

Synthesis and Structural Characterization of Cobalt Nanostructures in AAO Membranes

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Metallic nanostructures have attracted the interest of researchers due to their fundamental importance and potential applications in nanodevices, sensors and catalysts. Co-AAO nanocomposites were obtained by using a sol-gel method that uses ultrasonic vibrations to induce the penetration of a colloidal solution through the pores of an anodized aluminum oxide (AAO) template. The AAO template, with the sol into its pores, was annealed at 648 K. The entire dip-anneal-dip process was repeated three times. Finally, the metal nanostructures were formed by further annealing at 873 K in hydrogen atmosphere for 1 h. The morphology and structure of Co-AAO were investigated by using SEM, HRTEM, XRD and EPR methods.

Keywords: AAO, cobalt nanostructures, structural characterization, medical field

The recent theoretical studies and experimental techniques led to the discovery of new materials, processes and phenomena at nanoscale sizes. Such innovative research provides new opportunities in the development of nanosystems and nanostructured materials. Their usefulness in a variety of important applications such as: electronic devices, detection, mechanical and magnetic nanoscale [1, 2], information storage systems [3, 6], due to the optical, electrical, magnetic and catalytic properties, are widely recognized.

A low-cost technique for fabrication of metallic nanostructure arrays is the deposition of nanodots, nanowires, nanorods, nanotubes or nanocylinders in self-assembled anodized aluminum oxide membrane (AAO) from colloidal solutions or electrodeposition [7-13]. It was established that the pores ordering and structure can be controlled by the nature of the electrolyte, the voltage applied during the anodization and electrolyte temperature.

Due to their properties and possible advanced applications, metallic nanostructures attracted the interest of many researchers [14-26]. If some of the researchers have focused on their magnetic properties [27-31], others have studied the mechanism of formation of their formation [30-36].

It was shown that the size of the metal nanostructures depends on synthesis conditions and that elongated shape may give rise to significant effects and shape anisotropy [35]. When the magnetic field is applied parallel to the long axis of the magnetic nanowires, the resulted coercive field is inversely proportional to the pore's diameter and the squareness of the hysteresis loop can be increased.

Cobalt nanostructures are interesting due to the large magnetocrystalline anisotropy that lies along the c-axis (cobalt is the only magnetically uniaxial crystal). Various parameters including shape, size, and texture strongly influence the magnetic properties and it was shown that they can be controlled during fabrication process [37-39]. Certain experiments shown that fcc phase of cobalt nanowires can be changed to hcp phase by varying the pH

of the solution during fabrication and that the easy axis of magnetization can be tuned either perpendicular or parallel to the wire long axis by changing the length of wires [36-41]. It was experimentally observed that Co wires with small diameters (20 nm) have an isotropic saturation (same value with the field parallel or perpendicular to the wires) and was concluded that the magnetization behavior is a result of a competition of demagnetization of the individual wires and dipole-dipole interaction between the wires.

The present study is focused on the synthesis of cobalt nanostructures using aluminum oxide template (AAO) and on their structural characterization by using scanning electron microscopy (SEM), high resolution electron microscopy (HRTEM, EDX), X-ray diffraction (XRD) and electron paramagnetic spectroscopy (EPR).

Experimental part

There are a variety of techniques for self-assembly used to obtain metallic nanostructures. The chemical techniques use nanoporous membranes, which have a quasi-regular network of pores with pore diameters between 10 nm to several hundred nm.

In this study, metal nanostructures were synthesized by immersing the AAO template in a colloidal solution submitted to an ultrasonic vibration.

Preparation of AAO

An important factor in achieving an ordered distribution of the pores is the surface roughness (may initially be in the nm). In order to reduce the surface roughness, the aluminum foil (with a thickness of 0.2 mm and 99.99% purity) was degreased with acetone, annealed at 773K for 5 h and subjected to a mechanical grinding process. The resulted foil was used as an anode in an aqueous solution of oxalic acid (concentration of 0.3%) and as cathode a led foil was used. For the anodization process a constant potential of 50 V was applied at room temperature for 10 hours.

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The scheme of the experimental arrangement is shown in figure 1.

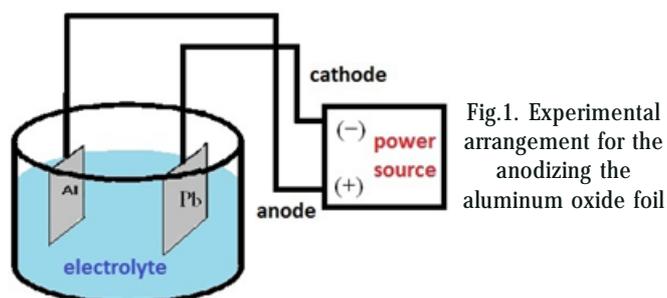
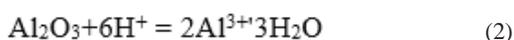
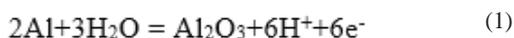


Fig.1. Experimental arrangement for the anodizing the aluminum oxide foil

The anodization process comprises three chemical reactions that take place at the anode (aluminum oxidation (1), aluminum dissolution (2)) and cathode (hydrogen evolution (3)) electrodes:



The resulted anodized aluminum oxide foil (AAO) was corroded in an aqueous solution of CuCl_2 in order to remove the metallic aluminum.

In order to enlarge the pore diameter, AAO foil was immersed in a phosphoric acid solution (concentration of 6 mass %) for 40 minutes at a temperature of 303K.

Synthesis of cobalt nanostructures using AAO template

The AAO foils obtained through the anodization process were used as template for the synthesis of Co nanostructures. For this purpose, colloidal solutions (0.8 M), formed from ethylene glycol (as solvent), citric acid (as etching agent) and cobalt acetate, were obtained by heating the mixture at 303K for 10 hours in a thermostat [41].

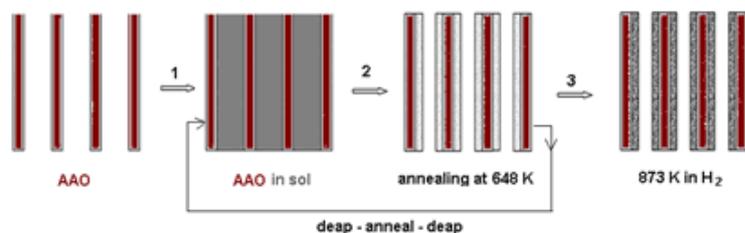


Fig. 2. Metallic nanotubes synthesis process: 1) AAO matrix filled with solution; 2) annealing at 648 K; 3) reduction under hydrogen atmosphere.

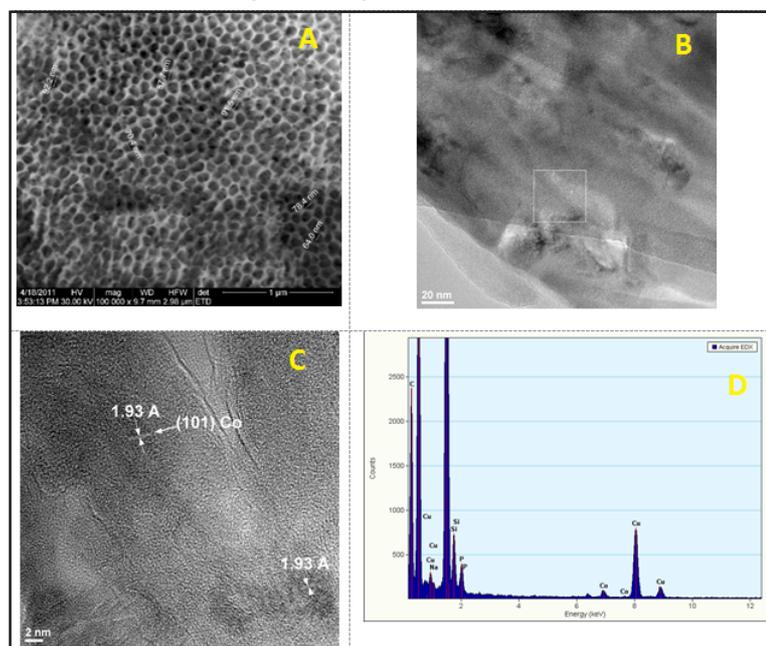


Fig. 3. a) and b) SEM image of Co nanostructures formed in AAO; c) HRTEM image - (101) crystalline planes of hcp Co; d) EDX spectrum of Co-AAO.

For nanostructures synthesis the AAO template was immersed in the sol for about 10 min. The sol penetrated the AAO pores by means of ultrasonic vibration. The AAO template, which incorporated the sol into its pores, was taken out and the template was heated from the room temperature to 648 K with a heating rate of 1.5 K min^{-1} in open air. The entire dip-anneal-dip process was repeated three times for each sample. Finally, the metal nanostructures were formed by further annealing at 873 K in hydrogen atmosphere for 1 h.

The procedure of metallic nanostructures synthesis is schematically shown in figure 2.

The morphology of AAO template and of metallic nanostructures formed inside the pores of AAO was investigated using a scanning electron microscope QUANTA INSPECT F.

The structure and elemental chemical composition of cobalt nanostructures were investigated by the mean of a high-resolution transmission microscope TECNAI G2 with and EDX detector. The nanocomposite structure and magnetic properties were investigated using a X'PERT Pro MPD diffractometer (CuK α radiation) and a X-band CMS 8400 spectrometer operating at 9.407 GHz.

Results and discussion

SEM images of the anodized template matrix having into the pores Co nanostructures evidenced pore sizes between 60 to 90 nm (Fig. 3. a), suggesting that the nanostructure's length is smaller than the AAO pore lengths.

HRTEM analysis of nanostructures grown into AAO matrix allowed evidencing the crystalline planes belonging to Co nanostructures. Fig. 3.c) shows the (101) crystalline planes of hcp Co. The image was taken on the nanotube wall, as is shown if Fig. 3. b). The cobalt peaks evidenced by EDX analysis indicate the presence of cobalt in AAO pores (Fig.3.d). The other signals originate from the substrate materials. The elemental chemical composition

allowed determining the chemical formula of AAO matrix as Al_2O_3 and the content of cobalt as 0.17%.

XRD pattern, registered with the AAO pores parallel with the X-Ray direction, evidenced only the (002) peak attributed to hcp structure of cobalt (Fig.4). No other XRD peaks belonging to hcp crystalline planes or other crystalline phases were observed, suggesting that cobalt nanostructures have a strong preferential crystallographic orientation, with c axis parallel to the pore axis. The unit cell parameter, c, as determined from the 2θ value of (002) XRD peak, has the value $c=0.4041$ nm. Using the interplanar distance evidenced by HRTEM analysis, the unit cell parameter a was determined as $a=0.2533$ nm ($c/a=1.603$). A medium nanostructure diameter of 88 nm was determined with the formula $D=(0.9 \times 1.54)/(w \times \cos\theta)$, where w is the width of the diffraction peak, in radians, at a height half-way between background and the peak maximum. This value is in good agreement with the values observed in SEM analysis. The geometrical confinement of small diameter pores favored the growth of single crystals [36, 41].

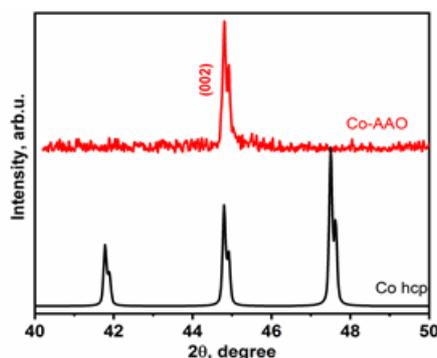


Fig. 4. XRD of Co nanostructures

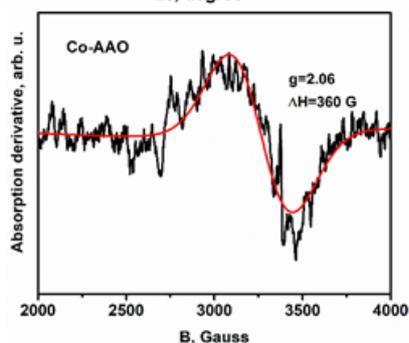


Fig. 5. EPR spectrum of Co-AAO

EPR measurements were performed at room temperature for sample different orientations. The Co-AAO sample was oriented with the AAO surface perpendicular to the plane of static-magnetic field. The sample was rotated in the plane of static magnetic field, in order to investigate the magnetic anisotropy. No change in the EPR signal was observed. Figure 5 shows the EPR spectrum of Co-AAO for the sample oriented with AAO pores parallel with the magnetic field direction and parallel with c axis. The signal observed at $g=2.06$ with a line width of 340 G can be characterized as superparamagnetic signal or as a ferromagnetic isotropic signal due to nanostructures with low L/D ratio (L- nanostructure length, D - nanostructure diameter). The EPR signal is weak, because of the small amount of magnetic material present for the measurements and has symmetric Gaussian line.

The superparamagnetic (SPM) state is characterized by random fluctuations of the magnetization due to thermal excitation. It appears in ferromagnetic nanostructures, which are sufficiently small and thus single domain (For cobalt spherical nanoparticles, a diameter size of 80 nm represents the maximum mono-domain magnetic size

[11]), typically in the nanometric range (1-100 nm). SPM occurs at temperatures below the Curie transition where exchange interaction is effective, and spins are coupled. Also, the literature showed for cobalt nanostructures with ferromagnetic properties that the angular dependence of the resonance field depends on the aspect ratio, L/D (L-nanowire length, D nanowire diameter) flattening with the decrease of it. In our case, due to the low content of cobalt in the AAO matrix is possible to have nanostructures with low L/D ratio with c axis parallel to the pores.

To acquire more information about the magnetic properties of cobalt nanostructures formed into the AAO pores, EPR measurements as a function of temperature will be performed and discussed in a future paper.

Using the same synthesis method, future experiments will be developed for more deep-anneal-deep processes and different post-annealing treatments, in order to control the shape of obtained nanostructures.

Conclusions

Cobalt nanostructures were synthesized using an AAO template that was immersed in a sol for about 10 min, under ultrasonic vibration, submitted to an annealing process at 648K and an another one at 873 K in hydrogen atmosphere for 1 h. SEM, HRTEM and XRD investigations evidenced a low content of cobalt nanostructures with a low L/D ratio, highly textured, with c axis parallel to the pore axis. EPR investigations, performed at room temperature, in a plane perpendicular to (002) crystallographic plane, evidenced an isotropic signal. To elucidate this result future measurements as a function of temperature are necessary. Further researches will be focused on preparing titanium, silver and gold nanotubes following the same procedure due to their uses in medical field, as these nanomaterials possesses unique characteristics such as biocompatibility, osseointegration, smart drug delivery and antimicrobial properties.

References

- 1.KOVTYUKHOVA, N.I., MALLOUK, T.E., Chem. Eur. J., **8** (19), 2002, p.4354.
- 2.PATOLSKY, F., ZHENG, G., HAYDEN, O., LAKADAMYALI, M., ZHUANG, X., LIEBER, C.M., Proc. Natl. Acad. Sci. U.S.A., **104**, 2004, p. 14017.
- 3.GUDIJKSEN, M.S., LAUHON, L.J., WANG, J.F., SMITH, D.C., LIEBER, C.M., Nature, **415** (6872), 2002, p. 617.
- 4.CUI, Y., WEI, Q.Q., PARK, H.K., LIEBER, C.M., Science, **293** (5533), 2001, p. 1289.
- 5.THURN-ALBRECHT, T., SCHOTTER, J., KASTLE, C.A., EMLEY, N., SHIBAUCHI, T., KRUSIN-ELBAUM, L., GUARINI, K., BLACK, C.T., TUOMINEN, M.T., RUSSELL, T.P. Science, **290** (2126), 2000, p. 2126.
- 6.LIANG, H.P., GUO, Y.Q., HU, J.S., ZHU, C.F., WAN, L.J., BAI, C.L., Inorg. Chem., **44**, 2005, p. 3013.
- 7.MARTIN, C.R., Science, **266** (5193), 1994, p. 1961.
- 8.MARTIN, C.R., Chem. Mater., **8** (8), 1996, p. 1739.
- 9.HUCZKO, A., Appl. Phys. A., **70** (4), 2000, p. 365.
- 10.PENG, K., HUANG, Z., ZHU, J., Adv. Mater., **16**, 2004, p. 73.
- 11.BOUZIANE, K., ROUSSIGNÉ, Y., CHÉRIE, S.M., STASHKEVICH, A.A., VASQUEZ, M., BRITEL, M.R., CHERKAOU, M., Sensor Lett., **11** (xx), 2013, p. 1.
- 12.PIROTA, K.R., NAVAS, D., HERNANDEZ-VELEZ, M., NIELSCH, K., VAZQUEZ, M., J. Alloy Compd., **369** (1), 2004, p. 18.
- 13.SOUSA, C.T., LEITAO, D.C., PROENCA, M.P., VENTURA, J., PEREIRA, A.M., ARAUJO, J.P., Appl. Phys.Rev., **1** (3), 2014, p. 031102
- 14.MIHALACHE, G., DARTU, L.E., DARABA, O.M., BIRGAOANU, A., DASCALESCU, R., NICHTUS, S., FOLESCU E., International Journal Medical Dentistry, **8** (4), 2014, p. 260. SARKAR, J., KHAN, G.G., BASUMALLICK, A., Bull. Mater. Sci., **30** (3), 2007, p. 271.

15. PORTNEY, N.G., OZKAN, M., *Anal. Bioanal. Chem.*, **384** (3), 2006, p.620.
16. TIAN, F., ZHU, J., WEI, D., *J. Phys. Chem. C.*, **111** (34), 2007, p. 12669.
17. HANGARTER, C.M., NOSANG M.V., *Chem. Mater.*, **17** (6), 2005, p. 1320.
18. ANTON, E., BOTNARIUC, N., ANCUTA, E., DOROFTEI, B., CIOBICA, A., ANTON, C., *MEDICAL-SURGICAL JOURNAL-REVISTA MEDICO-CHIRURGICALA*, **119**, no. 2, 2015, p. 410.
19. DOROFTEI, B., ZLEI, M., SIMIONESCU, G., MAFTEI, R., CUMPATA, S., EMERSON, G., *Reproductive Health*, **12**, 2015, article 38. DOI: 10.1186/s12978-015-0031-x
20. BENGHIAC, A.G., BUDACU, C., MOSCALU, M., IOAN, B.G., MOLDOVANU, A., HABA, D., *ROMANIAN JOURNAL OF LEGAL MEDICINE*, **25**, no. 2, 2017, p. 174.
21. BOSINCEANU, A., PADURARU, O.M.; VASILE, C., POPOVICI, I., TANTARU, G., OCHIUZ, L., *Farmacia*, **61**, no. 5, 2013, p. 856.
22. GUDRUMAN, A.D., BIBIRE, N., TANTARU, G., APOSTU, M., VIERIU, M., DORNEANU, V., *Rev. Chim (Bucharest)*, **64**, no. 4, 2010, p. 393.
23. APOSTU, M., TANTARU, G., VIERIU, M., PANAINTE, A.D., BIBIRE, N., AGOROAEI, L., *Rev. Chim (Bucharest)*, **68**, no. 4, 2017, p. 683.
24. DOLOCA, A., TANCULESCU, O., TRANDAFIR, L., CIONGRADI, I., STOLERIU, S., MOCANU, R., IFTENI, G., *Mat. Plast.*, **53**, no. 3, 2016, p. 370.
25. TRANDAFIR, L.M., BACIU, G., CONSTANTIN, M.M.L., MASTALERU, A., TEMNEANU, O.R., MIHAI, B., NOVAC, O., FRASINARIU, O.E., IVAN, A., TUDORACHI, N.B., AL HIARY, R., MOSCALU, M., *Rev. Chim. (Bucharest)*, **69**, 11, 2018, p. 3048.
26. ACHITEI, D.C., VIZUREANU, P., DANA, D., CIMPOESU, N., *Metalurgia International*, **18**, special issue 2, 2013, p. 104.
27. PATHAK, S., SHARMA, M., *Adv. Mat. Lett.* **3** (6), 2012, p. 526.
28. CANTU-VALLE, J., BETANCOUR, T I, SANCHEZ, J.E., RUIZ-ZEPEDA, F., MAQABLEH, M.M., MENDOZA-SANTOYO, F., STADLER, B.J.H., PONCE, A., *J. Appl. Phys.*, **118** (2), 2015, p. 024302.
29. PAN, H., LIU, B.H., YI, J.B., POH, C., LIM, S.H., DING, J., FENG, Y.P., HUAN, C.H.A., LIN, J.Y., *J. Phys. Chem. B.*, **109**, 2005, p. 3094.
30. LIM, J.H., ROTARU, A., MIN, S.G., MALKINSKI, L., WILEY, J.B., *J. Mater. Chem.*, **20**, 2010, p. 9246.
31. SELLMYER, D.J., ZHENG, M., SKOMSKI, R., *J. Phys.: Condens. Matter.*, 2001, **13** (25), R433.
32. MAAZ, K., KARIM, S., USMAN, M., MUMTAZ, A., LIU, J., DUAN, J.L., MAQBOOL, M., *Nanoscale Res Lett*, **5** (7), 2010, p.1111.
33. CAO, H.Q., WANG, L.D., QIU, Y., WU, Q.Z., WANG, G.Z., ZHANG, L., LIU, X.W., *Chem. Phys. Chem.*, **7**, 2006, p. 1500.
34. SAEKI, R., OHGAI, T., *Materials*, **11** (12), 2018, p. 2355.
35. MAAZ, K., KARIM, S., USMAN, M., MUMTAZ, A., LIU, J., DUAN, J.L., MAQBOOL, M., *Nanoscale Res Lett.*, **5** (7), 2010, p. 1111.
36. IVANOV, Y.P., CHUVILIN, A., VIVAS, L.G., KOSEL, J., Chubykalo-Fesenko, O., Vázquez, M., *Sci. Rep.*, **6** (23844), 2016, p. 1.
37. KOZLOVSKIYA, A.L., SHLIMASA, D.I., MASHENTSEVAA, A.A., ZDOROVETSA, M.V., KADYRZHAN, K.K., *Petroleum Chemistry*, **56** (10), 2016, p. 956.
38. NARAYANAN, T.N., SHAJUMON, M.M., AJAYAN, P.M., ANANTHARAMAN, M.R., *J. Phys. Chem. C*, **112** (37), 2008, p. 14281.
39. CHO, J.U., WU, J.-H., MIN, J.H., KO, S.P., SOH, J.Y., LIU, Q.X., KIM, Y.K., *J. Magn. Mater.* **303**, 2006, p. e281.
40. STRIJKERS G.J., DALDEROP J.H.J., BROEKSTEEG M.A.A., SWAGTEN H.J.M., DE JONGE W.J.M., *J. Appl. Phys.*, **86**, 1999, p. 5141.
41. PAN, H., LIU, B., YI, J., POH, C., LIM, S., DING, J., FENG, Y., HUAN, C.H.A., LIN, J., *J. Phys. Chem.*, **B109**, 2005, p. 3094.

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