



Short Communication

Self-organized growth of magnetic nanoporous thin film by alloy anodization

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ABSTRACT

Anodization of alloys containing Al, Ni, Co and Fe as main constituents is reported here for the first time for formation of thin film of self-organized magnetic nanoporous structure. Fluoride concentration, anodization potential and the amount of water in the ethylene glycol electrolyte are very critical parameters to produce the well-aligned nanostructure. Further, the presence of Al in the alloy to protect the ferrite nanostructure by controlling the selective dissolution of oxide layers of Ni, Co, Cu was essential.

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1. Introduction

Interest in the fabrication of nanometer-sized fine structures is ever increasing due to the potential application of these nanostructures in electronic, optical, and micromechanical devices. Among other nanomaterials, metal oxide nanostructures are gaining great attentions as most of the metal oxides are semiconducting materials with typically wide band gaps [1]. Apart from the semiconducting behaviour, some of these metal oxides of Fe, Co and Ni show magnetic properties. Recent reports showed that magnetic nanostructures have potential biomedical applications such as biomolecular separation, MRI image contrasting agent and drug delivery system [2]. Various techniques have been developed and employed to fabricate such nanostructures by wet chemical methods. Among them, anodization of metals is a simple and well established technique to form highly self-ordered metal oxide nanoporous or nanotubular structures with high aspect ratios [3–6]. Nanoporous structure of anodized alumina is a typical example of such self-ordered growth of a metal oxide nanostructure reported by Masuda and Fukuda [7]. Thereafter, there has been many ongoing efforts to synthesize self-ordered nanoporous or nanotubular structures of various transition metal oxides especially TiO₂ by anodizing the metals [3–6]. Along with the anodization of various metals, the anodization of metallic alloys has also been reported to fabricate ordered nanostructures of their mixed oxides using fluoride ion containing electrolytes [3,4,8–14].

Meanwhile, many efforts have been carried out to prepare ferrite films with ordered structure by anodization of corresponding alloy films, especially electrodeposited iron-based magnetic alloy film in an aqueous KOH electrolyte [15]. However, the ferrite film did not show self-organized nanostructures, and it is still remained as an important issue in the field of alloy anodization. In the present work, we explored possibilities of preparing self-organized nanostructures of ferrite composites by anodizing alloys consisting of Al, Fe and other magnetic metals like Ni, Co, etc., in an electrolyte containing fluoride ion. By optimizing experimental parameters such as fluoride concentration and anodization potential, we could achieve the formation of self-organized porous ferrite film on an “Alnico” alloy surface. To the best of our knowledge, this is the first successful attempt to fabricate self-organized nanostructure of ferrites by the anodization of alloys.

2. Experimental

All chemicals were reagent grade and used as obtained from the manufacturers. Aluminum–nickel–cobalt (“Alnico”) alloy disc (13 mm × 6 mm) purchased from ALDRICH was used as the substrate for anodization. The composition of this alloy was examined with an energy dispersive X-ray analyzer (EDX) and was found to contain Al 14.09 at.%, Ti 0.20 at.%, Fe 49.34 at.%, Co 19.60 at.%, Ni 13.96 at.% and Cu 2.80 at.%, respectively. The analytical result is within the range of data provided by the manufacturer. The alloy substrate was polished to a mirror-finish surface using SiC abrasive papers with different grit size ranging from #600 to #4000 in wet conditions. Then, the polished substrates were sonicated in

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acetone, isopropanol and methanol followed by deionized (DI) water and dried in a stream of Ar-gas. This substrate was contacted with a Cu back-plate and then pressed against an O-ring sealed opening in the wall of an electrochemical cell, leaving an area of 0.5 cm² in diameter exposed to the electrolyte. A two-electrode arrangement electrochemical cell with a Pt-sheet as a counter electrode and a DC voltage source regulator (*Korea switching*) was used for anodization. The ethylene glycol electrolyte containing various amount of HF was 'aged' while all other electrolytes in the present investigation were used as prepared. The aging of the electrolyte was done for 48 h by anodizing a Ti-sheet at 50 V against the counter electrode. After anodization, the samples were thoroughly washed with DI water followed by immersing them in DI water over night to leach out residual fluoride and other impurities adsorbed during anodization. The samples were dried in a stream of Ar-gas and characterized. A field effect scanning electron microscope (FE-SEM, Hitachi S-4800) was used to investigate the structural morphology of the anodized samples. The anodized film was also mechanically cracked to check the morphology of the different stages of the anodization. An energy dispersive X-ray analyzer (EDX) coupled to the Fe-SEM, X-ray photoelectron spectroscopy (XPS) and X-ray diffractometer (XRD) were used to investigate the chemical composition and crystal structure of the anodized film.

3. Results and discussion

A set of preliminary experiments was performed to find out a suitable electrolyte composition to grow self-organized nanostructures. The morphology of the anodized surface was heavily dependent on the composition of electrolytes. The conventional electrolytes of both aqueous and non-aqueous media gave non-uniform surfaces after anodization and cannot form ordered nanostructure on the surface. For the regularity of anodized ferrite, we prepared a specially designed ethylene glycol electrolyte, which was 'aged' at 50 V for 48 h. With the 'aged' electrolyte, the alloy surface turned into dark color by the application of voltage indicating the anodic film growth. The 'aging' of electrolyte was essential to grow this dark colored film. The 'aging' increases the conductivity of electrolyte by introducing [TiF₆]²⁻ ions and provides the optimal conductivity for typical nanostructuring by anodization [14].

The alloy contained Ni, Co, and Cu that can hardly resist to the etching by acidic conditions with fluoride ion than the other elements in the alloy. Therefore, the anodization was carried out in the 'aged' electrolytes, especially with low HF concentration at different applied potentials. The dark colored skin was started to appear on the anodized surface at 20 V after 3 h in the electrolyte containing 0.025 M HF. The SEM examination of this anodized surface showed a compact oxide layer as shown in Fig. 1a. The alloy surface is not much affected by the electrical etching process and did not give the expected morphological change. The result indicates that the fluoride ion concentration was not sufficient to attack and etch this compact oxide layer to develop pores during anodization. Then, we increased the HF concentration to 0.05 M with same applied potential and anodization time. The SEM image shows the initiation of surface etching process and the formation of some pores. However, they are randomly distributed all over the anodized surface without any ordered structure (Fig. 1b). To accelerate anodizing process, the anodization potential increased from 20 to 30 V, and its surface was also monitored by SEM. Interestingly, the voltage increase gave a sign of the initiation of regular pattern formation on the surface with morphological depth. Though it was not completely organized structure, pores of average diameter of approximately 35 nm can be seen on the anodized surface of the sample (Fig. 1c). Also the pore depth is getting deeper as surface morphology and porosity increase. To get to the optimum

conditions for self-organized pores, the anodization voltage increased to 45 V. Then, it is worth to note that the surface of anodized magnetic alloy shows highly ordered structure (Fig. 1d and e). Some of the pores are connected to each other on the surface, and the approximately 35 nm repeating unit can be observed clearly. The pores are interconnected and form 3-D architecture, and leave us a room for the future improvement of morphology modification. The cross-sectional view shows the vertical arrangement of the nanostructure of 1 μm thickness with self-ordered nanopores (Fig. 1f). The effect of the increase in anodization potential to 50 V was monitored using SEM and is shown in Fig. 2a. Here, the nanostructure surface was etched and the thicknesses of pore were thinner losing its regularity. As a result, based on the SEM image, the optimum anodization condition was 45 V for 3 h. The surface morphology was also very dependent on the moisture in the anodization conditions.

The concentration of HF generally an important parameter during the anodization process. The optimized HF concentration in this experiment is significantly low compared to the electrolytes usually used for the anodization of Ti and other metals/alloys [3,13,14]. The alloy under investigation contains elements of Ni, Co, and Cu which are relatively less stable than Al and Ti against HF and therefore, the HF concentration was maintained to its low level. To investigate the effects of selective chemical etching of the less stable element, the anodized nanostructure was mechanically cracked and the different stages of the pores were examined closely with a SEM (Fig. 2b). The magnified SEM view of the pores formed at the end of the anodization (Fig. 2c) showed the similar deformed surface morphology of the pores (i.e., not effectively connected to each other and losing its connectivity in the nanostructure network) as the top of the anodized surface which are formed in the beginning and being continuously exposed to the electrolyte during the anodization process (Fig. 1d). Therefore, the deformation on the self-organized pore network may be due to the field added chemical dissolution of less stable elements selectively from the alloy during anodization.

It was already known that the presence of a small amount of water facilitates the formation of a self-organized nanostructure in iron [16,17]. In the same line, water (1 M) was added to the electrolyte and anodization was performed at 45 V for 3 h. After the anodization, a self-organized microporous structure was observed, but it was different and looks rather an assembly of nanoparticles (Fig. 2d). Moreover, the size of pore became wider from nano to micro level due to the higher rate of field aided dissolution of the oxide network in the presence of water. Therefore, the final optimized conditions for the self-organized network formation of pores from an "Alnico" alloy were established as 0.05 M HF, 45 V, and 3 h.

Further investigation was performed to understand the anodization of individual component of the alloy and the effects of Al and Ti elements. A different type of alloy containing Ni (29 at.%), Co (17 at.%) and Fe (52 at.%), typically without Al or Ti ("Kovar" alloy, ALDRICH), was anodized to characterize the role of Al and Ti element during the anodization process. The result was quite clear that the nanoporous structure was not obtained at all, but only a plane surface after the anodization. The surface was rather bright showing a metallic shining surface due to electropolishing of the substrate under the anodization conditions same as those employed for the anodization of "Alnico" alloy. Generally, iron is readily anodized and can produce nanoporous or nanotubular structure in optimized conditions [16,17]. However, the above reference "Kovar" alloy did not produce any nanostructures on the anodized surface but it produced a plane polished surface even the anodization was performed at very mild condition (i.e., at very low fluoride concentration) and although it contained 52 at.% iron. This mean the iron content in the alloy is not enough even to protect itself

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