the diffraction patterns obtained using the digital X-ray diffractometer. Grains of the investigated material must be coarser than 1 μm , to be adequate for this investigation. The obtained results includes a description of the identified crystalline phases and the diffraction pattern together with the, identified patterns of the phases (Table 6).

A lack of a pure Mg pick in the investigated material is due to the fact, that such a pick can occur by a lowest Mg concentration of 3% in the alloy [46]. Some pick represents more than only one plain of one phase.

3.3. Light microscope investigation results

Metallographic investigations were performed on the light microscope Leica MEF-4A (Figs. 6 and 7). There was measured

the thickness of the oxide layer in various areas of each of the samples. The results of measurements, statistical analysis, are presented in Table 7.

3.4. Hardness measurement results

Hardness measurements were performed on an automatic hardness tester Zwick of the ZHR type, using a penetrator in the form of sintered carbide ball with a diameter of 1/16 inch. The results of hardness measurements are presented in Tables 8 and 9.

3.5. Scanning electron microscope investigations

On the Figures 9-13, mage on the scanning electron microscope Opton DSM-940, equipped with an adapter for energy analysis of scattered X-ray Oxford Link ISIS EDS X Ride there is presented the structure of the Al_2O_3 layer.

Table 7.

Thickness of the anodised layer for chosen samples

Sample designation	Minimal thickness. μm	Maximal thickness. μm	Average thickness. μm	σ
Degassed	26.1	108.3	65	32.7
Not degassed	65	207.5	136.25	27.95

Table 8.

Hardness measurement results for the alloy EN-AC AlSi12+2%Mg, non anodized

	Degassed sample			Not degassed sample	
	HRF hardness for sample No 1	HRF hardness for sample No 2	HRF hardness for sample No 3	HRF hardness for sample No 1	HRF hardness for sample No 2a
Average value	82.71	79.24	86.64	82.84	84.57
Standard deviation	7.860089	4.912614	2.663415	5.383968	9.919907

Table 9.

Hardness measurement results for the alloy EN-AC AlSi12+2%Mg, anodized

	Degassed sample			Not degassed sample	
	HRF hardness for sample No 1	HRF hardness for sample No 2	HRF hardness for sample No 1	HRF hardness for sample No 2	HRF hardness for sample No 1
Average value	89.66	93.2	87.61	87.53	87.81
Standard deviation	2.139159	2.870153	3.405698	6.066493	4.535649

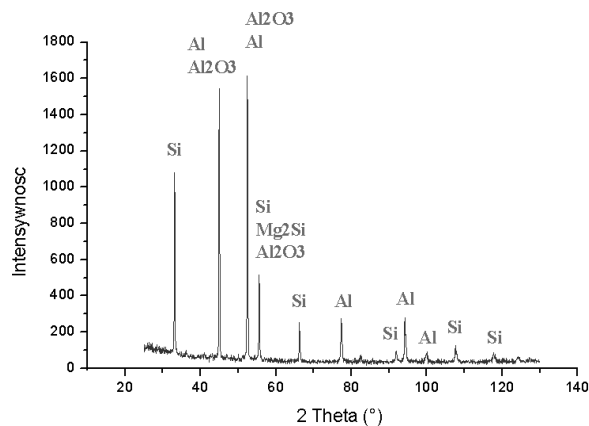
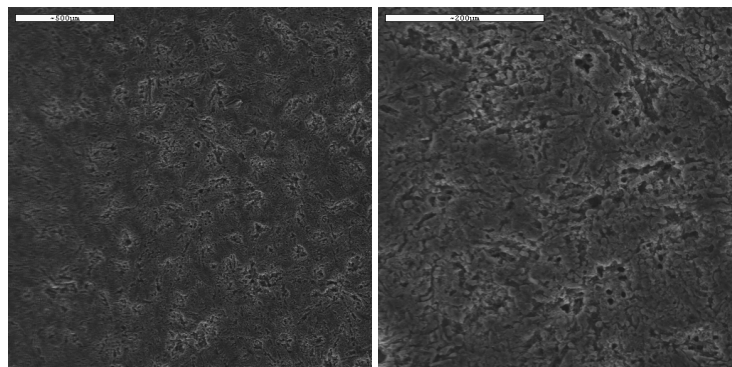


Fig. 8. X-Ray diffraction pattern for the anodised alloy AlSi12+2%Mg

Fig. 9. Al_2O_3 layer produced on the surface of the composite EN-AC AlSi12+2%Mg; SEM

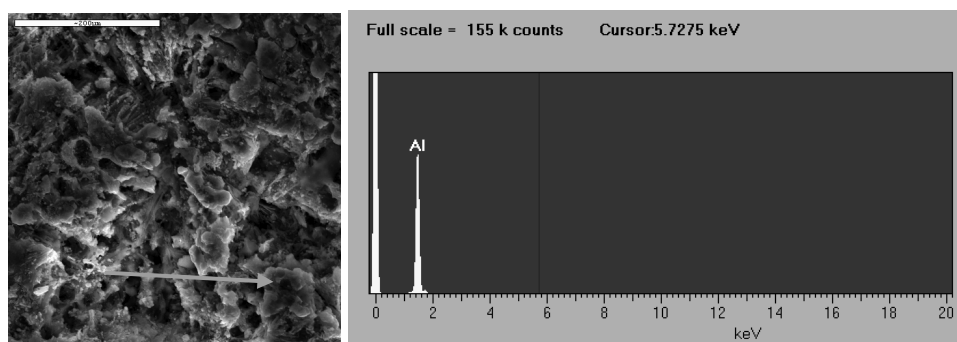


Fig. 10. Al_2O_3 layer produced on the surface of the composite EN-AC AlSi12+2%Mg; SEM, point-wise EDS analysis

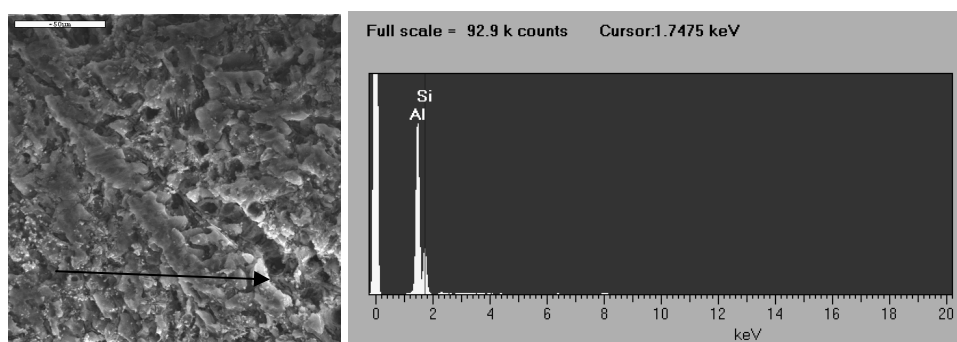


Fig. 11. Al_2O_3 layer produced on the surface of the composite EN-AC AlSi12+2%Mg; SEM, point-wise EDS analysis

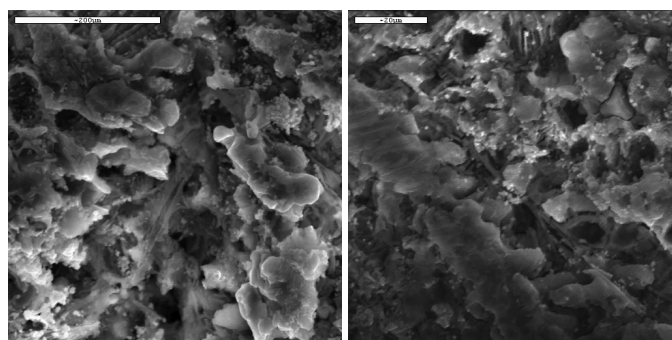


Fig. 12. Al_2O_3 layer produced on the surface of the composite EN-AC AlSi12+2%Mg; SEM

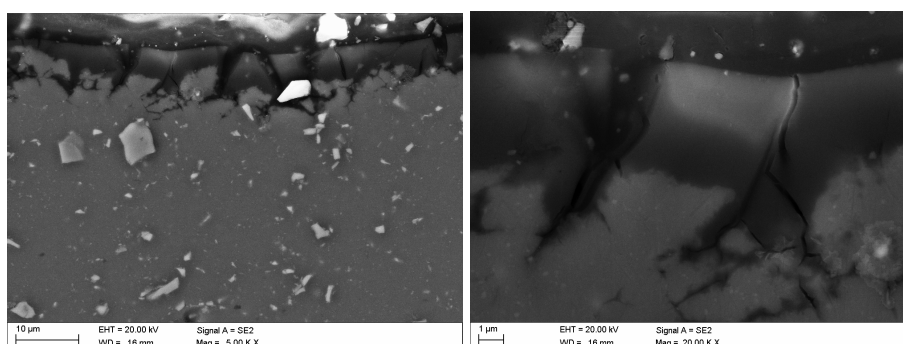


Fig. 13. Anodic layer on the surface of the composite EN-AC AlSi12+2%Mg; SEM

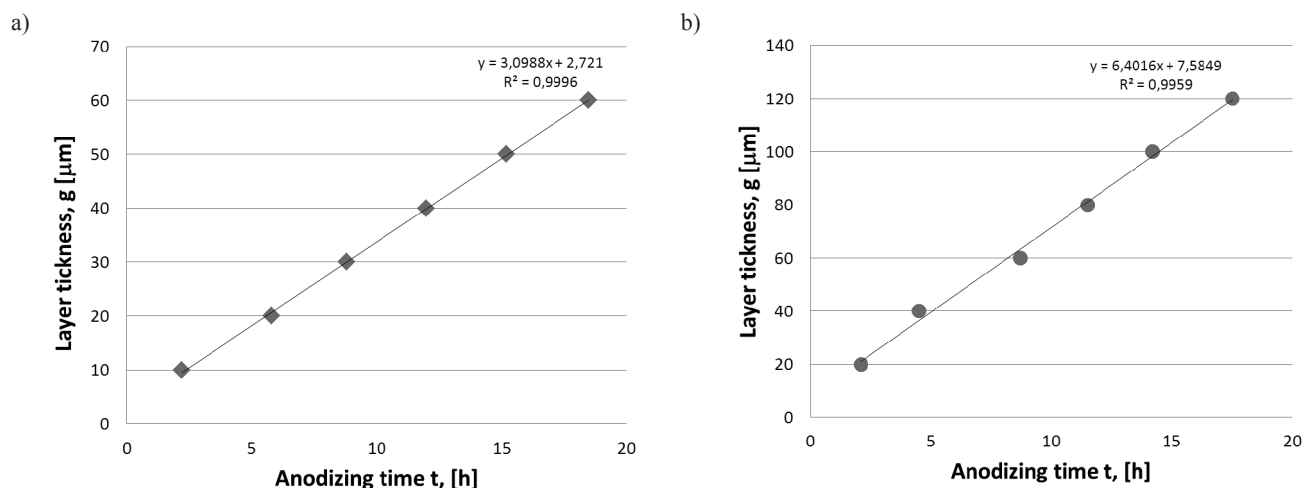


Fig. 14. Anodisation time t [h] influence on thickness of the anodic layer [μm], a) degassed composite, b) not degassed composite

The process of accumulation anode layer in terms of time after the approximation (Fig. 14) may be taken as a linear function [37]. The chart below shows the change in the thickness of the resulting layer at a time. As the final thickness of all the assumed average value of measurements.

4. Conclusions

The investigation results reported in Table 3 allows unequivocally to determine, which of the tested alloys in combination with an appropriate manufacturing method (pressure or sand casting) has the highest abrasion resistance. The best results should give a combination of the sand cast AlSi9Cu3 alloy and high pressure AlSi12 alloy.

The test results in the table we can observe that the anodized alloys, both AlSi9Cu3 and AlSi12 show less weight loss in comparison to nonanodized ones. It can be seen that the casting method also influences the resistance to abrasion. The sand cast alloys exhibit shows less weight loss during the test carried out, therefore, they have greater resistance to abrasion.

Based on the carried out investigations it could be found, that after the same anodizing time the thickness of the anodic layer is higher for not degassed material.

Based on the hardness measurement results, it can be concluded, that the samples after the anodisation process have greater hardness compared to those that have not been subjected to this process. The highest difference was recorded for the sample hardness of the alloy EN-AC AlSi12+2% Mg degassed, marked with number 2. After anodizing its hardness has increased to 13.96 HRF.

When comparing the hardness according to the degassing level, it can be seen that the anodized and degassed samples prior to casting have a higher hardness.

Anodic oxidation processes of aluminum are currently being developed mainly in order to increase competitiveness in the automobile, electronics, and other industries. A strong competition for aluminum anodic oxidation process are the painting technologies (mainly powder spraying). However, one of

still unsolved problems is the occurrence of filiform corrosion on the coated aluminum surface. Moreover, taking into account the recycling ability of aluminum products with oxide coating, it can be concluded that oxidation/anodisation remains the leading method of surface finishing of aluminum [31].

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