

# Cobalt Deposition Into a Nanotemplate Made of Anodized Aluminum Alloys

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**Abstract** — Well – ordered nanotemplates were obtained by anodisation of pure Al and Al-alloys in sulfuric acid. A bottom-up filling up of these templates with Co nanowires was investigated. The growth of cobalt nanowire arrays in the anodic aluminum oxide layers (AAO) was done under AC electrodeposition mode. The optimal AC mode under Vp-p = 30 V was in the range of 150 – 200 Hz. The uniformity of pore filling can be achieved only for several micrometers of nanowires.

**Index Terms** — Co, nanotemplate, AAO, AC deposition.

## I. INTRODUCTION

Porous anodic aluminum oxide (AAO) membranes formed by anodization of aluminum in acidic electrolytes are one of the most versatile templates for nanofabrication. A simple, self-organization achieved by a two-step Al anodization in sulfuric acid, oxalic acid and phosphoric acid solutions does not require any sophisticated and expensive technology. . A high purity aluminum foil (min 99.99% of Al) is used mostly as starting material. There are only few reports dealing with the anodizing of aluminum alloys. The synthesis of AAO template on Al alloys is not a trivial issue and often requires specific conditions different from those typically applied in the case of anodization of pure aluminum.

The motivation for this work is to investigate the possibility to fabricate nanoporous AAO templates from aluminum alloys in a simple manner, and the use of these templates for manufacturing of Co nanowires arrays.

## II. ANODISATION of Al and its ALLOYS.

The following types of aluminum were anodized: pure Al (99.99%), commercial AA1050 alloy, commercial 6082 alloy and commercial 6060 alloy (Table 1) by two-step anodizing under identical operating conditions.

The pore ordering at the surface of the anodic alumina is low because the holes develop randomly during the initial stage of anodization. To improve the ordering of the surface of anodic porous alumina, a two-step anodization was introduced [1]. That process involves two successive anodization steps: the first one consists of a long-period anodization to form the highly ordered hole configuration at the oxide/Al interface, and the second one is performed after removal of the oxide formed in the first anodization step (Fig. 1).

After the removal of the oxide, an array of highly ordered dimples are formed on the Al, and these dimples can act as initiation sites for the hole development in the second anodization step.

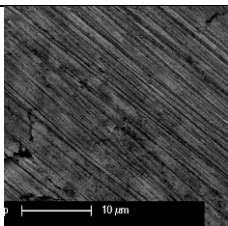
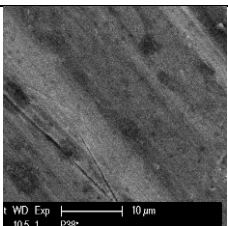
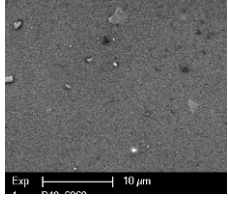
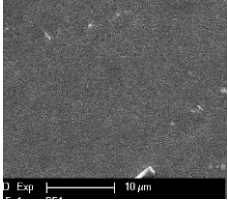
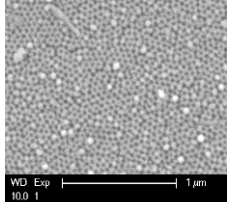
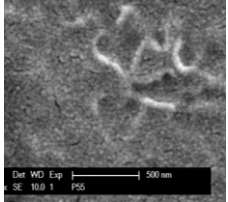
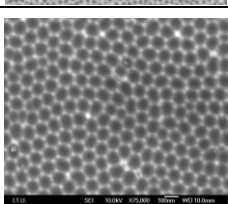
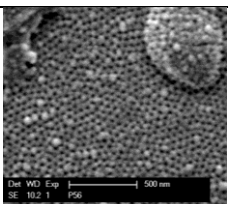
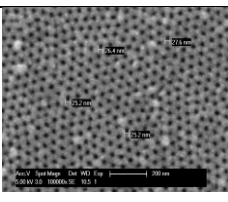
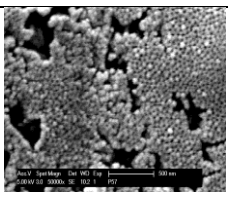
**TABLE 1.** Composition (wt.%) of the aluminum alloys.

Composition (wt.%)	AA1050	AA6082	AA6060
Si	0.25	0.7-1.3	0.30-0.6
Fe	0.40	0.5	0.10-0.30
Cu	0.05	0.10	0.10
Mn	0.05	0.40-1.0	0.10
Mg	0.05	0.60-1.2	0.35-0.6
Cr	-	0.25	0.05
Zn	0.07	0.20	0.15
Ti	0.05	0.10	0.10
Others (total)	0.03	0.15	0.15
Al	Min. 99.5	Balance	Balance

This process generates an ordered hole array throughout the entire oxide layer. This process can also be applied for the preparation of a porous alumina mask used for several types of nanofabrication techniques in which the ordered straight through-holes are essential [1].

In our research, a first and second anodizing step have been performed in a 20 wt % sulphuric acid electrolyte using a two electrode electrochemical cell set up equipped with a magnetic stirrer rotating at 500 rpm. The temperature was kept at  $\sim 0 - 1^{\circ}\text{C}$ ; anodization potential 21 V. After each anodization step, subsequent electropolishing and oxide removal steps, SEM images were taken in order to evaluate the influence of the condition on the each anodising step. In Table 2 the differences between pure Al and AA1050 alloys are given.

**TABLE 2.** Morphology of pure Al and AA1050 alloy after each step of AAO preparation

Steps	99.99 Al	AA1050
As-given		
Polished		
I anodization		
Oxide removal		
II anodisation		

Due to differences in surface temperature at high voltages during the anodizing steps, some stresses can be built up in the material and lead to inappropriate conditions for well-ordered pore growth. This can be seen e.g. for AA1050 alloy (Table 2), where some non-homogeneities and voids can be observed. Therefore a strict temperature control should be done to limit thermal stresses in materials. Characterization of the stress state of the materials (cold rolled, annealed, percentage of alloying elements, thickness of the sheets etc.) to be anodized is another parameter that should be taken into consideration.

Nevertheless, under strict control of anodizing parameters and avoiding the thermal stress of the material acceptable anodizing from the point of view of well-ordered pores can be achieved (Fig. 1). The thickness of the anodized layer was  $\sim 10 \mu\text{m}$  with a pore diameter of about  $\sim 20 - 25 \text{ nm}$ . It seems that the pores density of AAO surface is not largely affected by the type of aluminium alloys used. On the contrary, the degree of hexagonal distribution of the pores depends on the type of aluminum alloy anodized (Fig. 1). Alloying elements (Si, Mg) cause precipitates that can be noticed on the surface by SEM, especially for the 6060 alloy. Nevertheless a nanoporous structure can be obtained on all investigated aluminum alloys after the second anodization step.

Following the second anodization, the voltage was systematically reduced to promote a thinning of the barrier layer according to [2]. Barrier layer thinning was achieved in 2 steps:

1. reducing the voltage by  $2 \text{ Vmin}^{-1}$  from 21 V to 15 V,
2. by  $1 \text{ Vmin}^{-1}$  from 15 V to 10 V.

The barrier layer thinning was then continued for 5 min at this final voltage to stabilize the barrier layer thickness. By thinning the barrier layer the deposition process can be carried out due to decrease of oxide resistance.

### III. ELECTRODEPOSITION of Co ARRAYS.

The Co nanowires were electrodeposited from the electrolyte consisting of (g/l):

$\text{CoSO}_4 - 100$ , boric acid - 30, at a pH value of 3.8.

To fill up the template with Co an alternative current (AC) electrodeposition was carried out using a 200 Hz sine wave form (reductive time = oxidative time = 2.5 ms) in which the deposition voltage was  $30 V_{p-p}$  [2].  $V_{p-p}$  is the voltage between the reductive and oxidative voltages. These values were -15 V and 15 V, respectively.

A typical diagram of AC sine waveform at 200 Hz is shown in Fig. 2a. The deposition time was varied from 3 to 15 min. Also a pulse electrodeposition was carried out under deposition parameters:

$t_{\text{reductive}} = t_{\text{oxidative}} = 2.5 \text{ ms}$  and  $t_{\text{off}} = 30$  and 70 ms (see Fig. 2b).

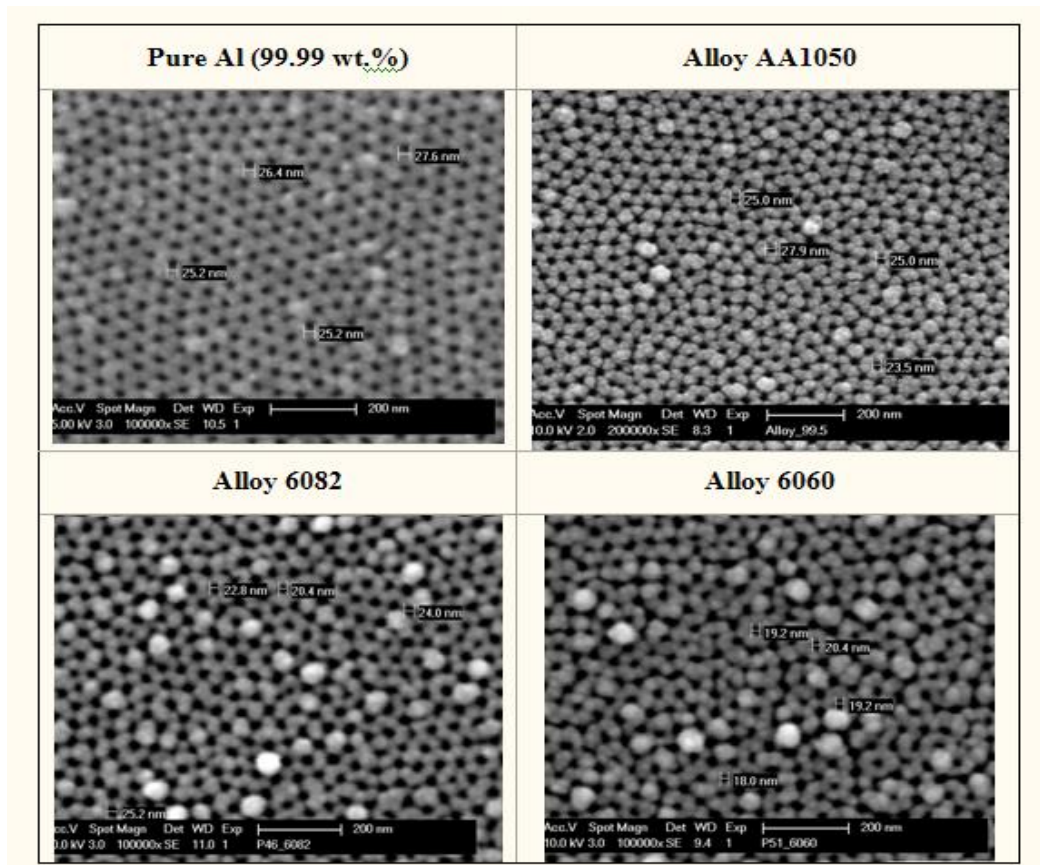


Figure 1. SEM images of the top-surface of Al alloys samples after second step anodization

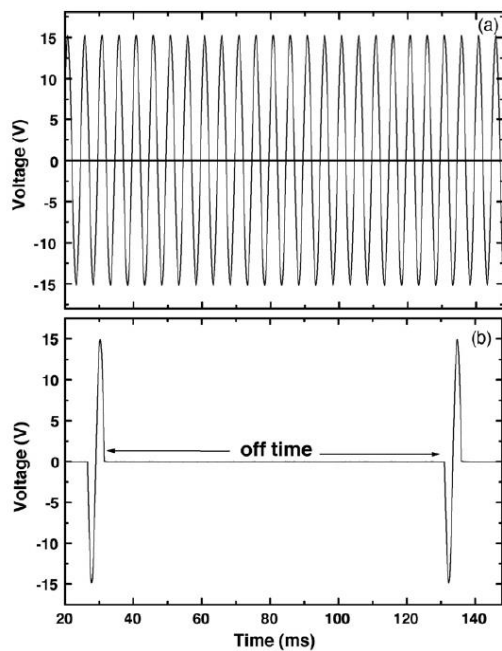


Figure 2. Schematic diagram of ac 200 Hz sine waveform (a) and pulse shape with off-time = 100 ms and reductive time = oxidative time = 5 ms (b).

Only using an AC electrodeposition at 200 Hz it was possible to obtain a total pore filling after 15 minutes (see, Fig. 3).

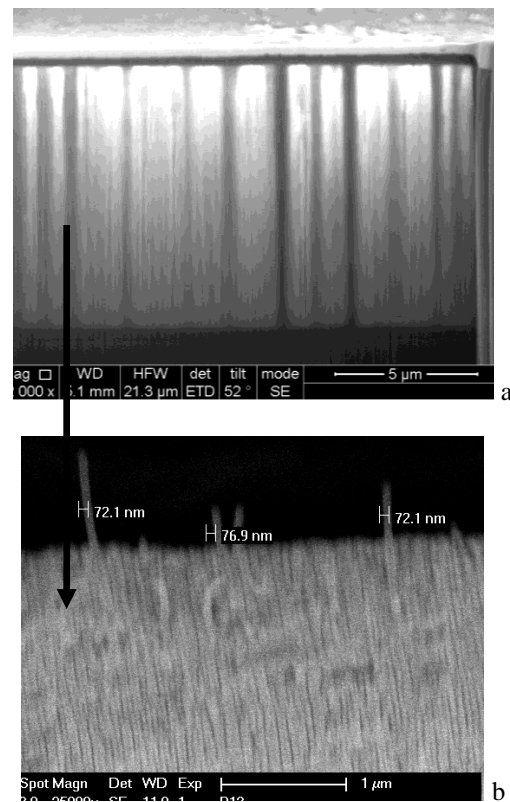
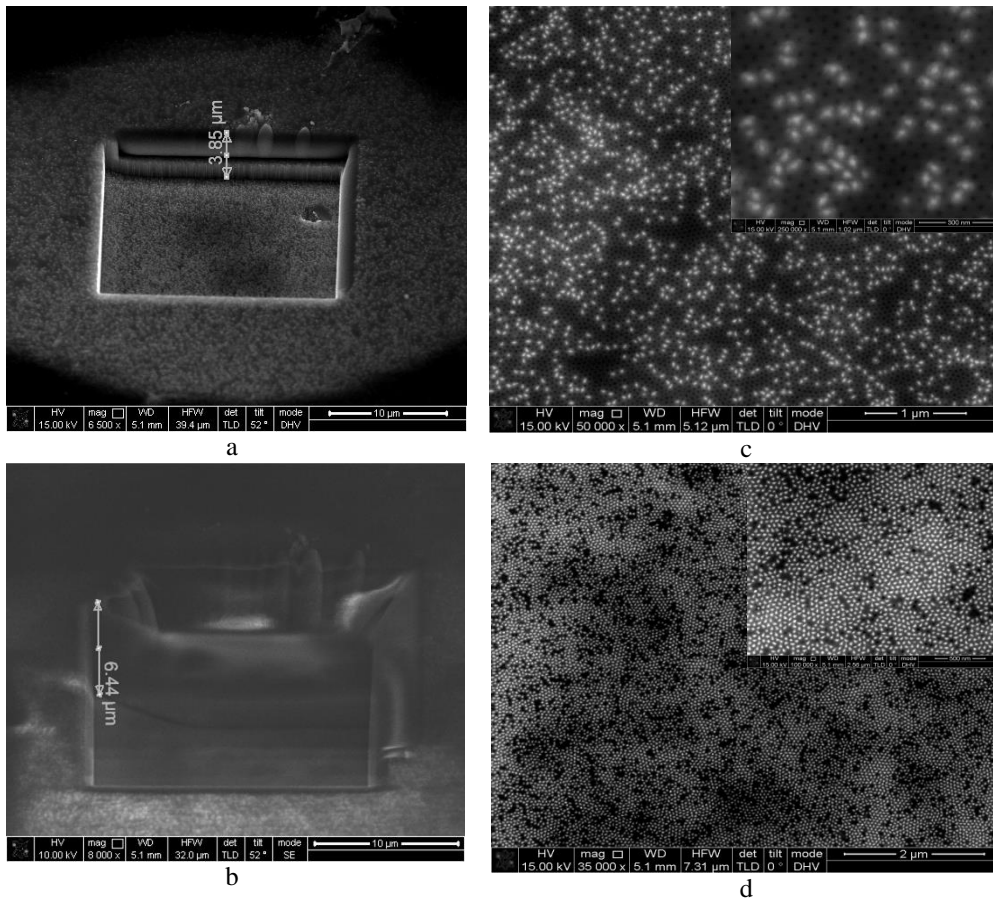


Figure 3. SEM images of cross section of AAO filled with Co using AC electrodeposition ( $f = 200$  Hz,  $t = 15$  min). a and b – are low and high magnifications of filled AAO correspondingly.



**Figure 4:** SEM images of the surfaces of 12  $\mu\text{m}$  ion-milled Co-filled AAO template as a function of the milling depth: 3.8  $\mu\text{m}$  (a, c) and 6.5  $\mu\text{m}$  (b, d), where c, d captions are the top-images of a, b cross-sections. The inserts in the c, d captions are the high magnification images of the relevant surface.

Although some voids or empty spaces can be observed on cross-section images (Fig. 3a). In order to investigate the membrane pores filling with Co, a FIB (focus ion beam) analysis was performed (Fig. 4) on sample obtained using for electrodeposition the the same conditions:  $V_{p-p} = 30 \text{ V}$ ,  $f = 200 \text{ Hz}$ ,  $t = 20 \text{ min}$ .

Thus, the images of pores filled as a function of depth beneath the initial electrode surface is presented in the Fig. 4, where in the a, b images are presented the depths of milled AAO from the top of the samples and in c, d images top surface in the groves formed are seen. The fraction of pores filled at 3.8  $\mu\text{m}$  below the surface is ca. 30% (Fig. 4a), while the fraction filled at 6.5  $\mu\text{m}$  below the initial surface is  $\sim 85\%$  (Fig. 4b). This fact denoted that uniform filling of Co is difficult to achieve on entire area of AAO and during electrodeposition evolving hydrogen blocks some pores. Thus, the uniformity of pore filling can be achieved only for several micrometers for Co nanowires growth.

#### IV. CONCLUSIONS

Well – ordered AAO from sulfuric acid was obtained. Also, it was possible to obtain AAO using industrial aluminum alloys. Different electrochemical

regimes were applied for template synthesis of cobalt nanowire arrays in home – made AAO under AC electrodeposition mode. The optimal conditions of AC mode  $V_{p-p} = 30 \text{ V}$  in the view of applied current frequencies (50 – 1000 Hz) are in the range of 150 – 200 Hz.

#### ACKNOWLEDGMENT

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