Porous anodic alumina formed on AA6063 aluminum alloy in a two-step process combining hard and mild anodization

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1. INTRODUCTION

Highly-ordered porous anodic alumina (PAA) is one of the most attractive templates for nanofabrication [1, 2]. Its geometrical parameters including pore diameter and pore arrangement, interpore distance, or PAA film thickness are easily controlled by anodizing conditions such as type of electrolyte, applied voltage, anodization time, or bath temperature [3, 4]. Usually PAA is fabricated on high-purity aluminium (99.999%) which by far hoists its production costs. Therefore, from economical point of view a replacement of the expensive high-purity aluminium for low-purity aluminium was considered [19]. In this process, a stable electrolysis is maintained at voltages much higher than the critical ones, and the problems related with heat dissipation are overcome by formation of a thick barrier layer at the beginning of the process during MA, before voltage is ramped to a target formation potential. Hard anodization was performed in oxalic [19–21], sulfuric [22, 23], and phosphoric [24] acid solutions. Thanks to the application of high potentials new self-ordering regimes, with interpore intervals in the range of hundreds of nanometers, were found. Well ordered PAA templates with the pore intervals in this range are of great interest for fabrication of optical devices operating in UV or visible spectral region [25–27]. The major drawback of PAA films produced in one-step HA is the irregular resulting top surface, which is a consequence of voltage increase at the beginning of the HA process. A parallel pore alignment from top to bottom of PAA’s film thickness can be obtained during so-called guided anodization. In the guided anodization regular hexagonal Al nanoconcaave arrays formed on aluminium after removing of the PAA produced in the first HA step are used as nucleation sites to maintain the ordered pore growth during second MA step, which is performed at constant voltage throughout the whole process [28, 29].

In this work, the effect of high-field anodization on geometrical parameters of porous anodic alumina formed on AA6063 aluminium foil is studied. The two-step process combining HA in 0.3 M oxalic acid solution and MA anodization in 0.1 M phosphoric acid solution is applied to fabricate PAAs in the voltage range between 120 and 180 V. The influence of ethanol on geometrical parameters of the PAAs was also tested. The analysis of the geometrical parameters as well as the current/voltage vs time transients suggested that alloying elements present in the AA6063 alloys play an important role in the relaxation of mechanical stresses at the metal/oxide interface occurring during the PAA’s growth. The effect contributed to comparable interpore distance $D_p$ values (between 270–370 nm) and similar regularity ratio parameter ($RR$) in the samples anodized in ethanol-free and ethanol-modified electrolyte, despite much higher average current densities registered for the former samples. The hexagonal pore ordering increased with the applied anodizing voltage.

Key words: hard anodization, guided anodization, porous anodic alumina (PAA).
2. EXPERIMENTAL

Commercially available AA6063 aluminium alloy sheet with a thickness of about 0.5 mm was cut into rectangular specimens of size 2 cm × 1 cm. Before the anodization process the Al sheets were degreased in acetone and ethanol and subsequently electropolished in a 1:4 mixture of 60% HClO₄ and ethanol at 0°C, and constant voltage of 20 V, for 2 min. Next, the samples were rinsed with ethanol first, then with distilled water and finally dried. As prepared Al coupons were insulated at the back and the edges with acid resistant tape, and serve as the anode. A Pt grid was used as a cathode and the distance between both electrodes was kept constant (ca. 5 cm). A large, 1 L electrochemical cell, a powerful low-constant-temperature bath, and vigorous stirring (750 rpm) were employed in the anodizing process. An adjustable DC power supply with voltage range of 0–300 V and current range of 0–5 A, purchased from NDN, model GEN750 TDK Lambda, was used to control the applied voltage, and APPA 207 TRUE RMS multimeters were used to measure and transfer the registered current and potential data to a computer.

The first anodization was carried out at 0°C in 0.3 M H₂C₂O₄ water-based solution and in ethanol-water 1:4 volumetric mixture. Anodizing voltages were ranging from 120 to 180 V. Prior to application of a given voltage, the samples were pre-anodized at 40 V for 10 min. Then, the voltage was slowly increased to a target value and the samples were anodized for 2 h. As obtained alumina was chemically removed in a mixture of 6 wt % phosphoric acid and 1.8 wt % chromic acid at 60°C for 3 h. Second anodization was performed in 0.1 M phosphoric acid solution with 1.4 v/v mixture of ethanol and water as a solvent, at 0°C under the same anodizing voltage as used in the first step.

Morphology of PAAs was studied using field-emission scanning electron microscope FE-SEM (FEI, Quanta) equipped with energy-dispersive X-ray spectrometer (EDS). The chemical composition analysis was performed at 20 kV, magnification of 2000, and with a constant distance of samples to the detector. In the case of PAA, the cross-sections were analysed. Each measurement was repeated three times and an average of the three measurements was taken to determine the chemical composition of a given sample.

To obtain geometrical parameters of the fabricated PAAs, Fast Fourier Transforms (FFTs) were generated based on three SEM images taken at the same magnification for every anodizing voltage, and were further used in calculations with WSxM software [30]. To estimate regularity ratio, radial average was generated from each FFT image. The regularity ratio $RR$ was estimated according to the following formula (1) [31]:

$$RR = \frac{H}{W_{1/2}} \cdot \frac{\sqrt{n}}{S^{3/2}}$$

where $n$ is the number of pores, $S$ is the analyzed surface area, $H$ is the maximum intensity value of the FFT intensity profile, and $W_{1/2}$ is the width of the intensity profile at half of its height. The average interpore distance $D_i$ was estimated as an inverse of the FFT’s radial average absissa from three FE-SEM images for each sample.

3. RESULTS AND DISCUSSION

Directly after electropolishing the AA6063 alloy samples were subjected to hard anodization. In Figure 1 the current density/voltage vs time curves measured during hard anodization in water-based oxalic acid solution (Fig. 1a) and in electrolyte with 4:1 v/v water to ethanol mixture (Fig. 1b) are presented. The HA method consists of two stages: anodization under the increasing voltage and a stable-voltage anodization. Voltage increase up to a target value $U_i$ is followed by the increase of the current density $i$. The sharp current increase was previously associated with ionization of charged particles (acid anions, in this case C₂O₄²⁻ anions) in the high electric field, which are being incorporated into the PAA framework and release primary electrons into the oxide conduction band [32]. These electrons are accelerated by the high electric field enhancing the average current flow. In the current transients at voltages higher than 140 V, the curves demonstrate two maxima, the second maximum being smaller than the first one. After reaching the first maximum, the current density decreases.

The decrease may be associated with a shift of equilibrium between the oxidation rate at the Al–Al₂O₃ interface and the dissolution rate at the Al₂O₃–electrolyte interface towards a faster oxidation rate. As a result of the faster oxidation rate, the oxide barrier layer becomes thicker, which is translated into a drop of the current density. As the voltage rises, the equilibrium is restored and the barrier layer gets thinner again recovering a smooth current flow, which is manifested in a second increase of the current density (the second maximum). After reaching the target voltage, the HA proceeds to the stable-voltage anodization, where the current density decreases exponentially owing to limited diffusion of the ionic species (e.g., C₂O₄²⁻) from the electrolyte to the electrolyte-oxide interface [32]. As compared to the HA of high-purity aluminium under the same electrochemical conditions (0.3 M oxalic acid solution, 0°C etc.) [29] the current densities are around two times smaller. The same trend was observed during mild anodization of high-purity Al foil...
and AA1050 alloy in sulfuric and oxalic acid solutions: the current values were always lower for the AA1050 samples [15]. Moreover, the current densities at the target voltages change negligibly with the voltage. It appears that there is a boundary \( i_b \) value which is not exceeded despite increasing of \( U \). The basically different current curves acquired for AA6063 anodization as compared to the currents registered during anodization of high-purity Al indicate a strong influence of impurities on the anodization process.

The rough composition of AA6063 was estimated by EDS analysis and is gathered in Table 1. The alloy contains Mg (--0.6 at. %), Si (--0.3 at. %), and Fe (--0.2 at. %) as principal alloying elements. Apart from the principal elements other elements including Cu, Ti, Zn, Mn, and Cr were also detected (the remainder). A relatively high amount of oxygen (--3 at. %) suggests that the alloy was partially oxidized in air. The influence of various elements on the process as well as on the resulted anodic alumina was analysed previously [33–36]. According to those analysis, the amount and distribution of insoluble impurities will strongly influence the quality of anodic oxide layers formed on the aluminium substrate under specific conditions. Moreover, the presence of various additives can affect both average ions migration rates through the barrier oxides and field-assisted dissolution of oxide. In the studied cases it is very probable that the impurities in the AA6063 alloy hindered the ion migration through the barrier layer resulting in the lower recorded steady-state current densities as compared to those registered for high-purity aluminium [29]. Furthermore, in contrast to the HA of high-purity aluminium, there is a negligible difference between the \( i_0 \) values reached at the \( U \), between the samples anodized in water-based electrolyte (Fig. 1a) and in electrolyte with 4:1 v/v water to ethanol mixture (Fig. 1b). The influence of ethanol is manifested, however, in \( i \), decaying process: in the case of anodization in water-based electrolyte the current decrease is more gentle than in the case of HA in electrolyte with 4:1 v/v water to ethanol mixture. The current density drops below 10 mA/cm\(^2\) after around 3500 s for the sample anodized in ethanol-free electrolyte (Fig. 1a), whereas in the ethanol-modified electrolyte the current exceeds the 10 mA/cm\(^2\) value well before 2000 s in the case of anodization at 120, 140, and 160 V, and after ~2250 s for the sample anodized at 180 V (Fig. 1b).

A steady-state anodization in ethanol-free electrolyte is carried out at the \( i_0 \) of 6–8 mA/cm\(^2\), whereas in ethanol-modified solution the \( i_0 \) attained at the stable-voltage anodization stage is around 3–5 mA/cm\(^2\). Accordingly, the average current density is higher in the case of samples anodized in water-based electrolyte as compared to the ones anodized in ethanol-modified acid solution (Fig. 2).

The lower currents registered during anodization in the presence of ethanol were ascribed to the ethanol cooling effect [24, 28, 32]. The cooling effect of ethanol was related with ethanol ability to lower the dissociation constant of the electrolyte and to decrease of temperature generated at the PAA barrier layer. These effects, in turn, lead to the reduction of the ion diffusion ability and smaller amount of acid anions in the barrier layer, and consequently to a relatively smaller contribution from the ionic current.

As formed anodic alumina was chemically removed and SEM images of the resulted nanoconcave arrays formed on aluminium are presented in Figure 3.

As compared to Al nanoconcaves formed on high-purity Al [29], the hexagonal pore arrangement is worse in all studied cases. There is also no clear ethanol influence on the pore ordering. The geometrical features of Al nanoconcaves, such as regularity of hexagonal pore arrangement and the pitch size, are directly transferred from Al concavities to the corresponding PAAs grown on their base during mild anodization in phosphoric acid solution at the same operating temperature (0°C) and at the same anodizing voltages. Therefore, the analysis of the SEM images of top part of the PAAs is equivalent with the SEM analysis of the Al nanoconcave arrays and will be presented below.

The current-time transients acquired during the second anodization step are given in Figure 4. The curves show typical behaviour for guided anodization where three stages can be distinguished: very high current density at the beginning of the process, its subsequent drop within 1–2 seconds, and finally its slower exponential decrease to a steady-state value within about 1 second. The three regimes can be attributed to the following phenomena: an electrolytic reaction of water at the beginning, very rapid barrier layer formation and, at the end, a stable pores growth. In the guided MA the stage related with the competition among pores, which in the current-time curve is manifested in a moderate current increase preceding the steady-state anodization [37, 38], is missing. This is due to the existing periodic pattern of nanoconcaves after the first anodization step at the aluminium surface that defines the pore nucleation sites and eliminates the pore competition. The growth position of the pores is limited by the pre-patterned design and is restricted to the inner corner/electrolyte interface, where a maximum dissolution rate of Al\(^{3+}\) is localized [39]. The time needed to proceed to the steady-state anodization is very short in the MA of AA6063 alloy. A similar process took about 2 minutes during the MA of high-purity aluminium [29]. This may indicate that the dissolution rate of Al\(^{3+}\) in the inner corner/electrolyte interface is much faster in the low-purity aluminium, which again underlines a different mechanism operating in anodization of the two types of aluminium.

The SEM images of resulting PAAs are presented in Figure 5. The pores in the PAAs are characterized by irregular shape with

| Table 1. Results of EDS chemical analysis of AA6063 foil and PAAs anodized at 120, 140, 160, and 180 V, at. % (Table 1 gives only approximate values) |
|------------------|--------|--------|--------|--------|
| **AA6063**       | **120 V** | **140 V** | **160 V** | **180 V** |
| Al               | 95.88  | 47.25  | 45.29  | 48.23  | 46.53  |
| O                | 2.53   | 51.42  | 53.63  | 50.64  | 52.21  |
| Mg               | 0.59   | 0.57   | 0.51   | 0.53   | 0.41   |
| Si               | 0.26   | 0.24   | 0.12   | 0.12   | 0.14   |
| Fe               | 0.22   | 0.06   | 0.05   | 0.04   | 0.06   |
| Remainder        | 0.52   | 0.46   | 0.40   | 0.44   | 0.65   |

Fig. 2. Average current density for the analysed samples as a function of a target voltage

Rys. 2. Średnia gęstość prądu dla analizowanych próbek w funkcji przyłożonego napięcia
The lower currents registered during anodization in the presence of ethanol-modified electrolyte [28]. Moreover, a number of the small pores seem to decrease. From the FFT analysis along with the radial average of the respective SEM images are presented in Figure 6. As can be seen there is no difference in the FFT rings appearance between the samples anodized on base of Al nanoconcavities prepared during HA in aqueous (Fig. 6a÷d), and ethanol-modified electrolytes (Fig. 6e÷h). The points in the corners of hexagons become, however, more distinct as the voltage increases. The interpore distances determined from the radial average of the respective FFT images for both sets of samples are gathered in Figure 7a. As expected the decreased interpore distance on applied voltage was also observed [44]. It was found that at high anodizing potentials the $D_c$ is not solely determined by potential $U_t$, but is also influenced by the current density $i_a$ (high electric field). The corresponding equation can be written as follows [23, 24, 44]:

$$
\frac{D_c}{U_t} = A + B \exp \left( \frac{i_a}{C} \right)
$$

(A, B and C are constants which are dependent on the anodization conditions). Upon increasing of $U_t$, $D_c$ increases with the $U_t$, as demonstrated in Figure 7a. On the other hand, the $\zeta$ parameter will decrease with the increase of the $i_a$. Accordingly, it can be seen in Figure 7a that while $D_c$ increases with $U_t$, $\zeta$ decreases with increasing $U_t$ (and with increasing average current density, Fig. 2), in agreement with Eq. (2). However, according to Eq. (2) when $U_t$ obtained after a two-step HA-MA process performed on high-purity aluminium in ethanol-free electrolyte ($D_c$ in the range of 250 and 300 nm) [29]. In the anodization of high-purity aluminium it was suggested that ethanol, in addition to a local cooling effect, most probably has some impact on stress relaxation which arises from the volume expansion associated with the oxidation reaction at the metal-oxide interface during the initial stages of PAA film growth [40, 41]. The volume expansion during PAA film formation at the aluminium/oxide interface is associated with a repulsive interaction force (mechanical stress) and increases with the current density. This mechanical stress has to remain within a certain range of acceptable values, in order not to deteriorate the pore arrangement [42]. At the same time the interpore distance increases. Although the effect of ethanol is clearly visible in the lower average current densities (Fig. 2), the comparable interpore distances in the samples anodizes with and without ethanol suggest that the alloying elements in AA6063 foil have a much stronger influence on the relaxation process than ethanol.

The $\zeta$ parameter, defined as $\zeta = D_c/U_t$, is in the range between 2.1÷2.3 characteristic for HA process (Fig. 7a). The $\zeta$ values of around 2.0 nm/V were also determined previously in various HA processes [19, 22, 23, 43]. The reduced $\zeta$ for HA process was explained by a reduced voltage dependence of pore diameter and the barrier layer thickness of PAA under high electric filed at the pore bottom. In HA processes a non-linear dependence of interpore distance on applied voltage was also observed [44]. It was found that at high anodizing potentials the $D_c$ is not solely determined by potential $U_t$, but is also influenced by the current density $i_a$ (high electric field).

![Fig. 3. SEM micrographs of Al nanoconcave arrays obtained after a removal of the formed oxides in HA carried out in ethanol-free (a÷d) and ethanol-modified (e÷h) electrolyte at 120 (a, e), 140 (b, f), 160 (c, g), and 180 V (d, h); the 1 μm bar is for all images](image)

Rys. 3. Mikrografie SEM nanowęględrin Al otrzymanych w wyniku anodowania twardego HA w czystym elektrolucie (a÷d) i w elektrolucie modyfikowany-
nym etanolem (e÷h) odpowiednio dla napięć HA 120 (a, e), 140 (b, f), 160 (c, g), and 180 V (d, h); wskaźnik 1 μm dotyczy wszystkich mikrografii SEM

![Fig. 4. Current density vs time transients recorded during the second mild anodization for the samples anodized on base of the Al nanoconcave arrays prepared in HA process conducted in ethanol-free electrolyte with increasing average current density, Fig. 2), in agreement with Eq. (2). However, according to Eq. (2) when $U_t$ obtained after a two-step HA-MA process performed on high-purity aluminium in ethanol-free electrolyte ($D_c$ in the range of 250 and 300 nm) [29]. In the anodization of high-purity aluminium it was suggested that ethanol, in addition to a local cooling effect, most probably has some impact on stress relaxation which arises from the volume expansion associated with the oxidation reaction at the metal-oxide interface during the initial stages of PAA film growth [40, 41]. The volume expansion during PAA film formation at the aluminium/oxide interface is associated with a repulsive interaction force (mechanical stress) and increases with the current density. This mechanical stress has to remain within a certain range of acceptable values, in order not to deteriorate the pore arrangement [42]. At the same time the interpore distance increases. Although the effect of ethanol is clearly visible in the lower average current densities (Fig. 2), the comparable interpore distances in the samples anodizes with and without ethanol suggest that the alloying elements in AA6063 foil have a much stronger influence on the relaxation process than ethanol.

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Fig. 5. SEM micrographs of PAAs (top view) fabricated on base of the Al nanoconcave obtained in HA process conducted in ethanol-free (a–d) and ethanol-modulated (e–h) electrolyte at 120 (a, e), 140 (b, f), 160 (c, g), and 180 V (d, h); the bar 1 μm is for all images

Rys. 5. Mikrografie SEM anodowego tlenku aluminium (widok z góry) wytworzonego na bazie nanowgłębień Al otrzymanych w wyniku anodowania twardego HA w czystym elektrolicie (a–d) i elektrolicie modyfikowanym etanolem (e–h) odpowiednio dla napięć MA 120 (a, e), 140 (b, f), 160 (c, g), and 180 V (d, h); wskaźnik 1 μm dotyczy wszystkich mikrografii SEM

Fig. 6. Results of Fast Fourier Transforms, FFTs along with FFTs intensity profiles (below a given FFT image) of the respective SEM images of PAAs presented in Figure 5

Rys. 6. Wyniki szybkiej transformaty Fouriera FFTs wraz z profilami intensywności (poniżej odpowiednich obrazów FFT) wygenerowane na podstawie odpowiednich mikrografii SEM anodowego tlenku aluminium przedstawionych na rysunku 5
is kept constant, $i_0$ is a key parameter governing $D_c$. This means that under constant $U$, $D_c$ should decrease with increasing current density. Despite higher average current densities in acid-only electrolyte as compared to ethanol-modified one (Fig. 2), the $D_c$ values are comparable. This behaviour may be linked with similar $i_0$ values reached at $U$ for both sets of samples (regardless of the voltage value) and again may indicate that the stress relaxation process and the factors influencing the relaxation can be essential in elucidation of this phenomena. Therefore, analysis of Eq. (2) supports the assumption that the insoluble impurities in AA6063 contribute to mechanical stress relaxation at the metal/oxide interface during PAA growth, and partly replace ethanol in stress relaxation in the samples anodized in acid-only electrolyte.

The degree of pore ordering was estimated based on Eq. (1). The analysis is summarized in Figure 7b. As in the case of $D_c$, the $RR$ are comparable for both sets of samples, although it seems that the parameter becomes a little bit larger at higher voltages for samples anodized in ethanol-modified electrolyte, in contrast to what was found in HA-MA anodization of high-purity aluminium [29]. Moreover, the $RR$ parameter increases around two times with the applied voltage in both cases. In general, the $RR$ values are lower than the corresponding values determined for PAAs formed on high-purity aluminium [29]. This signifies that the impurities (the alloying elements) in the AA6063 alloy influence not only to the interpore distance but play also a significant role in degrading of pore ordering. Recently, a new method for characterizing the quality of less ordered PAA patterns in terms of uniformity, was developed [45].

In Figure 8 the PAA growth rate as a function of the applied voltage along with the respective SEM images of PAA cross-section are presented. The PAA growth rate increases with voltage as the ion migration rate through the barrier layer becomes faster under the higher electric field. However, in reference to the PAA growth rate on pure aluminium [29], the rate of the anodic oxide growth on AA6063 aluminium is lower. The lower rate is presumably caused by the presence of various amount of insoluble alloying elements in aluminium, which can block the entrance of electrolyte ions to the barrier layer and thus slow down the oxidation process. The EDS analysis of the PAA cross-sections suggests that quite a portion of alloying elements transfer to the oxides (Tab. 1). Particularly Mg is the element which seems to be easily incorporated in the PAA framework. Also Si traps quite easily in the PAA walls. On the other hand, the amount of Fe in the PAAs is much lower than in AA6063 sheet implying that this element generally does not incorporate to the PAA matrix. The inclusion of Mg and Si into the PAA matrix were previously observed and were associated with a formation of a non-uniform layer thickness and a scalloped substrate/oxide interface [34-36]. The features are also observed in the studied samples. Moreover, it was shown that the elements, such as Si, are also anodized during MA, forming Si particles surrounded by Si oxide. Owing to significantly reduced anodization of Si alumina invaded beneath the Si particle and eventually occluded the partially anodized Si particle in the film [36]. This gave rise to a non-uniform growth of the aluminium oxide pores.

The effect can be also seen in Figure 9 which presents the SEM images of the top and bottom parts of the resulted PAAs. Although generally the pores are well ordered throughout the whole PAAs thickness, occasionally the parallel arrangement of pores is disturbed by the presence of entities originating from the alloying elements. Furthermore, the long-range pore ordering is improving with the voltage increase. The voltage of 180 V is close to the self-ordering phenomenon occurring in 0.1 M phosphoric acid solution.
and the proximity to this condition in cooperation with the guidance of periodic concavities in the aluminium surface aided the parallel pores growth throughout the entire layer. Therefore, it can be concluded that a formation of a long-range ordered porous alumina on low purity AA6063 aluminium alloy is possible at high electric fields.

4. CONCLUSIONS

Two-step process combining HA and MA anodization of AA6063 aluminium alloy at voltages 120÷180 V in water-based oxalic acid solution and in electrolyte with 4:1 v/v water to ethanol mixture resulted in fabrication of porous anodic alumina with interpore distance between 270 and 370 nm, respectively. The presence of impurities influenced the current density vs time curves as well as the hexagonal pore ordering. The analysis demonstrated that the alloying elements in the AA6063 play an important role in the relaxation of mechanical stresses at the metal/oxide interface occurring during the PAA’s growth. The effect contributed to comparable $D_c$ values in the samples anodized in ethanol-free and ethanol-modified electrolyte despite much larger average current densities in the case of the former samples. Moreover, the impurities lowered
the hexagonal pore arrangement as compared to the arrangement in the PAAs prepared on high-purity aluminium. The pore ordering was improved under application of higher anodization voltages. The porous anodic alumina obtained under anodization of low-cost AA6063 alloy can be applied for instance in various filtration systems or in a large scale nanofibers production applicable particularly in the fields where the interpore distance corresponding to the spectral UV/blue range is important.

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Porowata anodowy tlenek aluminium wytworzony na stopie aluminium AA6063 w dwuetapowym procesie łączącym twardą i miękkie anodowanie

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Słowa kluczowe: anodowanie twarda, aluminium techniczne, anodowanie sterowane, etanol, porowaty anodowy tlenek aluminium (ATA).

1. CEL PRACY
Porowaty anodowy tlenek aluminium (ATA) jest jedną z najczęściej używanych matryc do wytwarzania szerokiej gamy nanostruktur z różnych materiałów znajdujących zastosowania w optoelektronice, przemysł medyczny oraz medycynie. Do produkcji wysokiej jakości nanomateriałów jest wymagana matryca ATA charakteryzująca się dużym stopniem heksagonalnego uporządkowania nanoporów oraz ich równoległym ułożeniem wzdłuż całego przekroju. Anodowanie twardy (wysokoprądowe) jest procesem, który skutkuje wytworzeniem matryc ATA o takich właśnie cechach. Ponadto proces ten dokładnie skracza czas wytwarzania matrycy oraz powoduje rozszerzenie zakresu możliwych do osiągnięcia parametrów geometrycznych ATA, tj. odległości między porami. Zwykle najlepszej jakości matryce uzyskuje się przez anodowanie aluminium o wysokiej czystości (5N). Wysokie koszty uzyskania aluminium czystego Al powodują, że poszukuje się materiałów alternatywnych do produkcji ATA, takich jak stop aluminium. W pracy przeprowadzono dwuetapowy proces anodowania łączący anodowanie twardze (HA) w pierwszym etapie i anodowanie miękkie (MA) w drugim na stopie aluminium AA6063. Łączone procesy HA i MA umożliwiają uzyskanie heksagonalnie ułożonych, równoległych porów w całym przekroju matrycy ATA. Przeprowadzono kompleksową analizę matryc ATA wytworzonych w różnych napięciach z zakresu 120–180 V. Zbadano wpływ etanolu na proces anodowania i budową matryc przez porównanie krzywych prądowych zarejestrowanych w trakcie anodowania z parametrami geometrycznymi oraz stopniem uporządkowania nanoporów obliczonych metodą FFT.

2. MATERIAŁ I METODYKA BADAN
Blacha z aluminium AA6063 (próbki o wymiarze 2 cm × 1 cm) została wyelektropolowana w mieszaninie 1:4:60% HClO₄ oraz etanolu w 0°C, przy stałym napięciu równym 20 V, przez 2 min. Następnie tak przygotowane próbki poddano anodowaniu w 0,3 M roztworze wody w temperaturze 0°C, przy napięciu z zakresu 120–180 V. Anodowane były dwie serie próbek: I seria była anodowana w czystym roztworze wodnym, II seria w roztworze zawierającym 1:4 w/w wody do etanolu. Uzyskany tlenek wytworzył w I etapie (HA) usunięto w mieszaninie 6% mas. wodorowego i 1,8% mas. wody chromowego w 60°C przez 3 h. Następnie próbki zostały poddane II etapowi anodowania (MA) w 0,1 M roztworze wodorowego kwasu chromowego, w temperaturze 0°C oraz ich samych napięciach, co zastosowane w I etapie. Na podstawie mikrografii SEM warstwy powierzchniowej analityzowanych próbek wygenerowano obrazy FFT. Z wygenerowanych pierścieni FFT obliczono odległości między porami Dₜ oraz parametr uporządkowania nanoporów RR.

3. WYNIKI I ICH Dyskusja
Uzuwane wyniki pokazały, że matryce ATA wytworzono na aluminium AA6063 charakteryzują się gorszym stopniem uporządkowania nanoporów w porównaniu z ATA wytworzonym na czystym Al. Pierwiastki stopowe obecne w AA6063 powodują perturbację w uporządkowanym wzroście matrycy ATA. Dodatkowo zaobserwowano, że obecność pierwiastków stopowych przyczyniła się do znacznego obniżenia gęstości prądowej w odniesieniu do gęstości prądowej zarejestrowanej podczas anodowania czystego Al, co prawdopodobnie było spowodowane spowolnieniem dyfuzji jonów w warstwie barierowej przez obecne tam nieczystości. Nie zauważono znaczącego wpływu etanolu na proces anodowania, jak i na parametry geometryczne matrycy ATA w odróżnieniu do wyraźnego wpływu tego modyfikatora na proces anodowania czystego aluminium. Ponieważ mechanizm porządkowania porów matrycy jest ściśle związanym z pojawieniem się naprężeń ściskających na granicy metal/tlenek podczas wzrostu tlenku (duża różnica stałych sieciowych pomiędzy Al i Al₂O₃), efekt ten wytłumaczyło silnym wpływem pierwiastków stopowych, co w skali 120÷180 V, dla serii próbek poddanych HA w czystej wodzie oraz MA w 0,3 M roztworze kwasu szczawio- wego. W efekcie nie wystąpiły odpowiednie warunki mechaniczne do formowania się zwartej, heksagonalnie uporządkowanej matrycy ATA. Stopień heksagonalnego i wzdłużnego uporządkowania porów polepszył się wraz ze wzrostem przyłożonego napięcia do gęstości prądowej zarejestrowanej podczas anodowania.

4. PODSUMOWANIE
Stop aluminium AA6063 poddano dwuetapowemu procesowi anodowania łączącemu HA w 0,3 M roztworze kwasu szczawio- wego oraz MA w 0,1 M roztworze kwasu fosforowego w napięciach z zakresu 120–180 V. Badano wpływ etanolu na proces oraz parametry geometryczne uzyskanych matryc ATA. Analiza zarówno krzywych prądowych w funkcji czasu, jak i parametrów geometrycznych matrycy ATA pozwoliła na sformułowanie wniosku, że pierwiastki stopowe obecne w AA6063 w znaczący sposób przyczyniają się do relaksacji naprężeń mechanicznych generowanych podczas wzrostu tlenku na granicy metal/tlenek. W efekcie ATA charakteryzowały się podobnymi wartościami parametru Dₜ (270–370 nm) oraz podobnym stopniem uporządkowania nanoporów zarówno dla serii próbek poddanych HA w czystym elektrolucie, jak i modyfikowanym etanolem, pomimo większej średniej gęstości prądowej w porównaniu z ATA wytworzonymi na czystym aluminium.