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ELECTROCHEMICAL PREPARATION OF Co-Cu ALLOY NANOWIRES AND THEIR CHARACTERISATION

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ABSTRACT. In this study, Co-Cu alloy nanowires were grown in anodic aluminium oxide (AAO) template obtained through one-step anodisation method of aluminium-magnesium alloy (Al 95%) in oxalic acid solution at constant voltage of 40 V. The electrodeposition of Co-Cu alloy nanowires into the 10 μm thickness of AAO template with pore average diameter of 40 nm was studied using a single bath containing both cobalt and copper ions. The galvanostatic reverse pulse plating was chosen as preparation method of Co-Cu alloy nanowires at room temperature. The optimal operation parameters required during the preparation method were established by cyclic voltammetry (CV) experiments. The electrochemical deposition was performed at current densities ranging between 20-50 mA/cm^2 during 60 min. The physical and chemical properties of Co-Cu alloy nanowires have been investigated through scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), X-ray fluorescence spectroscopy (XRF) and focused-ion-beam-microscopy (FIB) techniques.

Keywords: *Al, anodisation, AAO template, Co-Cu alloy nanowires, electrodeposition, reverse pulse plating, FIB, TEM.*

INTRODUCTION

Nowadays we witnessed a development of high density information on magnetic storage. It has been demonstrated that ferromagnetic wires having a high aspect ratio can be prepared using porous alumina (Al_2O_3) as template [1].

Various magnetic wires have been synthesized using different methods and types of templates. In our days the electrodeposition of Co alloys nanowires with Ni, Fe or Cu is intensively studied due to the special properties of these

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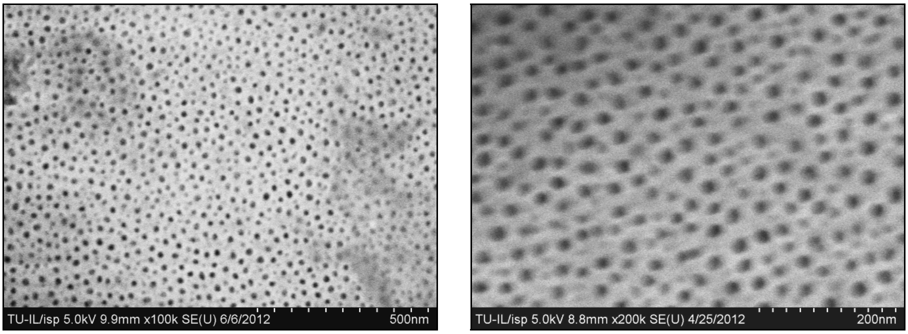
alloys [2-4]. In particular, the magnetoresistance and giant magnetoresistance (GMR) of these alloys is of great interest [5,6]. The controlled production of Co-Cu alloy nanowire arrays has attracted a great interest recently owing to their application in technologies related with magnetic information storage [7]. Piraux was the first who observed a GMR around 15% at room temperature in Co/Cu alloy nanowires [8]; after that, Blondel et al. obtained a GMR of 14% for Co/Cu and 10% for FeNi/Cu multilayered nanowires [9]. Evans et al. showed that the Co-Ni-Cu/Cu multilayer nanowires grown in AAO templates present a 55% GMR at room temperature and 115% GMR at low temperature [10].

The purpose of this research was to synthesis Co-Cu alloy nanowires in AAO template, without separation of the aluminium and by thinning the barrier oxide layer [11], by pulse reverse plating method. This deposition technique was chosen because its advantages: adjustment of pulse current density to obtain alloys with specific composition and uniform deposits over the entire aria of the sample [12].

For this, the AAO template was obtained through one-step anodisation of $AlMg_3$ substrate in an acidic solution. The structure and the morphology of the nanowires obtained were also studied.

RESULTS AND DISCUSSION

In Fig. 1a and b it can be seen the effect of the aluminium substrate (97% purity) pretreatment on the pore arrangement due to the anodisation process. The figure shows typical SEM micrographs of AAO template surface formed through aluminium anodisation and after reducing the thickness of the barrier layer.



a) b)

Figure 1. SEM micrographs of AAO template surfaces of self-ordered pore arrays obtained from oxalic acid at 40 V for 20 min (100000× and 200000× magnifications)

The average pore diameters for AAO template obtained in one-step anodisation method from oxalic acid solution were ca. 40 nm, and the pores were generally distributed in a honeycomb shape, in a hexagonal lattice. The results are in agreement with the literature [19]

The second step in the preparation process of metallic nanowires was to study the main characteristics of deposited Co, Cu and Co-Cu alloy by means of the CV technique [20].

Fig. 2 shows typical cyclic voltammograms of AAO template electrode obtained in oxalic acid recorded in Cu^{2+} (Fig.2a), Co^{2+} and Co-Cu ions solutions (Fig.2b) during one cycles. For all CV measurements, the potential scanning was started at 1.0 V towards the negative potential direction until –2.0 V was reached, and then reversed to the starting potential, at 10 mV/s scan rate.

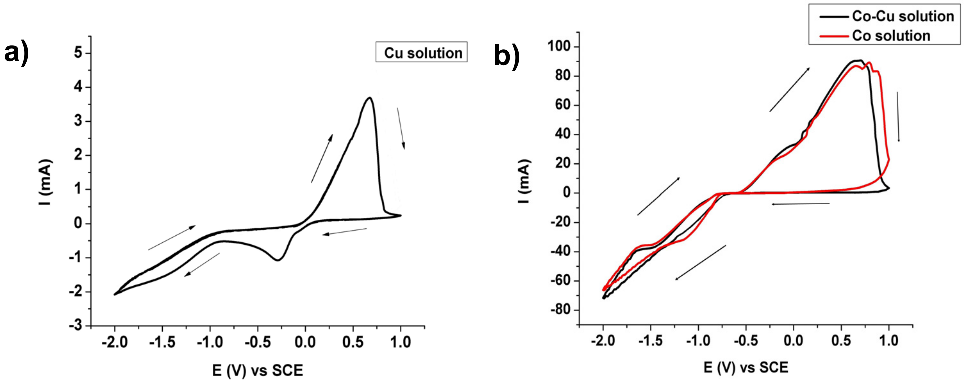


Figure 2. Cyclic voltammograms obtained in: (a) 0.99 g/L $CuSO_4$, (b) 119 g/L $CoSO_4$ and 0.99 g/L $CuSO_4$ + 119 g/L $CoSO_4$

Fig. 2a shows cyclic voltammogram of 0.99 g/L $CuSO_4$ solution with a cathodic scan limit of –2 V. Specific cathodic and anodic peaks coresponding to copper are formed in Cu^{2+} solution. Therefore, the apparent reduction and dissolution peaks are observed at –0.281 and 0.6 V respectively. Over –1.1 V vs. SCE the current increase can be associated with water decomposition and hydrogen formation processes.

Cyclic voltammograms of AAO template electrode obtained in Co and Co-Cu solutions are shown in Fig. 2b.

Cobalt electrodeposition process occurred under –1 V potential. In the direct scan from –1.1 to –2 V vs. SCE a current increasing could be observed due to the strong hydrogen evolution. The hydrogen production occurs because cobalt is less noble than the hydrogen, as can be seen in standard reduction potential of cobalt. In the reverse potential scan we can observe first a very small shoulder due to the hydrogen oxidation around 0 V potential (25 mA) followed by an intense peak centred at a potential around 0.65 V (80 mA) corresponding to the dissolution of the previously deposited Co.

From the direct scan of AAO template in Co-Cu solution it can be seen that the current increases from ca. –0.65 V. A first cathodic reduction peak and an anodic dissolution peak at –1.2 and 0.7 V respectively were observed.

The information acquired from cyclic voltammetry was used to establish the PRP conditions, namely, the values of the currents to be used in the cathodic and anodic pulse sequences.

During the electrochemical deposition process, the metallic phase is produced by the Co^{2+} and Cu^{2+} reduction reaction in sulphate solution. The main electrochemical reactions during the Co^{2+} and Cu^{2+} depositions [21] from aqueous solution are the following:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (1)$$

$$Co^{2+} + 2e^- \rightarrow Co \qquad (2)$$

There are also several possible side reactions that can occur simultaneously:

$$O_2 + 2H^+ + 4e^- \rightarrow 2H_2O \qquad (3)$$

$$H^+ + 2e^- \rightarrow H_2 \qquad (4)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (5)$$

Other literature sources describe the electrodeposition of metallic nanowires by using direct current [22], or pulse plating [23]. In this study, our goal was to prepare Co-Cu nanowires by galvanostatic PRP due to its advantages over the other methods mentioned above in the literature, as it will be described in the following.

The potential response and current used in the PRP depositions as function of time are shown in Fig. 3.

In our case, after 60 ms (pulse plating period), the plating current (-0.05 A) is interrupted by a shorter reverse-plating period (10 ms; 0.05 A current) when a lightly dissolution of the deposited layer during pulse-plating period occurs.

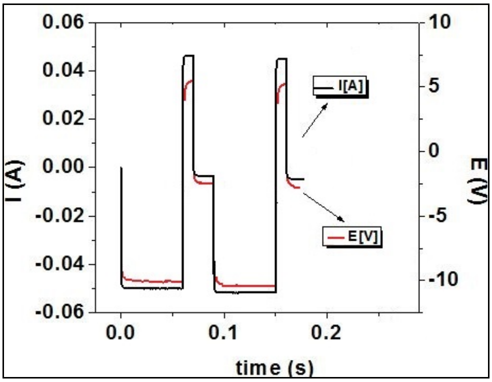


Figure 3. The form of the current used and of the potential response of the system in a sequence of PRP deposition

During off-time period when zero current is applied the ions migrate in the bath preparing for an uniform distribution in deposition time [24].

The ions of the active species diffuse in the channels and then the formation of the nanowires starts.

The HRTEM (high resolution TEM) images of Co-Cu alloy nanowires electrodeposited by PRP at a 50 mA/cm^2 current density were separated from AAO template and the results obtained are shown in Fig. 4. TEM preparation procedure of Co-Cu alloy nanowire specimens includes the following steps: dissolving of the AAO template in 1 M NaOH solution [25], rinsing by distilled water, centrifuged of the obtained suspensions with nanowires. At the end of this procedure, a drop of suspension containing Co-Cu alloy nanowires was put on a gold grid for the TEM investigations.

The nanowires diameter (about 40 nm) and their length (about 1.60 µm) correspond to the alumina nanopores shape and size precisely.

Fig. 4c confirmed the typical internal structure of Co-Cu alloy nanowires, obtained when the TEM microscopy. The bright zone here corresponds to the Co-rich phase and the darker regions indicate the Cu. One can also observe in Fig. 4 c that the deposits seem to be crystalline.

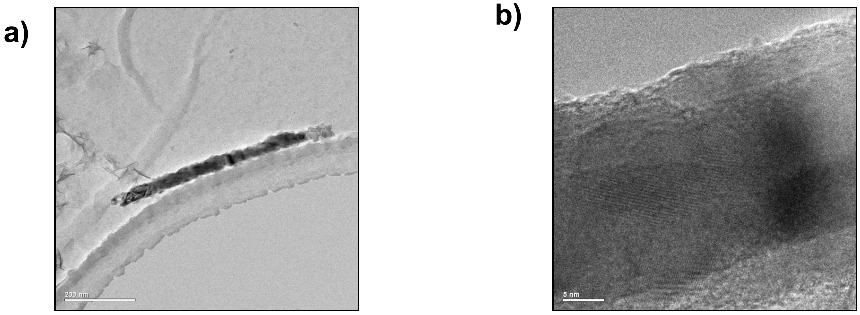


Figure 4. TEM images of Co-Cu alloy nanowires prepared by PRP method at 50 mA/cm² cathodic pulse in AAO template. Scale bar: (a) 200 nm, (b) 5 nm

The elemental composition of Co-Cu alloy samples electodeposited by PRP method was analyzed by means of XRF (Fig. 5) and EDS (Figs. 6 and 7). The alloy composition was determined in cross-section and locally on nanowire surface.

Fig. 5 indicates the variation in Co and Cu concentration in the alloy nanowires as a function of the current density used in the cathodic step, as given by XRF analysis.

The increasing current density implied the incorporation of more Co in the nanowires. Cu concentration decreases with increasing of the current density. One explanation for this behavior is that the Cu deposition is mass transport controlled, while the Co deposition is under mixed control.

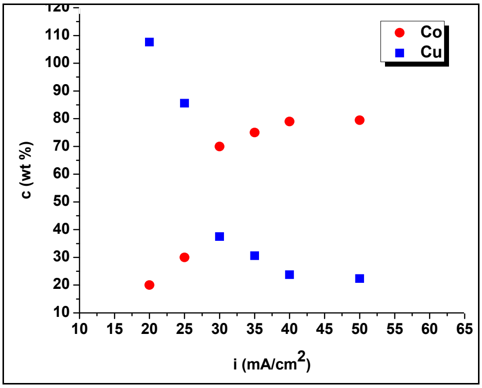


Figure 5. Evolution of Co and Cu concentrations from alloy nanowires as function of current density determined by XRF

The metals concentration of Co-Cu alloy nanowires obtained at 50 mA/cm^2 current density from a sulphate solution with 3.8 pH has been measured also by EDS analysis (Fig. 6).

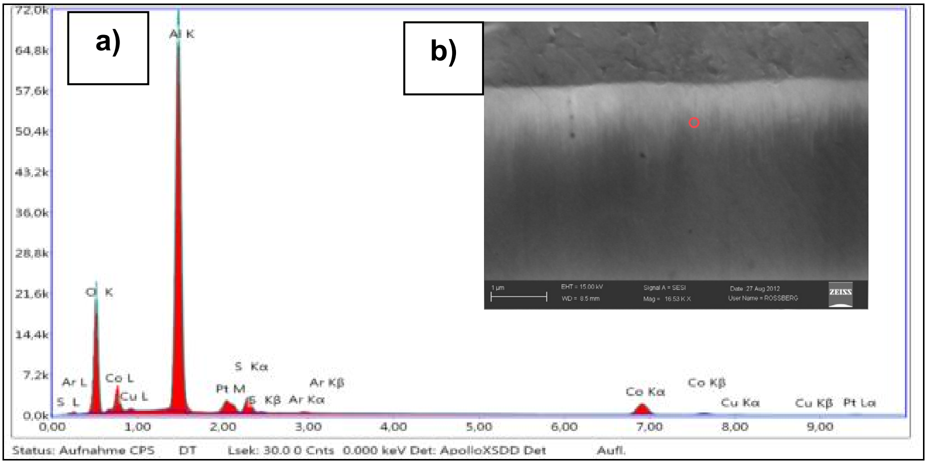


Figure 6. Cluster Co-Cu alloy nanowires embedded in AAO template: a) EDS analysis and b) FIB image in cross section (at upper right side)

The EDS spectrum of Co-Cu alloy nanowires within AAO template in one spot is given in Fig. 6a and consists of significant elementary peaks (Table 1).

EDS qualitative analysis marks out the presence of Co and Cu peaks arisen from the deposition, oxygen and aluminium peaks appeared from the AAO template while platinum peak appear due to the sputtering process (the samples were sputtered with Pt before the FIB and EDS analysis, in order to increase their conductivity). Five minutes sputtering time was sufficient to obtain a continuous and uniform platinum thin film.

Table 1. Co-Cu alloy nanowires EDS quantitative analysis

Element	Wt. (%)	At. (%)
Co	16.1	6.9
Cu	1.4	0.6
Al	44.0	41.3
O	30.1	47.8
Pt	4.8	0.6

The formation of Co-Cu alloy nanowires in the pore structure in cross section was studied by means of FIB technique. Fig. 6b illustrates FIB micrograph of cluster metallic nanowires still integrated into the porous AAO template, maintaining the above described working conditions.

EDS peaks (Fig. 6a) are in according to XRF results (Fig. 5) marking out a large amount of Co and a small concentration of Cu by a locally detection (Fig. 6b, spot 2).

The nanowires electrodeposited in AAO template at 50 mA/cm^2 current density were ca. 1.60 µm lengths and 40 nm diameter, as described also above. EDS on single Co-Cu alloy wire was also performed, in parallel to TEM, after the AAO template was dissolved in NaOH (1M) to expose the wires(Fig. 7a). Fig. 7b indicates high resolution TEM of individual alloy nanostructure.

The single Co-Cu alloy nanowires contained 80 wt.%-Co and 20 wt.%-Cu, as indicated by the EDS (Fig. 7a).

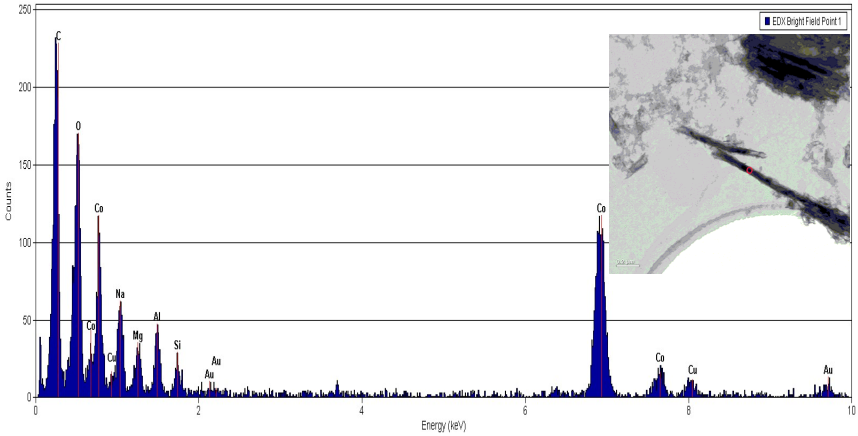


Figure 7. Individual Co-Cu alloy nanowire: a) EDS spectrum and b) TEM image (at upper right side)

Therefore, XRF results (Fig. 5) were in good agreement with EDS analysis of individual metallic alloy nanowires, which means that the material is chemically homogeneous.

However, the qualitative EDS examination on bigger area in a cross-section of the sample had indicated the presence of Al and O, beside the Co and Cu.

The XRD patterns (Fig. 8) of the annealed Co-Cu alloy nanowire samples have been recorded at room temperature, in order to study the relationship between the structure of the nanowires, their composition and the annealing temperatures. These deposits were prepared in the same conditions as those used for the foregoing analysis, at higher current density (50 mA/cm^2), when maximum Co concentration was observed.

The metallic nanostructures were annealed at temperatures below the melting point of aluminium (680ºC), namely, at 150, 300 and 350ºC respectively. This study is useful to explain the crystallographic variation influenced by the annealing temperature and chemical composition.

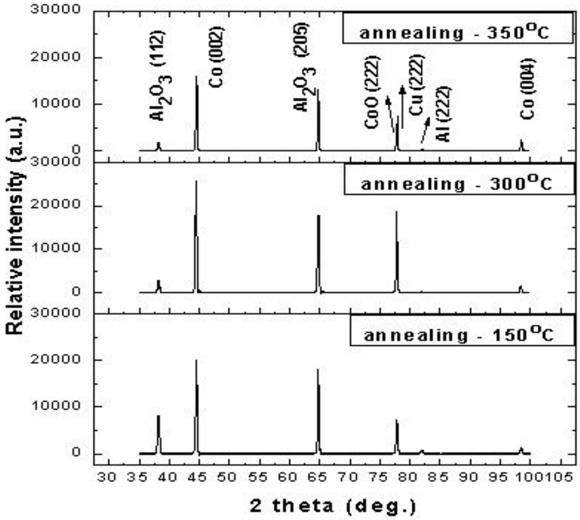


Figure 8. XRD patterns of Co-Cu alloy nanowires deposited at 50 mA/cm^2 current density and annealed at 150, 300 and 350ºC temperature

Bragg's reflections for Co-Cu alloy nanowires are observed at 2θ values of 38.06°, 44.6°, 64.0°, 77.54°, 77.8°, 81.72°, 98.71°. The crystalline planes of Al_2O_3, Co, Cu, aluminium and CoO could be identified. Aluminium peak resulted from the substrate used for AAO template and Al_2O_3 derived from under-layer used for nanowires respectively.

The annealed electrodeposited alloys contain the $\varepsilon-Co$ phase with hexagonal close-packed lattice (hcp) and Cu phase with face-centred cubic (fcc) lattice. According to the Joint Committee on Powder Diffraction Standards (JCPDS) card the more important phases in this study have been identified as 00-001-1278 for Co and 00-004-0836 corresponding to Cu phase respectively. CoO peak with fcc lattice according to JCPDS 00-001-1227. CoO characteristic line formation can be attributed to the metallic Co annealing.

Noticeable changes in phase composition and peak broadening are observed over the range of annealing temperature. The highest intensity peaks of Co and Cu respectively appeared when the deposits have been annealed at 300ºC. Thereby, it's about the Co peak corresponding to the (002) reflection and the (222) plane of Cu which is lower than Co. Therefore, a correlation between the chemical composition (Co:Cu 4:1) and fine crystalline structure (Figs. 5, 6, 7) could be made. As the annealing temperature of the samples increases, the amount of $\varepsilon-\mathrm{Co}$ phase diminishes and an obvious peak corresponding to Co (004) structure increases in intensity.

Reduced intensity peaks at higher temperatures (above 350ºC) could be observed indicating the weak Co–Al_2O_3 interactions. In this case, the observed increase in the peak broadening is due to decreasing CoO crystallites grain size compared to average Al_2O_3 pore size.

EXPERIMETAL DETAILES

The AAO template was synthesized by one-step anodisation method. Al_2O_3 layer was grown on the aluminium-magnesium electrodes (circular sector shaped), in oxalic acid solution at 40 V constant voltage [13]. In these experiments the counter was a net platinum electrode, and the $AlMg_3$ substrates were the working electrodes.

In order to electrodeposit the wished metallic nanowires in the AAO template, the last one must be conductive. After anodisation an Al_2O_3 barrier layer is formed in the AAO templates, that is not conductive and that hinders the tries to electrodeposit any metal onto it. Therefore the Al_2O_3 barrier layer was thinned electrochemically by successive reduction of the anodisation voltage and pores diameter widening was obtained in sulphuric acid [14].

The surface morphological features of AAO template were examined by means of scanning electron microscopy (SEM) technique using Hitachi S 4800 device operating at an accelerating voltage of 5 kV.

The deposition of Cu, Co and Co-Cu nanowires in the AAO template was firstly studied by cyclic voltammetry (CV), from sulphate based electrolytes. CVs experiments were performed in a three electrode cell: AAO template was the working electrode, and calomel electrode and platinum net were used as reference and counter electrodes, respectively. All measurements have been performed at room temperature.

The electrodeposition of Co-Cu alloy nanowires was performed from one electrolyte which contains both type of ions (Co^{2+} and Cu^{2+}), based on the previous reports of Yahalom and Zadok from 1986 for the Cu-Ni system [15].

The Co-Cu alloy nanowires were electrodeposited in AAO template by galvanostatic pulse reverse plating (PRP) method [16] using two electrode systems (platinum sheet as anode and AAO template as working electrode).

The bath composition was 119 g/L $CoSO_4$, 1 g/L $CuSO_4$, and 25 g/L H_3BO_3. The pH of solution varied between 3.8 and 4.0 and different current densities (20÷50 mA/cm^2) were applied. The deposition experiments were performed using a HEKA PG310 (Heka Elekronik Dr. Schulze GmbH) potentiostat/galvanostat.

The internal structure of nano-sized Co-Cu alloy wires (diameter < 40 nm) was examined using transmission electron microscopy (TEM).

The morphological caracteristics and chemical composition of Co-Cu alloy nanowires were investigated using the focused-ion-beam (FIB) microscopy, energy dispersive X-ray (EDS) and X-ray fluorescence (XRF, from Fisherscope, Germany) spectroscopies. For FIB and EDS techniques, a cross section in the AAO template was required. Thus, the samples were cut and embedded in epoxy resin. An accurate manually polishing of the cross-section of the nanowires was necessary and initiated with coarse polishing papers having different grains (from 800 to 4000) [17]. After each polishing step the samples were rinsed in distilled water.

Some of the Co-Cu nanowires were annealed in order to check if the structure of the wires changes with the temperature, fact that can influence their optical and magnetic properties, and thus, their industrial applications [18]. These deposits were prepared from sulphate solutions with pH of 3.8 at 50 mA/cm^2 current density. The annealing procedure was conducted, in air atmosphere, in a stove at different temperatures: 150, 300 and 350ºC for a period of 3 h.

The crystallographic characteristics of these samples were analysed by means of X-ray diffractometry (XRD). X-ray diffraction patterns were obtained from Philips PW 1830 diffractometer at room temperature using monochromated CuK_α radiation (λ = 1.54 Å). Routine patterns for phase identification were collected with a scanning step of 0.1° min^{-1} in 2θ over the angular range 30 and 100° with a collection time of 5 s per step.

CONCLUSIONS

The AAO template was obtained by one-step anodisation method of $AlMg_3$ substrates in oxalic acid solution at 40 V potential for 20 min. The roughness degree of substrate was the most important factor which could influence the nanopores linearity and symmetry respectively.

The AAO template morphology shows homogeneity and spherical shape of pores as well as a hexagonal lattice of nanopores. The average diameter of nanopores was of 40 nm, as indicated by SEM.

The information acquired from cyclic voltammograms was used to establish the PRP electrochemical conditions. The galvanostatic PRP was used to obtain Co-Cu alloy nanowire depositions from acidic sulphate solution at 50 mA/cm^2 current density with fine structure and superior physical properties than many metals.

From XRF examination Co and Cu concentrations from alloy nanowires varied with the cathodic current density used in deposition. Cu was deposited preferentially at lower current density where as Co-rich alloy were obtained at higher current density due to the mass transport limitation of the Cu during the deposition process.

The shape, size and crystallographic orientation of clusters of Co-Cu alloy nanowires embedded in AAO template were studied by means of FIB microscopy. After the AAO template was dissolved, high resolution TEM analyses were performed. Nanowires of ca. 1.60 µm length were thus analyzed.

The chemical composition of an individual alloy nanowire was investigated using EDS and XRF spectroscopies. The quantitative assay of Co-Cu alloy nanowire indicated that they contain 80 wt.%-Co and 20 wt.%-Cu. XRF results were agreement with the EDS analysis, proving that the material is chemically homogeneous.

An annealing treatment of Co-Cu alloy nanowires was required to assure their thermal stability under 350ºC. This study is useful to explain the crystallographic variation induced by the annealing temperature.

The internal structure of the annealed Co-Cu alloy nanowire samples was studied at room temperature by means of XRD method. The crystallization process varied with the annealing temperature and Co and Cu concentration showing ε-Co phase with hexagonal close-packed lattice and face-centred cubic lattice of electrodeposited Cu.

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