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Synthesis of a Hard Anodic Oxide Coating with a Structure Allowing for Its Modification by Nanoparticles

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Abstract: A hard anodic oxide coating's characteristic porous structure allows for its modification by the incorporation of nanoparticles. However, achieving an appropriate microstructure requires an optimal pore arrangement and shape, which is influenced by the electrolyte composition, current densities, temperature, and processing time. To achieve pores with a diameter of about 50 nm and the most regular structure, a range of these parameters were tested. Using a two-stage manufacturing process had a beneficial effect on increasing the microporosity of the coating. The addition of phthalic acid at 0 °C did not increase the pore diameter, but allowed for the process to be carried out at higher temperatures. However, the coating produced at 20 °C had a larger pore diameter, but numerous defects. The coating obtained from the three-component solution had the most regular structure, but the smallest pore diameter.

Keywords: hard anodizing; oxide coating; wear resistance; pore diameter

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1. Introduction

The growing consumption of aluminium and its alloys in various industries recently has resulted in a growing interest and demand for hard anodic oxide coatings with a low friction coefficient and self-lubricating properties. Due to the characteristic structure of the oxide film, the surface of a hard anodic oxide coating has an absorptive capacity. Therefore, it can be modified by incorporating hard particles or particles acting as solid lubricants into the porous structure. To incorporate particles into the porous structure, the pores must be uniformly distributed and possess an appropriate shape and size. If the pore diameter is smaller than the size of the modifying particles, they will not integrate into the structure and will instead deposit onto the surface, providing only a temporary improvement of the tribological properties. Incorporating these particles into the coating structure can significantly extend the coating's lifecycle. Therefore, a critical aspect of the current research is to produce a hard anodic oxide coating with the appropriate microstructure.

The main parameters affecting the shape and size of the pores are the electrolyte composition, current parameters, temperature, and time of the process. The production of coatings with a well-defined structure is usually carried out at a relatively low current density in the kinetic regime, which is very time-consuming. The slow rate of the production of coatings with a suitable structure limits their use in industrial conditions. Therefore, hard anodizing at higher current densities is used to increase the rate of layer growth [1].

Hard anodic oxide coatings are produced by various types of electrolytes. These can be inorganic acids (e.g., sulfuric acid, phosphoric acid) or organic acids (e.g., oxalic acid; recently, selenic acid and etidronic acid have also been investigated), as well as mixtures of acids [2–5]. Depending on the electrolyte used, coatings with different pore diameters and uniformity can be obtained. Oxide coatings produced in a sulfuric acid solution with a concentration of about 20% are characterized by a pore diameter of 5–33 nm [1,2,6]. Coatings produced in oxalic acid have pores with a diameter of approx. 50 nm [7]. The coatings produced by Nielsch et al. in oxalic acid were also characterized by the highest uniformity of pore distribution [8]. The largest pore diameter can be obtained in phosphoric acid solutions. In a solution of 10% phosphoric acid, the pore diameter of a coating is 80–120 nm [9]; in a 0.4 M solution of phosphoric acid, pores with a diameter of 200 nm can be obtained [7]. However, coatings produced in phosphoric acid are characterized by a low thickness. Therefore, they are unsuitable for tribological applications. With larger pore diameters, the thickness of the elementary cell walls is smaller, and the wear resistance of anodic oxide coatings is lower. In turn, a larger pore diameter allows for the incorporation of more modifying particles [10].

Various additives are also used to improve the morphology of the coating, to affect the current stability of the process, or to allow for the process to be carried out at a higher or lower temperature. These include, for example, carboxylic acids, metal salts, alcohols, and glycerin. The addition of organic acids significantly improves the surface morphology of oxide coatings; the coating growth process becomes stable, and the porous structure becomes more regular and ordered [11]. Leontiev et al. [12] also showed that the addition of phthalic acid allows for the obtaining of coatings with a relatively large pore diameter and the carrying out of the process at room temperature. Therefore, for the production of hard anodic oxide coatings, it is necessary to adjust the production parameters accordingly in order to obtain pores with a diameter that allows for the incorporation of nanoparticles, but does not deteriorate the anti-wear parameters of the coating.

Two-step manufacturing processes are used to achieve the most uniform pore structure and distribution. Lee et al. found that the formation of an oxide layer at lower voltages prevents uncontrolled phenomena, such as a rapid increase in local current density, which causes burning of the oxide layer [7].

The processing temperature for hard anodic oxide coatings ranges from -10 °C to 10 °C. Typically, most processes are carried out at 0 °C. The need to use a low temperature is due to the exothermic nature of the process.

Various types of additives, e.g., the addition of phthalic acid, are used to increase the temperature during the hard anodizing process and thus prevent the secondary dissolution of the coating. A solution consisting of sulfuric acid, oxalic acid, and phthalic acid was used by Wang et al. [13]. This allowed them to obtain coatings with pores with a relatively large diameter.

The production of hard anodic oxide coatings with a well-defined, regular structure and precise pore diameter typically requires processes lasting several hours at low current densities [14,15]. However, this approach is not suitable for industrial applications, especially for the production of hard anodic oxide coatings modified with nanoparticles to improve the mechanical and tribological properties. Therefore, to produce a coating with a regular pore arrangement and diameter suitable for nanoparticle modification in a significantly shorter process time, alternative process parameters are being explored, including different electrolyte compositions, current densities, and temperatures.

The key elements of this work are the selection of the appropriate electrolyte composition and coating production parameters (i.e., time, temperature, and current densities), as they affect the shape and size of the pores, and thus the possibility of embedding modifying particles deep into the porous structure. The pore size directly affects the tribological and mechanical properties of the coatings, so the microhardness and abrasion resistance are also tested.

2. Materials and Methods

EN-AW 5754 aluminium alloy, used as the anode, was cut into 100 × 100 × 3 mm pieces. Analytical grade acetone (C_3H_6O, Idalia, Nicosia, Cyprus), sodium hydroxide (NaOH, Chempur, Piekary Śląskie, Poland), nitric acid (HNO_3, VWR, Gdańsk, Poland), 95% dihydrate oxalic acid ($C_2H_2O_4 \times 2H_2O$, Chempur), phthalic acid ($C_6H_8O_2$, Sigma

Aldrich, St. Louis, MO, USA), and 95% sulphuric acid (H_2SO_4, Chempur) were used. Before anodization, the aluminium alloy was degreased in acetone, etched in a 200 g/L NaOH solution for 5 min, followed by brightening in a HNO_3 solution for 2 min. An aluminium sheet was used as the cathode.

The primary goal of this work was to produce a hard anodic oxide coating with a pore diameter suitable for further modification. To achieve this, multiple factors were tested, including the electrolyte composition, temperature, time, and current density. Each of these parameters can directly affect the structure of a hard anodic oxide coating.

The hard anodic oxide coatings were produced from 3 different electrolytes, one component (1C), two component (2C), and three component (3C). The base solution was 27 g/L oxalic acid. According to the literature, it allows for the obtaining of pores with a diameter in the range of 50 to 100 nm. A 27 g/L concentration of oxalic acid is the most common concentration in the literature [16–20] for the production of hard anodic oxide coatings, which is why it was used in this work as the base electrolyte. To enable the process to be carried out at a higher temperature and to obtain pores with a larger diameter, 10 g/L phthalic acid was added [21,22]. Temperature variations in the electrolyte affect the porosity of the anodized sample. The rate of pore formation increases with temperature [18]. Using a three-component solution should ensure a better uniformity of pore distribution, so a mixture of oxalic, phthalic, and sulfuric acid was applied.

The concentrations of the ingredients in the three-component solution were selected based on the literature data [23].

Typically, hard anodic oxide coatings are produced at a temperature of 0 °C due to the exothermic nature of the aluminium oxide formation reaction on a metal surface. To manage the heat generated during oxidation, not only is a low temperature required, but also the intensive mixing of the bath to dissipate the heat from the metal surface. Therefore, the 1C_const coating was produced exclusively at 0 °C. Producing hard anodic oxide coatings at higher temperatures in standard electrolytes (such as oxalic, sulfuric, or phosphoric acid) can result in the uncontrolled dissolution of the coating.

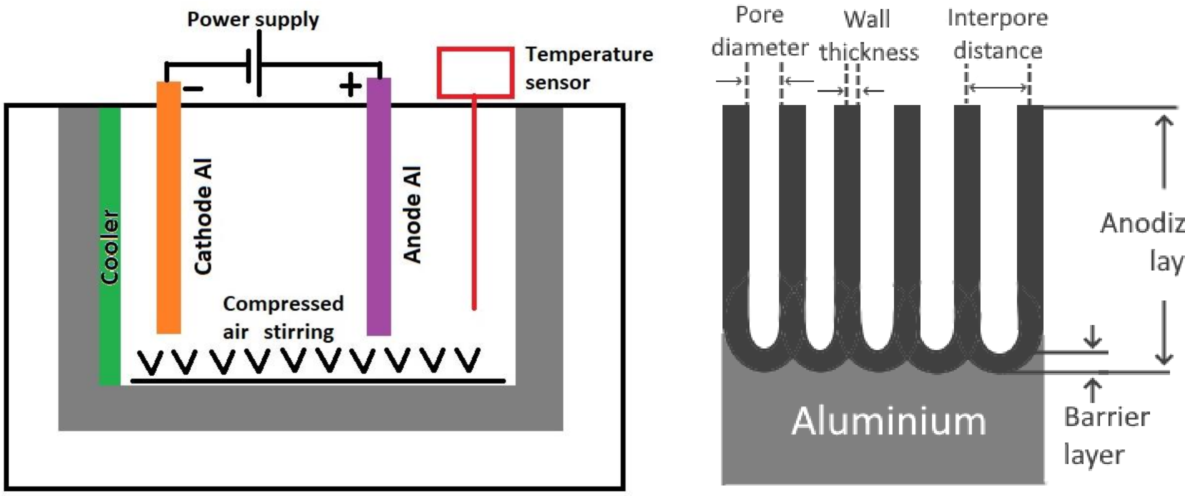
The anodizing process was conducted using constant and variable current densities (the current density was increased over time from 1.4 A/dm^2 to 4 A/dm^2) for different times and temperatures (Table 1). Standard industrial anodising processes require a constant current density of 2–5 A/dm^2. The 1C_const coating was produced at the standard 2 A/dm^2. Using variable current densities, i.e., a reduced current density of 1.4 A/dm^2 in the first stage and then increasing to 4 A/dm^2, allowed for the production of a coating with a more regular structure [24]. The process was extended to increase the thickness of the coatings produced.

Table 1. Anodizing process parameters.

Sample	Electrolyte Composition	Time [min.]	Current Density [A/dm^2]	Temperature [°C]
1C_const	27 g/L oxalic acid	45	2	0
1C_35_0	27 g/L oxalic acid	35	1.4/4	0
2C_35_0	27 g/L oxalic acid + 10 g/L phthalic acid	35	1.4/4	0
2C_35_5		35	1.4/4	5
2C_35_20		35	1.4/4	20
2C_75_0		75	1.4/4	0
2C_75_5		75	1.4/4	5
3C_35_20	30 g/L oxalic acid + 10 g/L phthalic acid + 60.7 g/L sulphuric acid	35	1.4/4	20

Figure 1a presents a schematic diagram of the laboratory set for coatings production, and Figure 1b the scheme of the ideal structure of an anodic oxide coating on aluminium. It consists of two layers: a thin barrier layer that adheres directly to the substrate metal and a top porous layer. The barrier layer is formed first during the electrolysis process;

it is non-porous and its thickness does not exceed 0.5%–2% of the total thickness of the coating. The proper layer is made of densely arranged hexagonal cells inside which a pore is located. The pore diameter, distance between pores, or wall thickness can be adjusted by appropriate selection of electrolysis conditions. Due to the characteristic structure of the oxide layer, the surface of the alumina can absorb. Therefore, it can be modified by incorporating nanoparticles into the porous structure to improve its coating properties. Nanoparticles with an average diameter of about 20–30 nm are considered for use as modifying particles. A characteristic phenomenon of nanoparticles is agglomeration, which is very difficult to eliminate. Therefore, it is assumed that the minimum pore diameter that allows for the modification of the coating with nanoparticles is about 50 nm.



(**a**) (**b**)

Figure 1. Schematic diagram of (**a**) laboratory set for coating production and (**b**) ideal structure of anodic oxide coating on aluminium.

The coating thickness was measured by the eddy current method using a Fischer Dualscope MP20E-S instrument. Ten measurements were made on each sample and the result is their average. The coatings were examined with a scanning electron microscope (HR-SEM), Inspect F50, with a field emission gun (FEG). Prior to the SEM examination, a 10 nm thick layer of carbon was deposited onto the surface of the samples by magnetron sputtering, using a low vacuum coating system, Leica EM ACE200. The microhardness HV0.01 of the coatings was measured for their cross sections using a Buehler Micromet 5103 low-load Vickers tester. Abrasion testing was performed using a Taber Abraser Model 5155 tester, CS-17 abrasive wheels, a load of 1000 g, and 10,000 cycles, according to the standard [25].

3. Results

Figure 2 presents the obtained thicknesses of the hard anodic oxide coatings. The thickness of the coatings ranged from 10 to 28.5 µm. The coating produced in 27 g/L oxalic acid solution at a constant current density (1C_const) was characterized by the highest thickness (28.5 µm). The addition of phthalic acid caused a decrease of 4 µm in the thickness of the coating (2C_35_0) compared to the coatings produced in oxalic acid solution (1C_35_0). The coating thickness obtained from the oxalic–phthalic acid mixture increased significantly with an increasing process time. In addition, increasing the electrolyte temperature to 5 °C contributed to a thicker coating (as observed for 2C_35_5 and 2C_75_5). In contrast, a rather rapid decrease was observed at 20 °C.

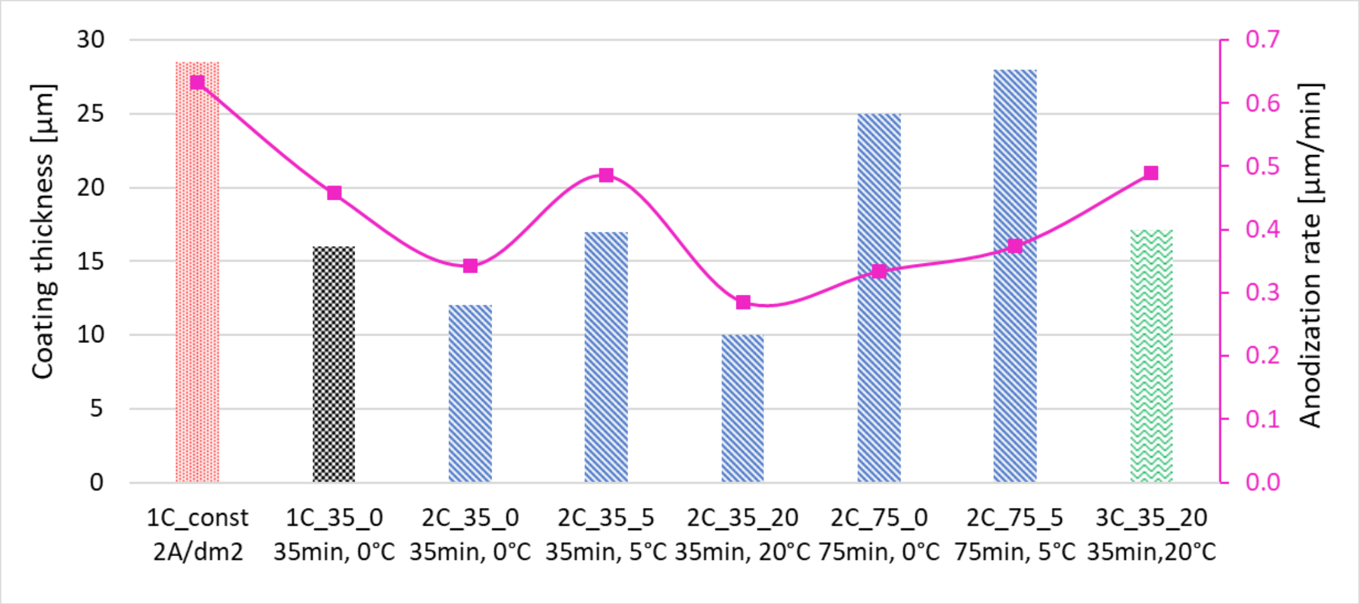


Figure 2. Coating thickness as function of applied process parameters (bar graph): red colour—constant current density 2 A/dm^2, oxalic acid; black colour—1.4/4 A/dm^2, oxalic acid; blue colour—1.4/4 A/dm^2, oxalic + phtalic acid; green colour—1.4/4 A/dm^2, oxalic + sulphuric + phtalic acid and anodization rate (line graph).

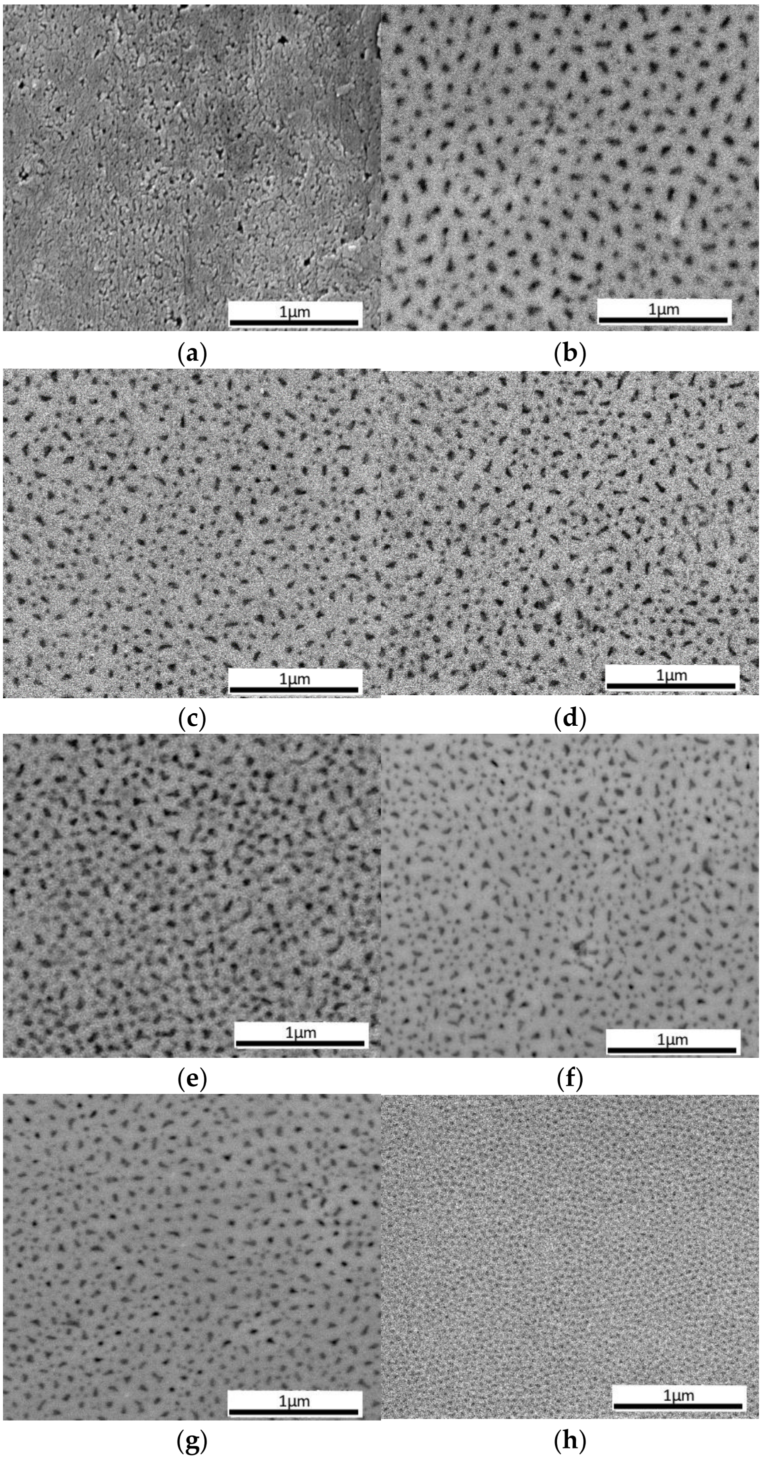
The coating thickness produced by the three-component solution (3C_35_20) was higher compared to the two-component solution (2C_35_20).

To study the influence of the electrolyte type, current parameters, temperatures, and time on the pore diameter and their organization, SEM images were obtained.

Figure 3 shows the surface morphology of the produced coatings. The most compact structure was obtained for the coating produced in 27 g/L oxalic acid solution at a constant current density (Figure 3a). The coatings obtained from the 27 g/L oxalic acid solution with a variable current waveform had pores distributed evenly over its entire surface, but with a rather irregular shape (Figure 3b). Using phthalic acid also allowed for the anodizing process to be carried out at elevated temperatures, and the coating was not subjected to uncontrolled dissolution (Figure 3c–e). However, carrying out the process at a temperature of 20 °C caused the porous structure to become significantly defective (Figure 3e). Extending the process time did not significantly change the shape and distribution of the pores (Figure 3f–g). The use of a mixture of sulfuric, oxalic, and phthalic acids allowed for the obtaining of the required shape and arrangement of pores (Figure 3h).

The SEM-SE images (Figure 3) were processed in ImageJ (1.54g), a public domain software for image processing and analysis, to measure the pore sizes. First, each image was converted to an 8 bit mode, then calibrated by setting the scale. A specific area was selected and duplicated for analysis. Thresholding was applied, and the "Analyze Particles" function was used to calculate the average surface area of all the pores. From these measurements, the average radius was calculated using the formula for the surface area of a circle, followed by the average diameter of a single particle.

Figure 4 presents a graph of the obtained coating pore diameters. The expected pore diameter, which allows for the incorporation of modifying particles into the porous structure, was assumed to be about 50 nm. The lowest pore diameter, impossible to measure by SEM, was obtained for the coating prepared from the oxalic acid solution at a constant current density (1C_const). A diameter above 50 nm was obtained for sample 2C_35-20 (56 nm). With an increasing process temperature for the oxalic acid + phthalic acid solution, the pore diameter increased from 42 nm at 0 °C (2C_35_0) to 56 nm at 20 °C (2C_35_20). Increasing the process time did not significantly increase the pore diameter. The use of a mixture of sulfuric, oxalic, and phthalic acids allowed for the obtainment of the required shape and arrangement of pores, but the pore diameter was only 18 nm.



(**a**) (**b**) (**c**) (**d**) (**e**) (**f**) (**g**) (**h**)

Figure 3. SEM-SE morphology of coatings for (**a**) sample 1C_const; (**b**) sample 1C_35_0; (**c**) sample 2C_35_0; (**d**) sample 2C_35_5; (**e**) sample 2C_35_20; (**f**) sample 2C_75_0; (**g**) sample 2C_75_5; and (**h**) sample 3C_35_20.

The coatings made from the one-component oxalic acid solutions using a constant current density revealed the highest microhardness (557 HV0.01) (Figure 5). The highest microhardness was directly related to the coating structure, which in this case was the most compact and the least porous (Figure 3a). The use of a variable current density did not significantly affect the microhardness of the coating. The coatings produced from the two-component solutions, regardless of the applied temperature and time of the process, had similar microhardness values of approx. 429–463 HV0.01. Increasing the current density during anodizing usually results in a higher hardness of an oxide coating [26,27]. In the case of the alternating current process, in the first step the current density was lower (1.4 A/dm^2) and in the second step the current density was higher (4 A/dm^2), compared to the coating produced at a constant current density, 1C_const (2 A/dm^2). Perhaps this was the reason for their similar microhardness value.

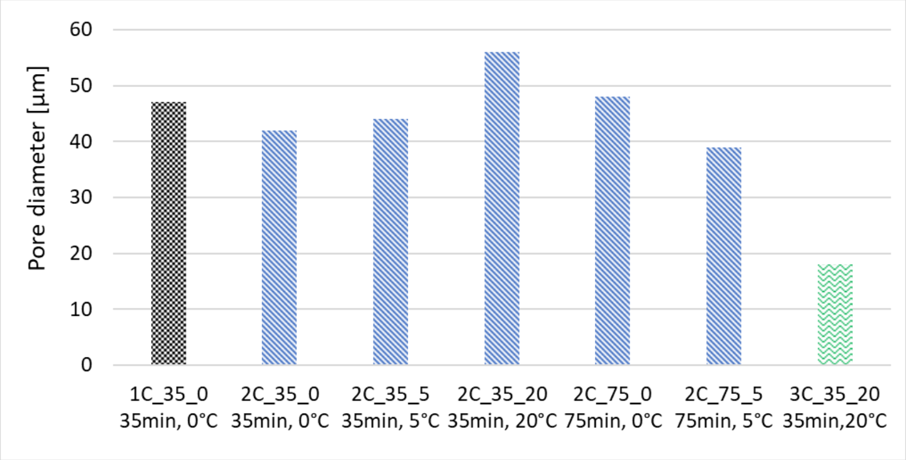


Figure 4. Average pore diameter as function of applied process parameters: red colour—constant current density 2 A/dm^2, oxalic acid; black colour—1.4/4 A/dm^2, oxalic acid; blue colour—1.4/4 A/dm^2, oxalic + phtalic acid; green colour—1.4/4 A/dm^2, oxalic + sulphuric + phtalic acid.

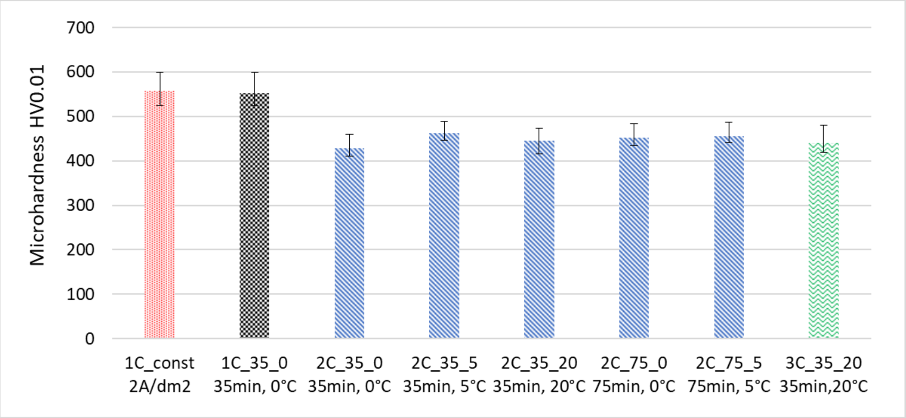


Figure 5. Coating microhardness as function of applied process parameters: red colour—constant current density 2 A/dm^2, oxalic acid; black colour—1.4/4 A/dm^2, oxalic acid; blue colour—1.4/4 A/dm^2, oxalic + phtalic acid; green colour—1.4/4 A/dm^2, oxalic + sulphuric + phtalic acid.

The coating obtained from the three-component solution was also characterized by a similar microhardness value of 441 HV0.01.

The hard anodic oxide coatings were tested according to the requirements of the Qualanod quality mark and the ISO standard [25]. This standard specifies that the maximum mass loss of a hard anodic oxide coating on a 5xxx series aluminium alloy should not exceed 25 mg, as indicated by the red line in the graph. All the coatings produced were tested using the Taber method and met this requirement regardless of the electrolyte used and the processing parameters (Figure 6).

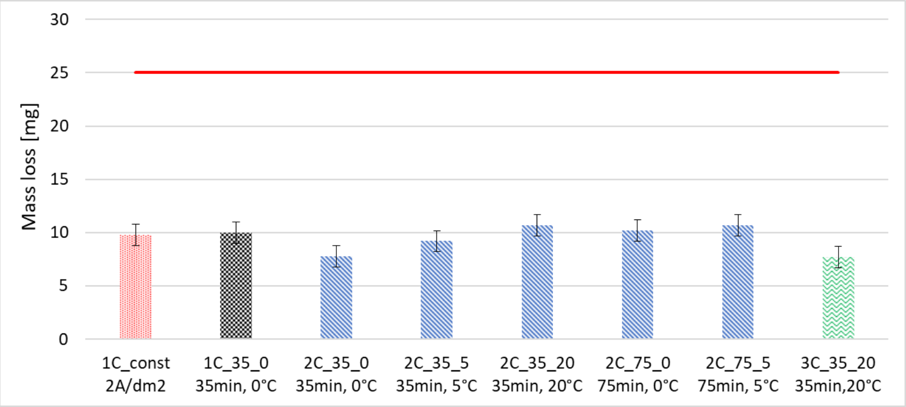


Figure 6. Mass loss of coatings after Taber test as function of applied process parameters: red bar—constant current density 2 A/dm^2, oxalic acid; black bar-1.4/4 A/dm^2, oxalic acid; blue bar-1.4/4 A/dm^2, oxalic + phtalic acid; green bar-1.4/4 A/dm^2, oxalic + sulphuric + phtalic acid. Red line—maximum weight loss permitted by the ISO standard [25].

4. Discussion

To produce hard anodic oxide coatings suitable for subsequent modification by incorporating particles into the porous structure, it is essential to use specialized electrolytes along with carefully selected process parameters, including the current density, temperature, and time. The electrolytes used to produce coatings for tribological purposes, i.e., with high wear resistance, allow for the obtainment of coatings with very low porosity. This fact was confirmed by the sample obtained in an electrolyte typically used for the production of hard anodic oxide coatings, i.e., the one-component solution of oxalic acid, under standard DC conditions (1C_const). Its structure was compact and the pores were very small, which could not be determined by an SEM (Figure 3a), but it had the greatest thickness and microhardness. For this reason, the electrolytes used to produce coatings that will undergo further modification must contain components that regulate porosity and hardness, and special current and temperature conditions must be applied.

One such additive may be phthalic acid, which is a carboxylic acid with two carboxyl groups (-COOH) and a benzene ring. The phthalic acid addition allows for the process to be carried out at a higher temperature without the coating burning. This is because organic substances block the access of an aggressive environment to the coating and inhibit the process of its secondary dissolution [28]. Studies of the anodizing process have shown that organic acids also have a significant effect on the morphology of the oxide layer. When added to an oxalic acid electrolyte, an organic acid can adsorb to the surface of the coating, restricting the diffusion of $C_2H_2O_4$ molecules toward the anode. This occurs in areas with a high electric field intensity, reducing the current density in active regions and promoting a more uniform electric field distribution across the coating. As a result, the coating grows more stably and the process can be carried out at elevated temperatures [11]. Compared to the coating produced from the one-component oxalic acid solution at 0 °C (1C_35_0), the addition of phthalic acid caused an increase in the thickness by 4 µm (2C_35_0). Wang et al. [29] indicated that organic acids can affect the increase in coating thickness, but only up to a content of 1%. Above this content, the coating thickness decreases. An increase in the process temperature to 20 °C (2C_35_20) caused the thickness of the produced coatings to decrease. Generally, an increase in the electrolyte temperature increases ionic mobility and electrolyte conductivity. Therefore, the growth rate of a nanoporous oxide increases, making the anodization less time-consuming [30]. However, in electrolytes containing additional carboxylic acids, the thickness of the produced coatings depends on the length of the aliphatic chain, which affects the ability of the electrolyte to cause the secondary dissolution of the oxide. Therefore, the coating thickness may decrease with increasing temperature [11,27]. Yoshimoto et al. [31] conducted studies with the addition of carboxylic acid. They found that the addition of percarboxylic acid allowed for the formation of an anodic oxide coating with a thickness of 100 µm. Without the additive, such a thick coating could not be produced, because above a thickness of 30 µm it "burned". The additive acted as an inhibitor of the dissolving of the film in the bath and of the burning. The anodic film was also characterized by a hexagonal cell structure. Compared to the film formed in the H_2SO_4 bath, the cells were almost uniform in size and the pore size of the cells was smaller. Also, Zhang et al. [11] studied the influence of organic additives in the anodizing bath. Porous anodic alumina membranes were fabricated using phosphoric and oxalic acid electrolytes, with the addition of 10 g/L organic acid. The experimental results indicated that the organic acid significantly reduced defects, leading to a more uniform oxide film growth. Additionally, a uniformly porous honeycomb structure was achieved.

With an increase in temperature to 20 °C (2C_35_20), an increase in pore diameter was observed; however, more defects were also noted. Also, Leontiev et al. [12] observed an increase in the number of defects in the coating structure with an increasing temperature. According to them, this may be because the electrolyte temperature significantly affects the kinetics of the anodizing process, shifting the boundaries of the kinetic regime to a mixed one, especially during the first low-current stage of the process, which has a significant impact on the ordering of the structure of the produced coating. On the other hand, this could be explained in terms of the observed relations between the anodizing temperature and both the pore diameter and interpore distance. As the anodizing temperature increases, the pore diameter also increases, while the interpore distance (as well as the pore density) remains constant. This could be attributed to the increased field-assisted dissolution of alumina at the oxide/electrolyte interface at higher temperatures [30].

The addition of carboxylic acids and the length of the aliphatic chain also influence the microhardness of the coatings [10]. The addition of phthalic acid caused a decrease in the microhardness of the coatings, regardless of the applied temperature and process time.

According to the literature, the greatest regularity of pore arrangement can be achieved by using three-component electrolytes [27]. The coatings produced in the three- component solution (3C_35_20) were characterized by the most uniform distribution and shape of the pores, but their diameter was only 18 nm.

The use of a two-stage process, where a lower current density (1.4 A/dm^2) was used in the first stage and a higher current density (4 A/dm^2) in the second stage, had a positive effect on increasing the microporosity of the coating. This is explained by the fact that the formation of an "initial" oxide layer at lower voltages provides a homogeneous site for pore nucleation at higher voltages. This prevents uncontrolled phenomena, such as a rapid increase in the local current density, which causes oxide layer burning and pitting. The homogeneity of the pore structure increases significantly at voltages above 110 V [7]. The positive effect of the two-step process on the increase in the anodic oxide coating structure was also demonstrated by Li et al. [19]. They prepared hard anodic oxide coatings in 27 g/L oxalic acid at 150 V (the voltage was initially increased from 40 V to 150 V). It was found that a high enough current density in the voltage-rise stage can induce rapid film growth, which causes the pores to enlarge rapidly and achieve a relatively ordered rearrangement.

5. Conclusions

Hard anodic oxide coatings with different microstructures were successfully produced on aluminium alloy 5754 using different process parameters, such as three electrolytes (oxalic acid solution, oxalic acid solution with 10 g/L of phthalic acid added, and a mixture of oxalic, sulfuric, and phthalic acids) and different current densities, temperatures, and times. The thickness of the hard anodic oxide coatings ranged from 10 to 28.5 µm, with the maximum thickness achieved in the oxalic acid solution (1C_const). The pore diameters ranged from 18 to 56 nm, with the smallest diameter undetectable by SEM. Using a variable current density (1.4 to 4 A/dm^2) allowed for the production of coatings with a more regular structure and larger pore diameter (47 nm) than a constant current, without significantly affecting the microhardness. Adding phthalic acid to the oxalic acid solution allowed for anodizing at higher temperatures, but resulted in larger, less uniform pores (up to 56 nm at

20 °C) and a 22% reduction in microhardness. A sulfuric acid–oxalic acid–phthalic acid mixture produced the most uniform pore structure, but with a smaller diameter (18 nm).

Extending the anodizing time resulted in an increase in coating thickness, but did not significantly affect the pore shape and distribution.

All the anodic coatings met Qualanod and ISO standards [25], which specify a maximum mass loss of 25 mg for anodic coatings on 5xxx aluminum alloys. Taber testing confirmed compliance regardless of the electrolyte or process parameters.

The recommended parameters for producing a modifiable hard anodic oxide coating are 27 g/L oxalic acid, 35 min, an initial current density of 1.4 A/dm^2 increasing to 4 A/dm^2, at 0 °C; this results in a pore diameter of ~47 nm with a uniform distribution but irregularity in shape.

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