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INFLUENCE OF PRIMARY SILICON PRECIPITATES ON ANODIZED ALUMINUM ALLOYS SURFACE LAYER PROPERTIES

Summary. In this work, we presented the influence of the anodizing method and parameters, as well as the chemical composition of the used aluminium alloys on the properties and microstructure of the anodic layer produced on aluminium alloys, in particular on the size and morphology of the primary silicon precipitates and the homogeneity of the resulting oxide coating. Aluminium alloys AlSi8 and AlSi12, produced using the die-casting method and subsequently subjected to anodic oxidation were used as test material. The microstructure of the obtained surface layer was analyzed by taking into account the primary silicon precipitates. The results of the hardness and abrasive wear test also show the influence of anodizing and electrolyte parameters on the structure and properties of the tested aluminium alloys.

1. INTRODUCTION

Anodizing is an electrochemical conversion of the aluminum surface to its oxide, while the metal is the anode in an electrolytic cell, existing since the early 1930s. The primary purpose of the process is to increase corrosion resistance by providing a barrier to corrodents. Several metals are capable of being anodized, including aluminum, magnesium, titanium, and tantalum. Anodized aluminum is used in many applications due to its low cost, esthetic qualities, and ideal mechanical properties. Acid anodizing produces a coating with a thickness of 0.00015–0.00025 inches, and pores in the coating can be sealed by immersion in a dichromate solution.

It is also used because of its thermal properties designed for producing of technical means of transport. This material can also be coated on other engineering materials with a possible usage of these coatings for producing of cooling cabins on vehicles, letting us to reduce fuel for maintenance of the given temperature. It has an important influence on transport quality and quality costs [1-4].

Unlike most protective coatings, anodizing permanently changes the outer structure of the metal. When aluminum is exposed to air, it naturally develops a thin aluminum oxide film that seals the aluminum from further oxidation. The anodizing process makes the oxidized surface much thicker, up to several micrometers. The anodized aluminum oxide coating is very hard, enhancing the abrasion resistance of the aluminum. The achieved depth of the oxide layer improves the corrosion resistance of the aluminum, while making cleaning of the surface easier. The porous nature of particular types of anodizing makes it possible to dye the aluminum in a variety of colors, making it more attractive [5-11].

For anodizing, different aluminum alloys are also used in these investigations: AlSi8 and AlSi12. Higher-purity alloys are always preferred for anodizing and anodize better, producing better finishes.

Alloying elements such as copper or silicon do not anodize and leave microscopic voids in the aluminum oxide film. Since the anodizing process converts the aluminum to aluminum oxide to form the anodized finish, higher-purity aluminum will yield a denser and harder layer of aluminum oxide. High concentrations of some alloying elements will also affect the surface finish and color of the anodized finish and will reduce the effectiveness of the sealing process, causing reduced corrosion and wear resistance and decreasing fade resistance in dyed parts [12-15].

Nowadays more and more producers decide to use aluminum. There is no industry sector that could not be used for this resource. According to Modern Trends and Challenges of Development of Global Aluminum Industry "…nearly all branches of global industry consume aluminum. Mechanic engineering, defense industry, aircraft engineering and shipbuilding, power production industry, fabrication of construction materials should be especially mentioned". That is why many see aluminum as a "strategic metal" on a global market.

Transport is the single largest sector for aluminum products in Europe, absorbing almost 40% of industry output. It is the largest percentage among all industries using this material. The public transport benefits from its use, which is always looking for optimal solutions based on savings and innovation. Anodized aluminum lightweight characteristics can reduce the weight of a range of vehicles from passenger aircraft to cars, increasing fuel efficiency and reducing CO_2 emissions. Anodized aluminum can be used in public transport because of its various advantages.

The growing demand for aluminum results, among others, from continuous technological development, which allows the wider and better use of its properties. Better properties of aluminum that we can obtain after anodizing improve its applicability. Using anodized aluminum will help to save money as well as reduce the negative impact on the environment [16-19]. The advantages of anodized coatings make them applicable in many industries, and for several decades.

Correctly made anode coatings, in addition to very good protective properties, give the surfaces an esthetic appearance, which is why they are often used in construction. Modern building facades, finishing details both inside and outside objects, window frames, doors, and even constructions of winter gardens or sports facilities—in each of these cases, anodized aluminum components will work perfectly. It is possible to anodize aluminum components for furniture companies and car manufacturers who appreciate both the beauty and durability of our solutions.

This is obviously not the only possible application. The anodized elements also reach the shipyards (after anodizing, some aluminum alloys do not corrode in chlorides) and electronic manufacturers (anodized non-conductive layer), and due to the high resistance of the oxide layer to abrasion, anodized materials (technical anodizing) are used in parts in moving machines, e.g., the aviation industry. Manufacturers of LED and lighting fittings also use anodized aluminum, for the production of both internal and external lamps.

The anodizing process, although complicated, exceeds the limits of "big industry" and becomes an everyday element of ordinary consumers. The aluminum anodizing process consists of the following steps:

- Pretreatment: This process removes accumulated contaminants and light oils.
- Rinsing: Multiple rinses, some using strictly deionized water, follow each process step.
- Etching (chemical milling): Etching in caustic soda (sodium hydroxide) prepares the aluminum for anodizing by chemically removing a thin layer of aluminum.
- Desmutting: Rinsing in an acidic solution removes unwanted surface alloy constituent particles not removed by the etching process.
- Anodizing: Aluminum is immersed in a tank containing an electrolyte.
- Coloring: Anodic films are well suited to a variety of coloring methods, including absorptive dyeing, both organic and inorganic dyestuffs, and electrolytic coloring.
- Sealing: In all the anodizing processes, the proper sealing of the porous oxide coating is absolutely essential to the satisfactory performance of the coating.

Anodized aluminum is used for the food industry (the anodized metal surface may come into contact with products intended for consumption), hence, it is available on the market aluminum pots or countertops, refrigerated counters, shelves, etc. This material is also increasingly appearing in jewelry, where it begins to be treated equally with other base metals, such as copper or titanium. Many colors and forms, as well as the high plasticity of aluminum as a plastic, combined with a unique set of features that leads to anodizing, make the possibilities of its use seem almost limitless today [20-29].

Aluminum is used in transportation because of its unbeatable strength-to-weight ratio. Its lighter weight means that less force is required to move the vehicle, leading to greater fuel efficiency. Although aluminum is not the strongest metal, anodizing helps to increase its strength. Its corrosion resistance is an added bonus, eliminating the need for heavy and expensive anti-corrosion coatings.

While the auto industry still relies heavily on steel, the drive to increase fuel efficiency and reduce CO_2 emissions has led to a much wider use of aluminum. Experts predict that the average aluminum content in a car will increase to 60% by 2025.

Not only Asia, but also Europe appreciates the advantages of aluminum. Alstom-EMU250 is an Italian train from the Pendolino family, which in 2014 appeared on Polish tracks. The boxes of its wagons are self-supporting and made of light aluminum alloys. The profiles used combine with each other by sliding in the so-called “Dovetail”, and the places where they are joined are welded by welding robots. Aluminum is an extremely plastic material that can be shaped in a very simple way. There are many methods of machining or joining, so you can easily choose the right method for the selected type of alloy, its thickness, and preferred shape. Aluminum components are successfully used in all kinds of transport, where machining of details is a very important issue.

The manufacturers of rolling stock depend on projects of light construction and individualized production, both in the scope of structural profiles as well as external and internal elements.

Aluminum is one of the main materials used in the construction of train bodies. Among the applications, side walls of the body, roof and floor panels, and parts connecting the floor with the sidewall of the train can be found.

The use of aluminum in the construction of wagons makes their surface uniform and smooth—and unlike steel, it does not “waver.” This means that after assembly, the scope of finishing works is smaller and the total production time is shortened. Beside smoothing of the surface, smutting can also occur, which can be encountered, e.g., in sealing processes, typically during hydrothermal sealing procedures. Smutting can result from the conversion of the coating surface to boehmite. Smutting is typically associated with high operational temperature and pH, long immersion time, aged sealing solution containing too much dissolved solids and breakdown components of additives, and shortage of antismutting agents and/or surface-active agents. Antismutting agents can inhibit the formation of boehmite on the coating surface without adversely affecting the sealing process within the micropores. Typical antismutting agents include, for example, hydroxycarboxylic acids, lignosulfonates, cycloaliphatic or aromatic polycarboxylic acids, naphthalene sulfonic acids, polyacrylic acids, phosphonates, sulfonated phenol, phosphonocarboxylic acids, polyphosphinocarboxylic acids, phosphonic acids, and triazine derivatives [27].

Cast aluminum parts in general will not anodize as well because of their tendency toward porosity. Pores do not anodize and contribute to the same type of problem that highly alloyed aluminum parts encounter. Good high-density castings without porosity will anodize with good results [16-19].

Dimensional growth during anodizing—as previously mentioned, anodizing is the process of electrochemically converting the surface of an aluminum part to aluminum oxide. Aluminum oxide occupies about two times the volume as that of raw aluminum, including the intermetallic phases present in the basic alloy, for this reason, it is important to investigate the influence not only of the anodizing parameters but also on the alloy chemical composition on the structure and properties of the obtained final product.

2. MATERIAL AND INVESTIGATION METHODS

2.1. Material

Investigations were carried out on the AlSi8 as well as AlSi12 aluminum-cast alloys. For both AlSi8 andAlSi12 alloys, the high-pressure casting method was used. The chemical composition of these alloys is presented in Table 1.

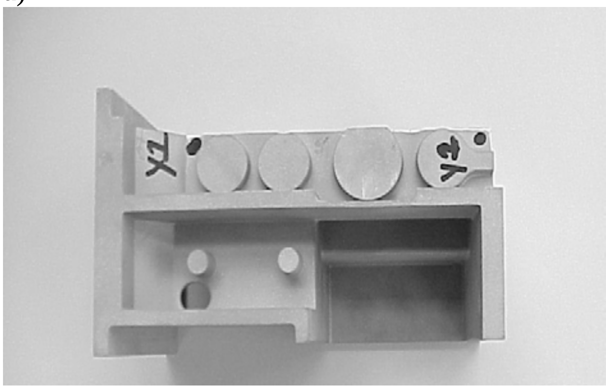
Table 1

Chemical composition of the investigated cast aluminium alloys AlSi8 and AlSi12

Alloy type	Elements concentration, % (mass)						
	Si	Mg	Cu	Mn	Fe	Zn	Al
AlSi8	7,8	0,03	0,03	0,13	0,3	0,1	Balance
AlSi12	12,5	0,05	0,05	0,5	0,6	0,1	Balance

For anodizing, two elements were selected, the AlSi12 high-pressure cast alloy and AlSi8 high-pressure cast alloy. Technological parameters of the anodizing process are shown in Table 2. The anodized elements of AlSi12 as well as AlSi8 high-pressure alloys are shown in Figs. 1a and 1b.

a)



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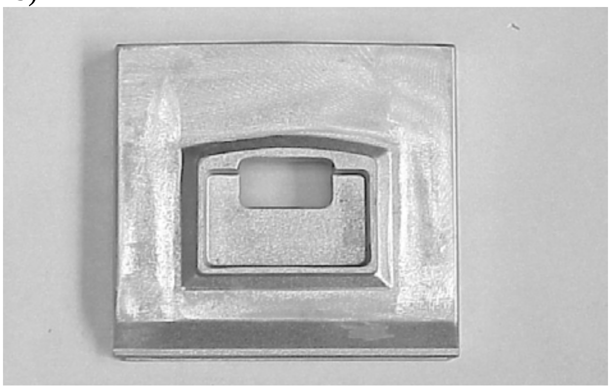

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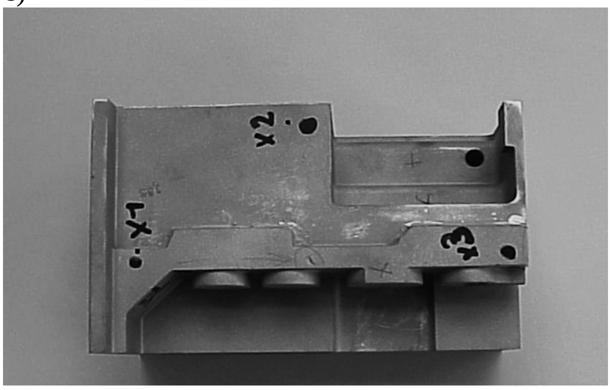

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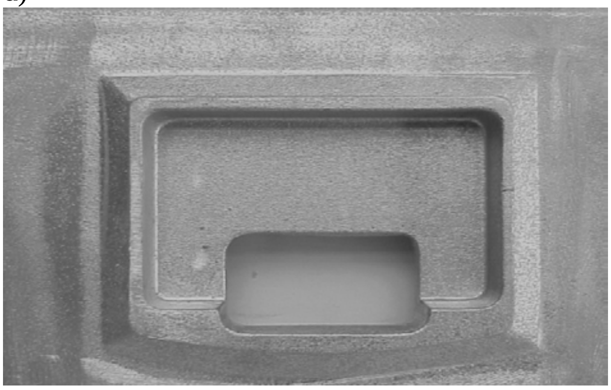

Fig. 1. Parts of housing used for anodizing in the state before anodizing: a) AlSi12, b) AlSi8 and after anodizing: c) AlSi12, d) AlSi8

2.2. Methods

To determine the influence of a kind of electrolyte on the homogeneity of pores in the oxide layer at the same conditions, the samples of the AlSi8 as well as the AlSi12 alloy were put under anodic treatment in the presence of the following electrolytes: 3% $H_2C_2O_4$, 4% H_3PO_4, 4% H_2SO_4, and 3% CrO_3. For final investigation, however, due to the initial quality of the obtained anodic layer, sulfuric acid 3% H_2SO_4 was chosen. The entire anodization process was carried out according to the parameters and conditions present in Table 2. It should be mentioned that all the given current conditions were the same for all tested acids, as well as the temperature value. In the case of other acids, some damages (Fig. 2) or discontinuities of the obtained alumina surface were observed.

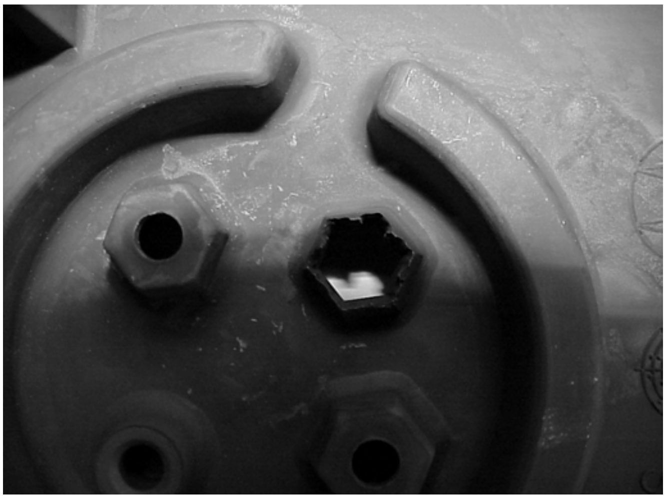

Fig. 2. Element damage occurred after anodizing in other acids than H_2SO_4

Table 2

Anodizing parameters applied for the investigated aluminium alloys

Parameter	Value
Electrolyte	H_2SO_4 with a concentration 295 ÷ 315 g/l
Temperature	–4÷ 2 °C
Pulse 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

For investigations of the microstructure, the following tests were carried out:

- Samples were cut on saw using the Discotom-2 saw model supplied by Struers.
- The specimens were mounted in Resin 4 using the press LaboPress-3 supplied by Struers.
- Grinding was performed on SiC paper (size 80, 120, 180, 240, 320, 400, and 600) using the grinding machine model Rotor-2 supplied by Knuth.
- Polishing was performed using the polishing machine model RotoPol-31 (with RotoForce-4, Multidoser, and Rotocom) all supplied by Struers. Polishing steps were performed according to the Metalog A Methods provided by Struers.
- The optical micrographs were obtained using a light microscope (model BX60M supplied by Olympus). The microscope was equipped with a camera supplied by Olympus and connected with the computer. The program "analySIS" was used to capture the photos.

- Wear test investigation: Abrasive wear tests were performed using the tester model ABR-8251 supplied by TCD Teknologi ApS. The tests were performed according to the specifications of the standard ISO 8251, presented below (Table 3):

Table 3

Conditions for the abrasive wear tests

Load	4.9 N (500 g)
Slide velocity	40 cycles/min
Abrasive wheel steps	400 steps/rotation
Wear area	12×30 mm
Humidity	63%
Temperature	23 ºC
Replicates	2

Wear resistance is expressed in mass loss [mg]. Each sample was weighed before and after the wear test. Data presented in Table 3 are average values.

3. INVESTIGATION RESULTS

Based on the result of the macrostructure investigations of the treated parts, a relatively large color change of the surface after anodizing was found (Fig. 1). The color change may result from different mechanisms, as there are

- Phenomenon of silicon smutting that causes the characteristic gray color observed, caused by silicon atoms present in the created alumina layer during anodization.
- Conventional hydrothermal sealing process was performed by immersion or exposure to hot water or steam at temperatures above 80° C to hydrate the anhydrous oxide (Al_2O_3) in anodic coatings to form boehmite-like crystals (AlO(OH)) according to the following reaction [1]:

$$Al_2O_3 \text{ (anodic coating)} + H_2O \rightarrow 2AlO(OH) \qquad [1]$$

- Carbon smutting [30]

In the case of the investigated material after anodizing, silicon smutting was the dominant mechanism because of a lack of sealing process as well as carbon content in the processing method. However, a difference in the smutting gradient of the treated surface was found, where the surface of the AlSi12 alloy appears darker (Fig. 1c) compared with the surface of the AlSi8 alloy (Fig. 1d). The surface of the alloys was nearly the same grey level for both the AlSi8 and AlSi12 alloys (Figs. 1c and 1d), the only difference was the silicon content, with a difference of 4%, which has caused silicon smutting.

The microstructure of the material used for anodization—presented in Figs. 2a and 2b, reveals the presence of needle-shaped primary silicon precipitates, of similar size for the AlSi8 and AlSi12 alloy, however, the amount is higher in the case of the AlSi12 alloy because of a higher Si content in the chemical composition.

Metallographic observations of the surface layer cross-section of the anodized material show that the structure of the anode layer presented in Fig. 2d (AlSi12) exhibits much higher homogeneity obtained by pore anodization compared with that shown in Fig. 2c (AlSi8). An influence on the amount and size of discontinuities has also been found. The structure shown in Fig. 2d presents only a low amount of small pores and their arrangement is more regular. The thickness measurements reveal the value of 9,7 μm for the AlSi12 alloy and 32,3 μm for the AlSi8 alloy, and also the standard deviation (Table 4) confirms that the layer obtained in the case of the AlSi12 alloy is more uniform and homogeneous.

Based on the analysis of the abrasive wear test, it was found that anodic treatment in general increases the abrasive wear resistance of the material. The highest wear resistance was achieved for the anodic layer with high thickness of 32,3 µm for the AlSi8 alloy. A partial removal of the coat was observed for all casts produced in high-pressure dye casting, where the thickness of the coat is lower than 10 µm. The samples made of AlSi12 alloy present higher loss in weight, both for the AlSi8 and AlSi12 alloys.

The results presented in Figs. 3, 4 and Table 5 indicate that anodized samples of the AlSi8 and AlSi12 alloy, are characterized by a lower loss in weight in comparison to the samples not anodized of 43% and 51%, respectively.

Table 4

Thickness of the alumina layer for the anodized and non-anodized material

Parameters	Alloy			
	AlSi8		AlSi12	
	Non-anodized	Anodized	Non-anodized	Anodized
Average value	0,3 µm	32,3 µm	0,45 µm	9,7 µm
Standard deviation	0,17 µm	9,74 µm	0,07 µm	3,5 µm

Table 5

Mass loss measured during the wear test

Alloy	Mass loss, mg	
	Anodized	Non-anodized
AlSi8	11,2	19,6
AlSi12	8,2	16,7

4. CONCLUSIONS

The investigated AlSi8 and AlSi12 cast aluminum alloys are suitable for anodic oxidation. In the case of the AlSi12 alloy, the obtained alumina layer is of lower thickness (9,7 µm) compared with the AlSi8 alloy (32,2 µm), however the layer is of higher homogeneity and more uniform.

The test results of the wear investigation show that anodized alloys, both AlSi8 and AlSi12, show less weight loss compared with non-anodized alloys. It can be seen that the structure of the layer affects the abrasion resistance.

It has been observed that a relatively large smutting occurred on the treated surface of the aluminium parts. This silicon-smutting phenomenon of the anodic surface causes the characteristic grey color to be observed—Fig. 1b, which is very intensive, even black on over-anodized samples (Fig. 2). Anodic desmutting should be applied after anodizing to remove any silicon or carbon smut formed during acid treatment.

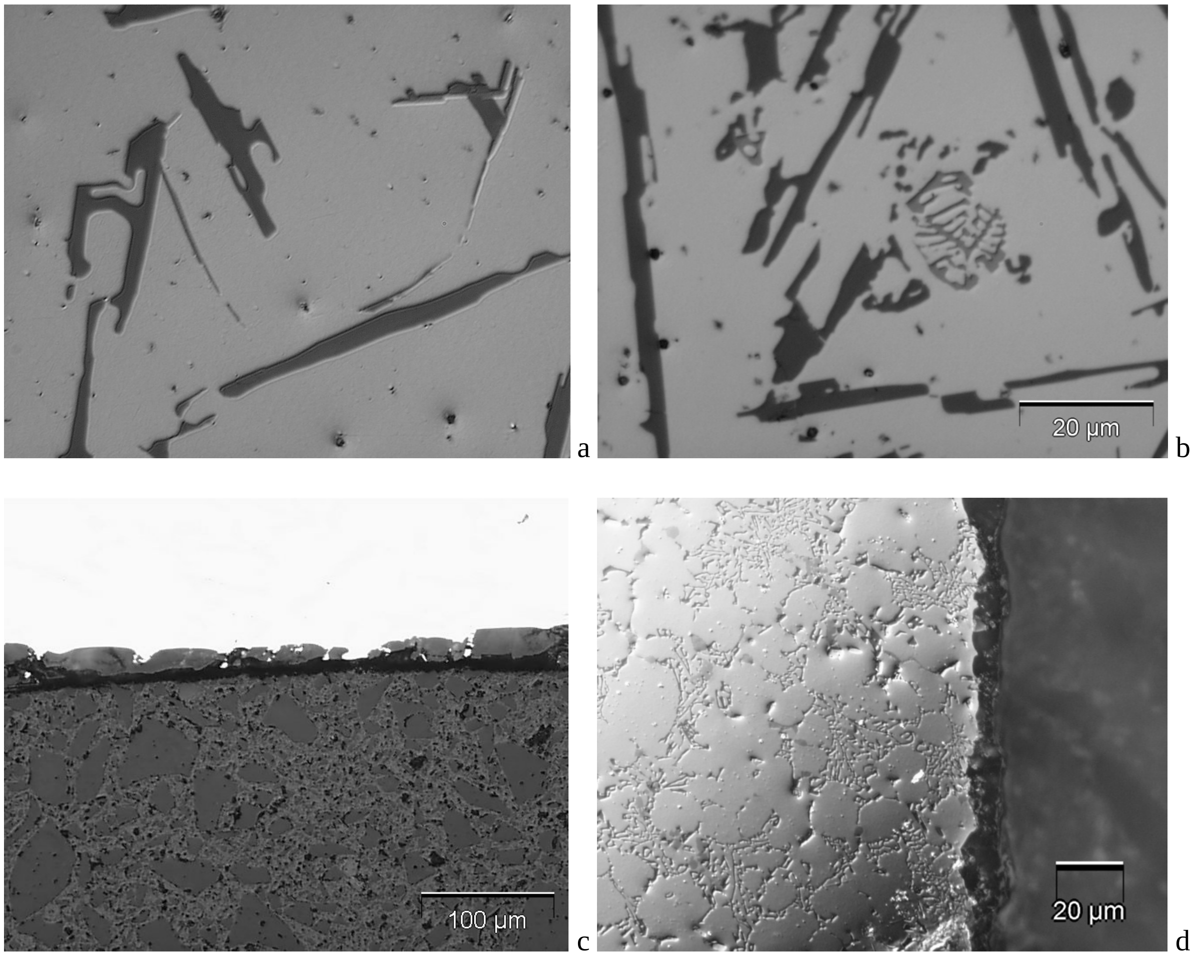

Fig. 3. Microstructure of the a) AlSi8 and b) AlSi12 cast aluminium alloy used for anodizing. Cross-section of the obtained surface layer after anodizing: c) AlSi8 and d) AlSi12

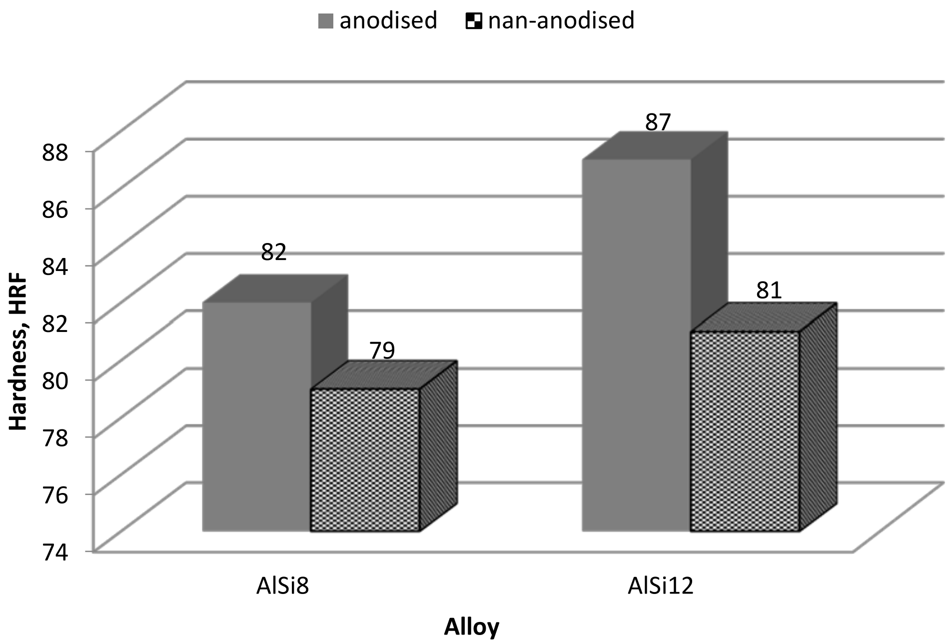

Fig. 4. Mass loss measured during the wear test of the anodized and non-anodized AlSi8 and AlSi12 alloys

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