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AL₂O₃-Me LAYERS OBTAINED BY THE ELECTROCHEMICAL METHOD

WARSTWY AL₂O₃-Me UZYSKANE METODĄ ELEKTROCHEMICZNĄ

Abstract

Fine membranes with controlled size of pores were produced by the two step anodizing process of the aluminium in oxalic acid solution. Highly ordered Co, Fe and CoFe nanowire arrays were prepared by two electrodeposition techniques: pulsed (PED) and potentiostatic electrodeposition (DC) into the anodic alumina membrane (AAM) templates. It has been observed that both experimental methods (PED, DC) enable the embedding of Co, Fe as well as CoFe alloy into the pores of the AAM with a high aspect ratio.

Key words: *anodic alumina membrane (AAM), electrodeposition, nanowires, alloy*

Streszczenie

Membrany z kontrolowaną średnicą porów zostały otrzymane w procesie dwuetapowego anodowania aluminium w roztworze kwasu szczawiowego. Wysoko uporządkowane nanodrutki Co, Fe oraz stopu CoFe uzyskano w procesie elektroosadzania metalu na membranie anodowego tlenku glinu (AAM), przy użyciu dwóch technik prądowych: pulsacyjnego (PED) i potencjostatycznego (DC) elektroosadzania na membranie. Zaobserwowano, że w obu eksperymentalnych metodach (PED, DC) jest możliwe wbudowanie Co, Fe oraz stopu CoFe w porach anodowego tlenku aluminium o wysokim współczynniku geometrii kształtu.

Słowa kluczowe: *membrana anodowego tlenku glinu (AAM), elektroosadzanie, nanodrutki, stop*

1. Introduction

An increased interest in nanostructured porous materials has been observed for the last years. Anodic alumina membrane (AAM) produced by anodization of pure aluminium has become an important template material for the fabrication of nanostructured materials [1]. Considerable attention has been focused mainly on nanotubes [2], nanowires [3], as well as nanoporous materials. It is particularly due to their unique electronic, magnetic, optoelectronic, biomedical and mechanical properties [4]. Various methods for metal incorporation into the membrane pores has been described in the literature. Among them the electrodeposition revealed as a simple and a low cost technique the production of large arrays of metallic nanowires. Such structures can be used successfully in the single-electron devices, nanoelectrodes and microfluidics [3, 5, 6]. Many research groups have investigated the electrodeposition of magnetic nanowires into AAM templates [4, 7÷9]. The effects of the AAM pore diameter, current density, kind electrolyte, pH of electrolyte and annealing on the structure and the magnetic properties of the nanowires were studied. The pulse current and potentiostatic methods as well as electrodeposition under the external magnetic field were also proposed [4, 10÷12]. Among the materials investigated, Co and CoFe based alloys have received particular attention, because of their high saturation magnetization and high Curie temperature [13÷15].

Two methods are used for the pretreatment of the alumina template before pulsed electrodeposition. One of them does not require either the aluminum substrate or the barrier layer dissolution. However, it results in the incomplete filling of the template nanoholes with the electrodeposited metal. The second method is more complex, but it provides for the incorporation of the metal nanowire with a high aspect ratio. In this method the aluminum substrate as well as the insulated barrier layer between the aluminum substrate and the porous layer at the outer part of the alumina film have to be removed. It was found that PED is particularly appropriate for the electrodeposition into the nanoporous templates, where the diffusion of the electrolyte through the pores is the rate determining process [16].

2. Experimental

The Co, Fe and CoFe nanowires arrays were prepared by the DC and PED electrodeposition. The nanometer – sized pores of anodic aluminum membranes were used the nanoporous anodic alumina membranes were prepared in a two-step anodizing process described by Masuda [17]. Prior to anodizing, a commercial aluminium sheet (99,999% purity) was degreased in acetone, annealed (argon atmosphere for 3 h at 500°C) to remove any residual stress, and electropolished at a constant-voltage of 48 V during 20 s at 16°C in a solution of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$. The polished foil was anodized in 0.3 M oxalic acid solutions at 40 V during 24 h at 2°C. After the first anodization, the membranes were etched in the phosphoric acid (5 wt.%) and then in the chromic acid (1.8 wt.%) to remove the irregular oxide layer. Subsequent anodization was conducted during 5 h at the same condition as in the first anodization step. After the second anodizing step the aluminum substrate was chemically removed by immersion in a diluted $\text{CuCl}_2 + \text{HCl}$ solution. The barrier layer at the bottom of the samples was

chemically removed in a 5 wt.% H_3PO_4 solution (15 min at 30°C) in order to prepare the membranes with open pores. The H_3PO_4 solution allows for the dissolving of the walls of the nanopores, resulting in the widening of the diameter of the nanopores [18]. The electrical contact to the membrane was ensured by the gold layer prepared by vapour deposition. The side was fixed by electrodeposited copper layer.

The Co, Fe, CoFe nanowire arrays were electrodeposited from the sulfate electrolytes with compositions listed in Table 1. A pH values of 3 and 2.8 were adjusted with H_2SO_4 . All experiments were carried out at room temperature.

Table 1. The composition of the electrolytes

Bath	C_{CoSO_4} [mol/dm ³]	C_{FeSO_4} [mol/dm ³]	$C_{\text{H}_3\text{BO}_3}$ [mol/dm ³]	pH
Co	0.5	0.0	0.3	3.0
Fe	0.0	0.5	0.3	2.8
CoFe	0.5	0.3	0.3	3.0

A three-electrode cell was used for the electrodeposition, with a platinum foil as counter electrode and a standard calomel electrode (SCE) as a reference. For the electrodeposition of the Fe the nanowire array pure iron foil as counter electrode was used. Electrodeposition was performed in the potentiostatic method, using an IPS Jassile potentiostat. Two different techniques were applied (PED and DC)

The morphology of the Co, Fe, CoFe nanowire arrays was examined by scanning electron microscope (SEM).

3. Results and discussion

3.1. Preparation of the AAM

Membrane preparation is the most important step for the fabrication of metallic nanowires. The diameter of the pores and its length can be controlled by the appropriate selection of the anodizing parameters (voltage and time) [6]. Pore diameter in the linear dependence of the anodizing voltage and pore length linearly depends on the anodizing time [1, 5, 6]. The number of pores per unit area square centimeter is proportional to the square of the anodizing potential [6]. The membrane was produced by the anodizing of the aluminum metal in the oxalic acid solution at a voltage of 40 V and 2°C . A typical current-time transient during the second anodization process is shown in Figure 1. The currents densities for the first and second anodization were similar.

In this step, the pores grow hexagonally and perpendicular to the metal surface. At the beginning of the process the current density decreases very rapidly from a high value 6,36 to 0,63 mA/cm². Then it increases gradually to the value of 0,95 mA/cm² and finally it remains at a constant level. The sharp decrease in the current corresponds to the alumina formation. The nanopores growth starts with the formation of the barrier layer, which finally becomes the bottom side of the nanopores. It corresponds to the minimum value of the current-time graph (Fig. 1). Later the rates of the pore growth rate and alumina formation become equal.

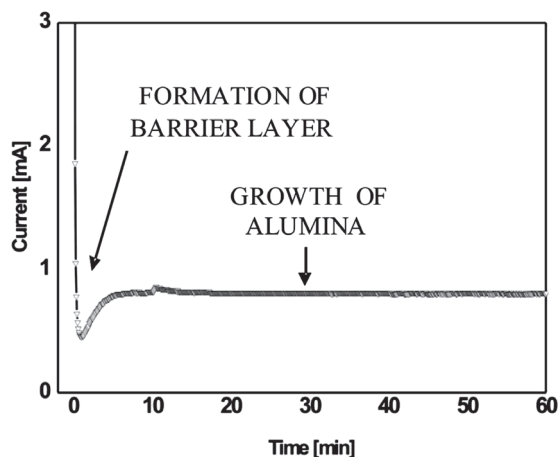


Fig. 1. Current-time curve for the second anodization process, in 0.3 M $\text{H}_2\text{C}_2\text{O}_4$ at a constant potential of 40 V, to = 2°C

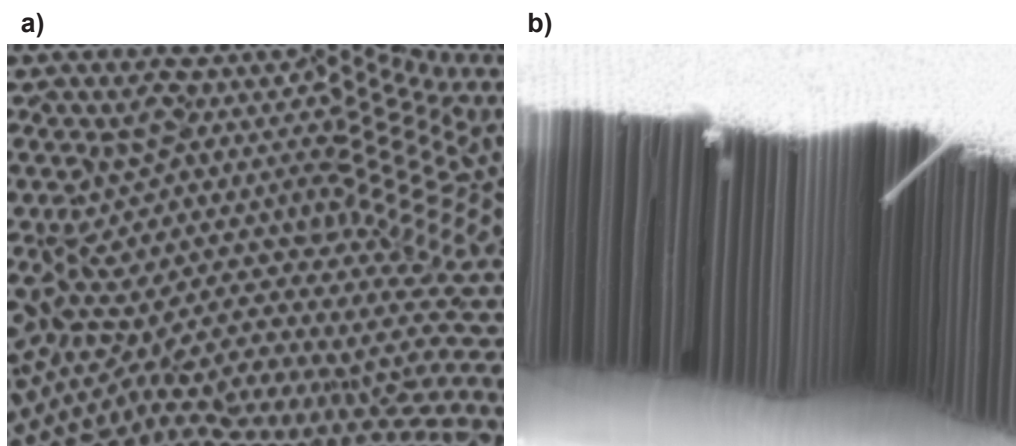


Fig. 2. SEM image of the AAM formed by a two-step anodization: a) top view, b) cross-section view

The SEM micrographs of the surface and the cross-section of the as-prepared nanoporous anodic alumina membrane are shown in Figure 2. It was observed a perfect hexagonal nanopore arrangement with uniform pore diameter. The measured pore diameter was between 60 and 80 nm and the interpore distance was 110 nm.

3.2. Electrodeposition

Cyclic voltammetry was applied to determine the optimal potentials for Co, Fe and CoFe alloy electrodeposition. The dependence of current density on potential $i = f(E)$ is obtained from cyclic voltammetry. This relationship is shown in Figure 3. The all potentials are given versus saturated calomel electrode (SCE).

The current density-potential plots show two characteristic regions for all investigated systems. The first region corresponds to the simultaneous deposition of the metals and it the reduction of the hydrogen ions. It was found that the cathodic process from

potentials of the $-850 \text{ mV}_{\text{SCE}}$, $-750 \text{ mV}_{\text{SCE}}$ and $-700 \text{ mV}_{\text{SCE}}$ for Co, Fe and CoFe system, respectively. The range current for the deposition CoFe alloy is wider and is shifted to more negative values. The scan in the region deposition was finished at the -1200 ; -1400 and $-1550 \text{ mV}_{\text{SCE}}$ for Co, Fe, CoFe, respectively. Above these potentials the hydrogen evolution was very high. The cathodic part of the CV curves was characterized by a gradual increase of the cathodic current. However it was observed, that the polarization of the cathodic processes were dependent on the system studied. The process was the most inhibited for the FeSO_4 solution. The second parts of the CV curves correspond to the dissolution of the metals deposited during the cathodic scan. The anodic peaks were at potentials of -470 ; -670 and $-590 \text{ mV}_{\text{SCE}}$ for Co, Fe, CoFe, respectively. The anodic peak for CoFe is shifted to more positive values in comparison to peaks for Co and Fe. Simultaneously, it higher units deposited of Co-Fe dissolution in comparison to the anodic currents of Co and Fe was observed. For every investigated bath have place completely dissolved of deposited metal at positive potentials.

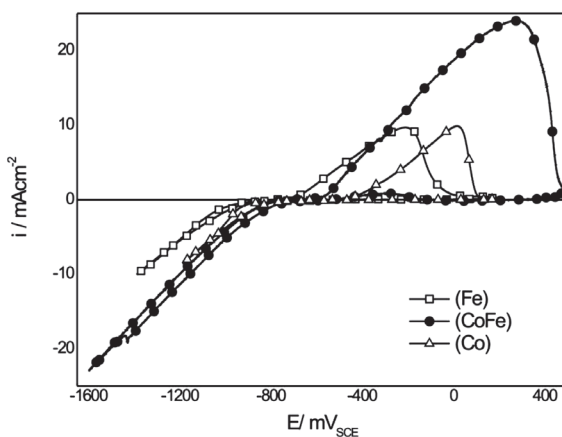


Fig. 3. Cyclic voltammograms for an electrolyte containing (●) 0.5M CoSO_4 and 0.3M FeSO_4 (□) 0.5M FeSO_4 (Δ) 0.5M CoSO_4 and boric acid; $dE/dt = 20\text{mV/s}$

It wasn't found any solid products on the gold electrode surface after finishing the measurements. Ranges of electrochemical potentials in which the deposition of Co and Fe as also codeposition both of metals is possible were determined according on the basis of cyclic voltammograms investigations. To determine the optimal conditions at which Co, Fe, CoFe alloy would deposit, depositions were performed on an Au electrode.

The decomposition was done according two different methods:

- at a constant current (DC) during 5 min in a potential ranges: -900 to -1250 mV for Fe, -1200 mV for Co and -1350 mV for CoFe,
- at using alternate rectangular cathodic and anodic pulses with different time duration (t_A , t_K) in a range of 10 to 170 ms.

On the basis of the quality of the received metallic layers optimal deposition conditions were selected. As a criterion of "good" deposit apply: compactness and quantity of pits on the layer surface.

The Co, Fe, CoFe nanowires were fabricated by electrodeposition for using two methods. The electrodeposition into the pore membrane is not straightforward, due to the vast number of high aspect ratio pores. If the rate of electrodeposition is higher than

that of the transport through the pores, the metal ion concentration decreases at the bottom of the pores. Consequently, hydrogen evolution becomes the dominant process, inhibiting the homogenous deposition and decreasing the pore filling factor and the current efficiency. In the Figure 4 see on began the charge of double layers was observed and following the electrodeposition of the metal. An 140 ms cathodic pulse (potential control) with relatively high current density was employed. The voltage response was about $-1.2 V_{SCE}$. In comparison to the potentiostatic deposition, relatively high current density is visible at the moment of the metal deposition which should increase the number of deposited pores and continuous nanowires. This current density was sufficient to deposit metallic cobalt, iron and alloy into the membrane, while the short pulse time prevented metal ion depletion and hydrogen evolution.

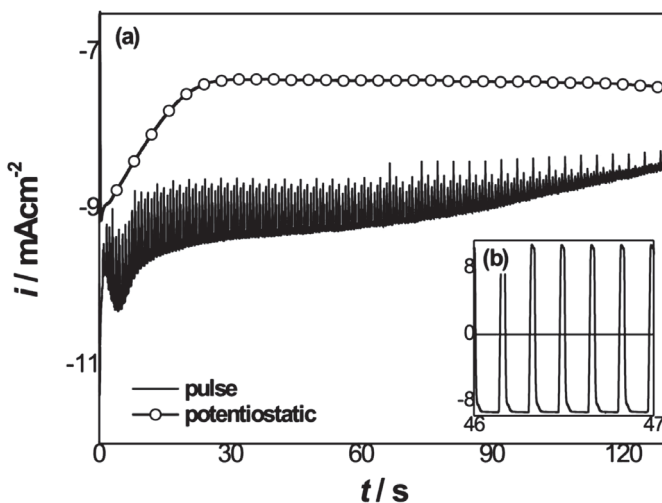


Fig. 4. Current-time curves for: a) DC and PED, at $E = -1,2 V$ vs. SCE and $E_a = 0 V$, $E_c = -1,2 V$ vs SCE, respectively, b) magnified area of the steady state from the PED transient

Figure 5 shows SEM images of the deposited nanowires. The sectional – view of the membrane with parallel Co, Fe, CoFe nanowires can be visible. It is well known that the length of the deposited nanowires depends on the time of the deposition process. The dimension of a nanowire is defined by the dimension of a pore.

The XRD patterns for the Co and Fe nanowire arrays are shown in the Figure 6. The diffraction peaks correspond to the (111), (200) and (220) face centred cubic (fcc) polycrystalline Co reflections, while the base centre cubic (bcc) reflections were found in the polycrystalline Fe and CoFe sample. Patterns of the Al_2O_3 and Au/Cu substrate were also detected.

The present studies show that it is possible to deposit a metal in deep holes by using both techniques. The appearance of hydroxides on the surface of a membrane has been revealed – see Figure 5d. This is due to the parasitic hydrogen evolution reaction, which interferes with the reaction of Co, Fe and CoFe alloy deposition.

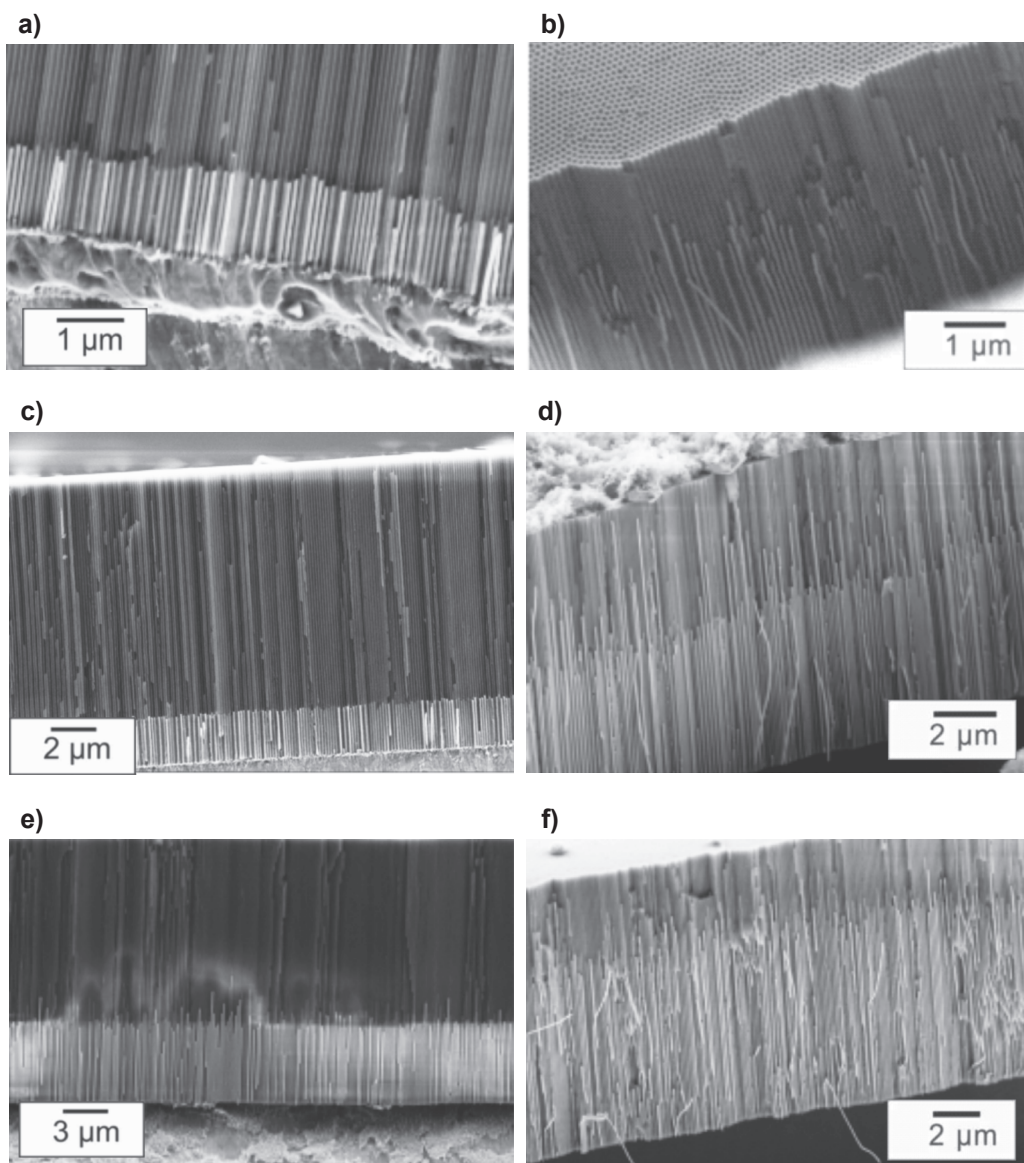


Fig. 5. Cross-section SEM images of membranes:

- Co nanowires: a) DC, $E = -1.2$ V, $t = 150$ s; b) PED, $E_a = 0$ V, $t_a = 20$ ms; $E_c = -1.2$ V, $t_c = 140$ ms,
- Fe nanowires: c) DC, $E = -1.2$ V, $t = 150$ s; d) PED, $E_a = -0.35$ V, $t_a = 20$ ms; $E_c = -1.2$ V, $t_c = 140$ ms,
- CoFe nanowires: e) DC, $E = -1.0$ V, $t = 150$ s; f) PED, $E_a = -0.35$ V, $t_a = 20$ ms; $E_c = -1.0$ V, $t_c = 140$ ms

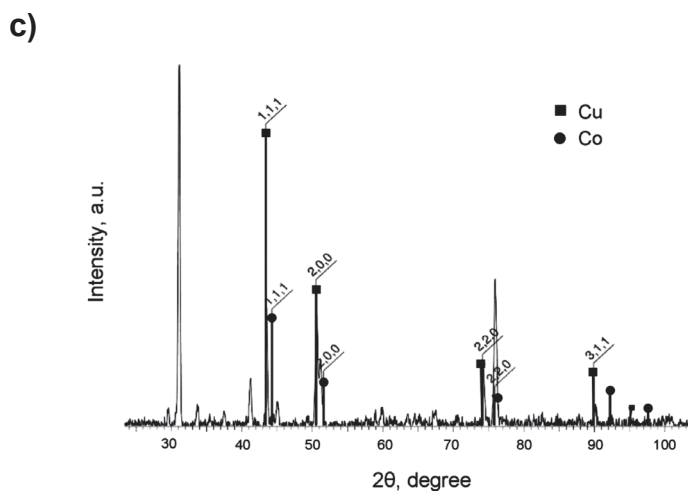
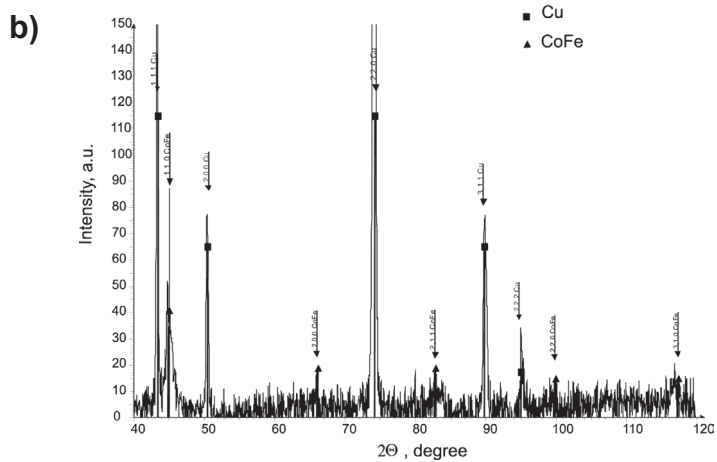
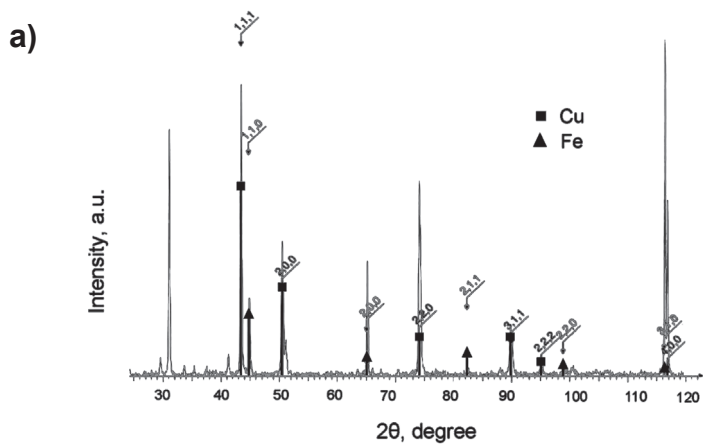


Fig. 6. XRD pattern of: a) Co, b) Fe, c) Co-Fe alloy nanowires arrays

3. Conclusion

In conclusion, fine membranes with controlled size of pores can be produced by anodising of aluminium in oxalic acid solution. The pores growth is parallel straight and facilitates the embedding of metals into pores. The potentials of electrodeposition the Co, Fe and CoFe alloy have been selected whereas for PED also times. The techniques of potentiostatic and pulsed electrodeposition have successfully been applied to fabricate Co, Fe and CoFe nanowires arrays deposited into AAM. The as-obtained nanowires have been investigated by SEM. The nanowires have a diameter of about 70 nm and exhibit height aspect ration. In case of both methods (DC and PED) the formation of the hydroxides on the surface of the metal was recognized.

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