DEPOSITION OF NICRMO NANOWIRES USING ANODIC ALUMINUM OXIDE TEMPLATE

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Abstract— This work aims to fabricate NiCrMo nanowires with wt% of 72.2, 19.5 and 8.3% respectively which closed to the composition of NiCrMo alloy that used in dental applications. The fabrication was done by electrochemical process using anodic aluminum oxide (AAO) as a template which prepared in 0.3M oxalic acid. The fabricated nanowires were characterized by XRD, SEM, EDS and TEM. The produced nanowires have 70-72 nm in diameter and 10-20 µm in length. The XRD pattern of fabricated nanowires indicates the formation of symmetric orthorhombic $Ni_{40}Cr_{18}Mo_{42}$ phase within Ni matrix with uniformly wire arrays at the same dimensions. These arrays were deposited in orderly pores of AAO as indicated by SEM and TEM techniques.

Index Terms—Nanowire, NiCrMo, Electrochemical method, AAO template.

I. INTRODUCTION

Nickel-chromium-molybdenum alloys are widely used in pollution control, chemical processing, marine, pulp and paper, and oil and gas industries for their resistance to corrosion by many aggressive media, high strength, ease of fabrication, and versatility. Most applications require that the alloy products be welded. Because of the differences in melting points of the elements within these alloys (especially molybdenum) and the rapid solidification and cooling rates associated with welding, elemental segregation often occurs in welds. At present, there is a huge anticipation that the realm of nanotechnology will soon be realized, and the life will become easier and more enjoyable – thanks to numerous new products and apparatus that will be operating on 'nano-facts' and nano-sized objects. For example, metal nanowires (MNWs) are likely to become an integral part of future nanodevices, at least as the elements interconnecting the functional components such as 'nano'-transistors. Additional to the provision of electrical connection to nano-circuits, the MNWs are expected to be utilized as the functional components in various applications ranging from high density perpendicular data storage to nano-sensors, from high-sensitivity nano-electrodes to meta-materials, and so on. Therefore, many authors highlighted on fabrication Ni nanowires and its alloys using electrodeposition method and other technique for various applications. Iraj and Gholamreza studied Ni-rich/Cu multi-layered nanowire of arbitrary thickness of the bi-layer which may be grown within a nuclear track-etched polycarbonate membrane by electrodepositing well-defined quantities of Ni and Cu in alternation [1]. Saidin et al. fabricated Au/Ni multilayered nanowires by electrochemical deposition [2]. Gheorghies et al. fabricated Ni-Co and Ni-Co/BaFe nanowires in AAO template [3]. Davis and Podlaha fabricated metallic CoNiCu and Cu nanotubes in polycarbonate membranes by electrodeposition. Nanowires were obtained in the high-efficiency electrolyte while nanotubes were generated from the low efficiency electrolyte [4].

Geng et al. synthesized NiSi nanowires by DC arc-discharge approach. Two important conditions, high temperature and enough Ni supply, are emphasized for the synthesis of the NiSi nanowires. Magnetic characterization was carried out and the results show that the NiSi nanowires exhibit ferromagnetic characteristics at room temperature [5]. Vijay and Roy investigated a novel superplastic deformation in an intermetallic B2-NiAl nanowire of cross-sectional dimensions of ≈20 Å with failure strain as high as ≈700% at 700 K temperature. Superplasticity is observed due to transformation from crystalline phase to amorphous phase after yielding of the nanowire [6]. Srdjan et al. described a novel fabrication method of single crystalline Mo nanowires and nanowire arrays. The method utilizes directional solidification of a NiAl-Mo eutectic alloy and its subsequent electrochemical processing. In the first step, a self-organized array of Mo nanowires embedded in a NiAl matrix is obtained. By combining the Pourbaix diagrams of the three elements involved, a strategy for selective removal of either of the two phases is derived [7].

Mohamed et al. fabricated NiFe nanowires with well-controlled diameters and compositions in various porous alumina templates by using a pulsed electrochemical deposition technique. The coercivity of the nanowire array is influenced by its texture and the amount of iron content in the alloy. The processes of magnetization reversal in Ni80Fe20 nanowire array are investigated. The temperature dependence of Ni80Fe20 nanowires coercivity is interpreted in accordance with magnetization fluctuation over a single energy barrier [8]. Martensitic phase transformation in bulk Nickle-Titanium (NiTi) (the most widely used shape memory alloy) has been extensively studied in the past. However, the structures and properties of nanostructured NiTi

remain poorly understood. Reza et al. studied the molecular dynamics simulations of structural transformations in NiTi nanowires. The tendency to reduce the surface energy in NiTi nanowires can lead to a new phase transformation mechanism from the austenitic B2 to the martensitic B19 phase [9]. Wei et al. studied a well-ordered and vertically-aligned metal (nickel (Ni)/zinc (Zn)) and metal oxides (NiO/ZnO) nano heterojunctions (NHJs) which grown inside the nanopores of anodic aluminum oxide template using electrochemical deposition and thermal oxidization. The electrical properties of NiO/ZnO NHJs show a rectifying behavior of a p-n junction, while the Ni/Zn NHJs show an ohmic behavior [10]. Rana et al. fabricated NiMo nanowires by electrodeposition using aluminum oxide template [11].

Because of importance of NiCrMo alloy in dental applications, we tried to investigate on fabrication of NiCrMo nanowires for medical application using AAO template and the fabricated nanowires were characterized by XRD, SEM, EDS and TEM.

II. PROCEDURE FOR PAPER SUBMISSION

A. Preparation of AAO Template

Aluminum sheet with thickness (0.5mm) was cut to circle shapes with (20mm) diameter to prepare anodic aluminum oxide template for depositing the nanowires. Cleaning with acetone has been done for Al specimens and to get more active Al surface, the Al specimens were treated with 3M NaOH and then electrochemically polished also done.

Oxalic acid with concentration 0.3 M was prepared in distilled water to use it as electrolyte for anodization. The anodization was achieved in two steps, in the first; the Al specimen was connected to the positive terminal of power supply to act as anode and stainless steel 316L as rod was used as cathode in electrochemical cell with applying 30V. The period time of first anodization was 8 hrs. at room temperature and then the specimen was treated with (H_3PO_4+$H_2Cr_2O_4$) mixture to open the pores for 1 hr at 60^{o}C.

The second anodization was achieved in the same electrolyte for 6hrs and then the specimens were wished with deionized water and ethanol. The immersion in acetone at 60^{o}C for 1 h was performed to remove the remained alumina.

B. Deposition of NiCrMo Nanowire

Nickel sulfate 0.30 M, chromium sulfate 0.08 M, sodium molybdate 0.008 M and boric acid 30 g/L were used as electrolyte to deposit the NiCrMo nanowires. The AAO template was acted cathode in electrochemical cell with Ni rode (purity 99.99%) acts as anode. The voltage of deposition was 1.8 V for 40 min.

Characterization of Nanowires

XRD technique was used to characterized the Al sheet, prepared AAO and fabricated nanowires with Cu as target at scan rate 40.0 (kV) and current= 30.0 (mA). Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and Transition electron microscopy (TEM) also used for characterization of fabricated nanowires. These inspections were achieved for partial and complete removal of template after deposition of nanowires. The partial dissolving of AAO was performed by 10% HCl and ethanol, while complete dissolving was by 6 M KOH solution.

III. RESULTS AND DISCUSSION

Figure (1) shows the XRD pattern of Al as substrate to prepare anodic aluminum oxide AAO as template which further used to deposit NiCrMo nanowires. XRD pattern of Al is a good agreement with JCPDS card (04-0787) at 2θ=38.473° (1 1 1), 44.739° (2 0 0) and 65.135° (2 2 0), while the XRD pattern of prepared AAO is a good agreement with JCPDS card (46-1215) at 2θ=45.716° (4 0 0) and 67.197° (0 4 6) as shown in Figure (2).

Figure (3) shows the side view of prepared AAO by SEM and TEM technique with ≈ 70 nm as diameter of formed pores which measured using J. Image program. By two-step anodization process, the hexagonally ordered porous alumina template has been obtained. The aluminum substrate was prestructured by anodizing in a solution of 0.3 M $H_2C_2O_4$ at room temperature. Fig. (3) indicates a highly ordered aluminum oxide pore structure.

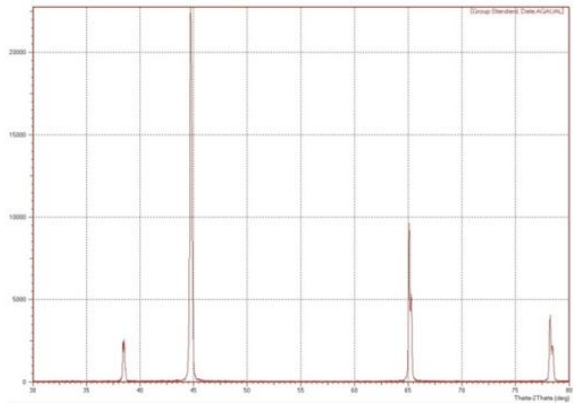


Fig. (1) XRD pattern of used Aluminum.

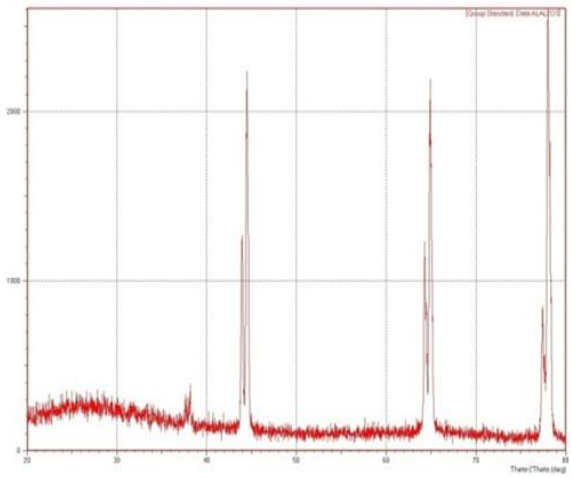


Fig. (2) XRD pattern of prepared AAO.

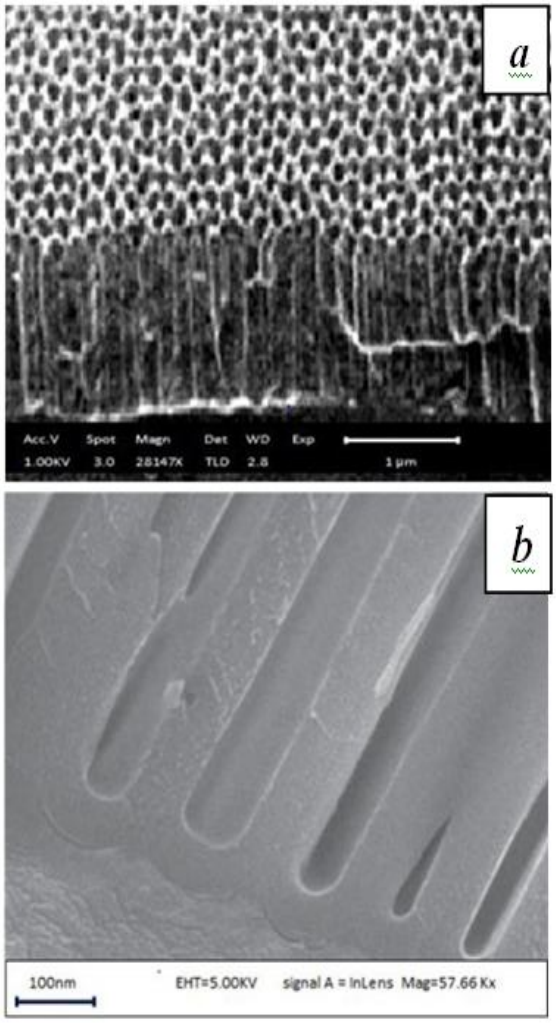


Fig. (3) SEM (a) and TEM (b) of pores in AAO.

XRD analysis of NiCrMo nanowires is presented in Fig. (4). The most intensive peak in the XRD spectrum for the nanowires is at $2\theta \approx 44^{\circ}$ which can be the result of matching of two peaks corresponding to Ni (0 1 1) ($2\theta = 44.521^{\circ}$ according to JCPDS card (45-1027) and Cr (1 1 0) ($2\theta = 44.392^{\circ}$ according to JCPDS card (06-0694). Other peaks are good agreement with JCPDS card (07-0050) at $2\theta = 41.187^{\circ}$ (4 2 0) and $2\theta = 74.200^{\circ}$ (4 11 0) to form $Ni_{40}Cr_{18}Mo_{42}$, in addition to appear a peak at $2\theta = 41.531^{\circ}$ (0 0 2) which attributed to pure Ni.

Figure (5) shows the SEM images of fabricated nanowires, these images indicate the nanowires were deposit in AAO pores. In plane view of partial removal for AAO (5-a), this image demonstrates the growth of multilayer and the black and white color can be distinguished between the individual layers as a Ni matrix and formed phase. In Fig. (5-b), can be shown the nanowires after completely dissolving the AAO template. Generally, the fabricated wires are ordered with fixed length ranged between 10 and 20 µm, this phenomena confirms the homogenous growth of nanowires under experimental conditions.

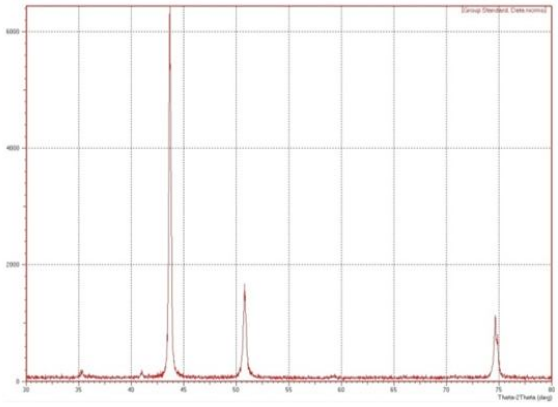


Fig. (4) XRD pattern of deposited NiCrMo nanowires.

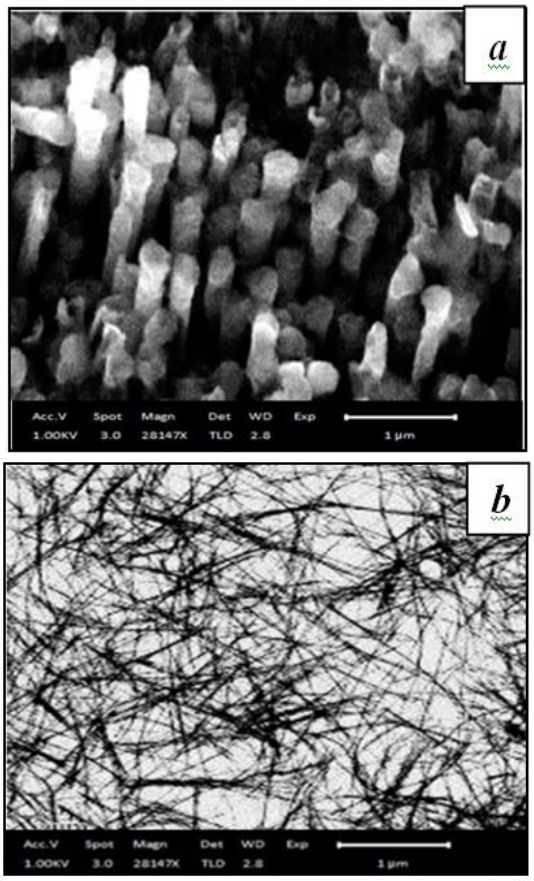


Fig. (5) SEM images for NiCrMo nanowires; (a) Plane view and (b) Complete dissolving of template.

The EDS analysis of NiCrMo nanowires is shown in Fig. (6) which indicates obtaining 72.2 wt% Ni, 19.5 wt% Cr and 8.3 wt% Mo that closely to composition of dental alloy NiCrMo and can be candidate the using of NiCrMo nanowires as biomaterial.

Fig. (7) shows TEM images of fabricated NiCrMo nanowires obtained after partial dissolving of template as arrays (a) and single nanowire (b). This figure shows the uniformly wire arrays with the same dimensions without distinguish the phases in nanowires. The image of single NiCrMo nanowire shows some white regions in Ni matrix (black color) which may be due to symmetric orthorhombic crystal of NiCrMo phase.

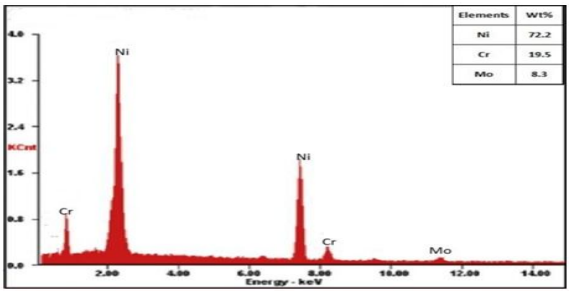
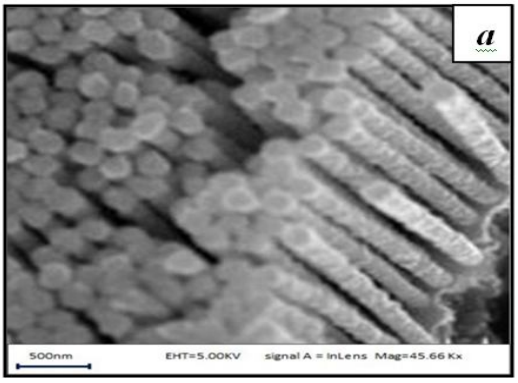


Fig. (6) EDS analysis of fabricated nanowires.



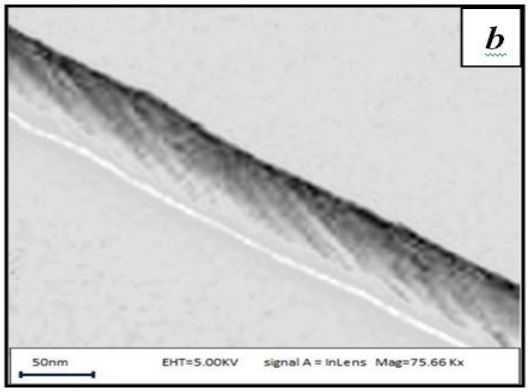


Fig. (7) TEM images for NiCrMo nanowires;
(a) After partial dissolving of AAO
(b) Single nanowire.

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