Anodic oxidization of Ti-Ni-Si amorphous alloy ribbons and their capacitive and resistive properties

M. Fukuhara^{1,2,*}, K. Sugawara³

¹ *New Industry Creation Hatchery Center, Tohoku University*

6-6-10, Aoba, Aramaki, Aoba, Sendai 980-8579, Japan

² *Green Device Laboratory, Institute for Nanoscience & Nanotechnology, Waseda University, Tokyo, 162-0041 Japan*

³ *Research Institute for Electromagnetic Materials, Sendai, Miyagi, 982-0807 Japan*

* Corresponding author. Tel. & Fax: +81 22 352 6601

Abstract

Amorphous titanium oxide film on Ti-Ni-Si amorphous alloy ribbons was prepared by anodic polarization process in ten kinds of electrolyte solutions. Addition of NH_4F in $(\text{NH}_4)_2\text{SO}_4$ solution accelerates an increase in current, *i.e.* formation of soluble Ti-fluoride complexes, resulting in the amorphous titanium oxide layers with nanometer-sized pores. Pore size decreases down to 12 nm with decreasing of applied voltage from 30 to 5 V. However, parallel capacitance C_p , series capacitance C_s , and RCs constant increase with decrease of pore size from 23 to 18 nm and then decrease in pore size region from 18 to 12 nm by formation of penetrating tunnels in the layer. It needs further enhancement of RCs for realization of superior electric storage capacitor.

Keywords : Electric storage devices; Amorphous alloys; Amorphous titanium oxide film; Nanometer-sized pores; Fluoride ions

1. Introduction

The storage of electrical energy is one of the topics currently attracting a great deal of interest in the field of scientific and technological research [1-6]. For the Japanese nation which contemplates a nuclear-power-free future after the tremendous disaster of the earthquake and tsunami, especially, the development of renewable-energy source including electrical storage is an urgent problem to be solved.

Following the capacitance studies of Ni-Nb-Zr-H amorphous alloys with femtofarad capacitance tunnels [7] and nanocrystalline de-alloyed Si-Al [8, 9], we have found that the de-alloyed and anodically oxidized amorphous Ti-Ni-Si alloy ribbons [10] show AC electric storage from 193 to 453 K with a voltage variation from 10 to 150 V, and DC

capacitance of $\sim 4.8 \text{ F}$ ($\sim 52 \text{ kF/cm}^3$) in discharging behaviors for voltage after 1.8 ks charging at DC current of 100 mA. In sharp contrast to conventional crystalline titanium oxide (TiO_2) for wide range of applications, including photocatalysis [11], optovoltaics [12], solar energy conversion [13], chemical sensors [14], bioprobes [15] and environmental pollution control [16], our distinguished amorphous titanium oxide supercapacitors are devices that store electric charge on their amorphous titanium oxide TiO_{2-x} surfaces that contain many 50-70 nm sized cavities with higher work functions of 5.5 eV [10, 17]. We assumed that the surface structure of the oxide consists of a distributed constant equivalent circuit of resistance and capacitance, analogous to active carbons in electric double-layer capacitors (EDLCs). The amorphous materials of interest are completely different from the conventional “wet” cells such as EDLC and secondary cells which are controlled by diffusivity of ions. We termed this device a “dry” electric distributed constant capacitor [8- 10].

We are interested in investigating anodically oxidized conditions of higher narrow canyon densities and higher electric resistivities for amorphous alloy supercapacitors. In this study, we report anodic oxidization conditions for amorphous titanium oxide coated Ti-15 at.% Ni-15 at.% Si alloy supercapacitors, with an aim to obtain further higher capacitances and resistivities. Little research about anodically oxidized titanium oxides for supercooled amorphous alloys, however, have been carried out. The formation of self-organized porous crystalline oxide nanostructures ($\pi\text{-TiO}_2$) has been electrochemically achieved mostly in fluoride ion containing electrolytes [18]. Recent researches for high aspect-ratio nanotubes have been eagerly investigated as one of the most functional materials such as gas sensing devices, solar cells, catalyst and biomaterials [19].

2. Experimental details

Ti-15 at.% Ni-15 at.% Si alloy ingots (nominal compositions) were prepared by arc-melting mixtures of Ti (99.95 % purity), Si (99.999 % purity) and Ni (99.95 % purity) in Ar atmosphere purified by Ti-gettering. Ribbon specimens 50 μm thick and 1 mm wide were prepared from the ingots by rapid solidification of the melt on a single copper roller in He atmosphere at a tangential velocity of 52.3 m/s, using a single-wheel melt-quenching apparatus (NEV-A05-R10S, Nisshin Giken). To prevent tight oxide from deterioration by formation of nickel oxides, we removed Ni elements from surface of the specimens for 288 ks in 1N HCl solution at room temperature, as de-alloying process. Subsequent anodic oxidation of the de-alloyed specimens were carried out for 3.6 ks in

various solutions at 5-30 V and 278 K. Table 1 lists the 13 kinds of oxidization conditions for the amorphous alloys. Specimen surfaces were examined by field emission scanning electron microscope (FESEM, S3800, Hitachi) at an operating voltage of 5-15 kV.

The specimen (1 mm wide, 40 μ m thick, and 10 mm long) with double-oxidized surfaces was sandwiched directly by two copper ribbons beneath two pieces of glass plates using a clamp. The capacitance of the specimen was measured using galvanostatic charge/discharge on a potentiostat /galvanostat (SP-150, BioLogic Science) at frequencies between 1 mHz and 1 MHz under a constant voltage of 10 mV at room temperature. All electronic measurements were carried out in an Al shield box, to prevent electromagnetism of the environment.

3. Results and Discussion

3.1. Anodic oxidization of the amorphous alloys

With an aim to obtain further higher capacitances and resistivities, we studied oxidizing conditions on surface characterization for the amorphous alloys using ten kinds of electrolyte solutions. The current-time curves during potentiostatic polarization at 30 V are shown in Fig. 1 (a) and (b). All curves are characterized by rapid increase and the following gradual decrease in the initial stage of anodization. However, curves (Fig. 1(a)) of NaOH and H₃PO₄ solutions then remarkably increase due to the dissolution reaction of the formed oxide layers [18] and O₂ evolution, while ones (Fig. 1(b)) of CH₃COOC₂H₅, H₂CrO₄, CH₃COOH, NH₃ and Na₂S₂O₃ keep the decreasing to a steady-state value. All specimens changed their surface color from metallic luster to ash color. The former samples are brittle and the latter ones showed lower resistance below 1 k Ω . The curves of H₂SO₄, (NH₄)₂SO₄, CH₃COONH₄ showed gradual increase. Although de-alloying process did not change the morphology of specimens, anodic oxidization changed surface of the specimens to amorphous titanium oxide. The representative X-ray pattern for H₂SO₄ solution was presented at inset of Fig. 1 (a). The XRD pattern of Ti-based amorphous alloy is characterized by a broad large peak of 40 deg., which corresponds to main peak of crystalline Ti [17]. However, we could not detect main peak of crystalline anatase phase at around 25 deg. Thus we regarded it as Ti-based amorphous alloy coated with amorphous titanium oxide layers. Furthermore, barrier-type, amorphous titanium oxide film structurally stabilized by incorporation of silicon species to much increased voltages [19].

Since the samples obtained by H₂SO₄ and (NH₄)₂SO₄ solutions showed high

resistance over 1 M Ω , we then carried out anodic oxidization by addition of NH₄F and NH₄ClO₄ electrolytes in anticipation of nanometer-sized porous making effect by fluoride [20] and chloride ions, respectively. Figure 2 shows the current-time curves in (NH₄)₂SO₄ - 0.005wt%NH₄F, -0.05wt%NH₄F and -1wt%NH₄ClO₄ solutions, along with ones in H₂SO₄ and (NH₄)₂SO₄ solutions. Addition of NH₄F and NH₄ClO₄ accelerate increase in current, *i.e.* formation of soluble Ti-fluoride complexes [21], but increase of the former is larger than that of the latter. Furthermore, the amount of NH₄F electrolyte is more effective to formation of the complexes.

Fig. 3 shows top views of SEM images of the surface morphology observed in (NH₄)₂SO₄, (NH₄)₂SO₄-0.005wt%NH₄F, (NH₄)₂SO₄-0.05wt%NH₄F and (NH₄)₂SO₄-1wt%NH₄ClO₄ solutions at 30 V. The samples obtained from (NH₄)₂SO₄ (a) and (NH₄)₂SO₄-1wt%NH₄ClO₄ (d) consisted of spherical aggregates of small particles with rough surfaces. On the other hand, the samples from (NH₄)₂SO₄-0.005wt%NH₄F (b), -0.05wt%NH₄F (c) consisted of the self-organized regular porous structures. This is known as spark-discharge [22], as same as in H₂SO₄ [10, 17].

3.2. Capacitive and resistive properties of anodic oxidized alloys

To decrease the pore size, we anodically oxidized the specimens under various applied voltage, using (NH₄)₂SO₄-0.005wt%NH₄F solution. The presentative microstructure of the specimen anodically oxidized at applied voltage of 5V is shown in Fig. 4. The pore size and resistance are presented at Fig. 5(a), as a function of applied voltage. The pore size decreases from 23 to 12 nm with decreasing the voltage. The morphology and the structure of porous layers are affected strongly by the chemical conditions (particularly the anodization voltage) and the solution parameters (in particular the HF concentration) [21]. On the other hand, resistance showed a curve with the lowest value, 1.5 k Ω at 15 V. Pore size dependences of C_p and C_s are shown in Fig. 5 (b). Both curves of C_p and C_s showed reverse “V” typed one. The values of C_s are 500 thousand times higher than ones of C_p. This means that this device is constructed as series capacitance. Since our device is characterized by RC constant with large resistance over 1 M Ω [11, 17], we evaluate RCs as a function of pore size. The results (Fig. 5 (c)) showed reverse “V” typed one, as well as Fig. 5(b). Although capacitance is expected to increase with decreasing pore size, capacitance of specimens with pore size below 18 nm decreases reversely. To elucidate the reason, we lastly observed cross section of the titanium oxide layer. The backscattered electron image (Fig. 5(d)) at 2 kV revealed an existence of some tunnels through the porous amorphous titanium oxide

layer with about 100 nm thickness to amorphous Ti-Ni-Si alloy. There is a possibility of penetration of metallic atoms in tunnels. Thus Cp, Cs and RCs would increase as the porous size decreases, provided that the tunnels are plugged with insulating matters. It needs further study such as two step oxidization. In addition, usage of Ti-based amorphous alloys without Ni is another selection, because very small amount of Ni remains in amorphous oxide layer.

Although researches by Shumuki *et al.* [18, 20, 21] have focused on self-organized TiO₂ nanotubes with high aspect ratio, our aim is to achieve amorphous titanium oxide supercapacitors with quick charging and long-time discharging. It would be not desirable for solid state supercapacitors to have high-aspect-ratio nanotube structure on the surface of the titanium oxide because of static electric repulsion among absorbed electrons.

4. Conclusions

Amorphous Ti-15 at.% Ni-15 at.% Si alloys prepared by the rotating wheel method were leached out for 288 ks in 1N HCl solution at room temperature and anodically oxidized for 3.6 ks in 13 kinds of solution at 5-30 V and 278 K, respectively. The specimens obtained by NaOH and H₃PO₄ electrolytes, which showed remarkable increase in current-time curves, are brittle, while ones of CH₃COOC₂H₅, H₂CrO₄, CH₃COOH, NH₃ and Na₂S₂O₃, which kept the decreasing to a steady-state value, showed lower resistance below 1 kΩ. Addition of NH₄F and NH₄ClO₄ electrolytes to (NH₄)₂SO₄ solution accelerate increase in current, but increase of the former is larger than that of latter. SEM images showed spherical aggregates of small particles with rough surfaces for (NH₄)₂SO₄ and (NH₄)₂SO₄-1wt%NH₄ClO₄ solutions, and the titanium oxide layers with the nanometer-sized porous structures for (NH₄)₂SO₄-0.005wt%NH₄F and (NH₄)₂SO₄-0.05wt%NH₄F ones. The pore size decreases down to 12 nm with decreasing applied voltage from 30 to 5 V. However, Cp, Cs and RCs decrease from 18 nm by formation of penetrating tunnels in titanium oxide layer deposited on the amorphous alloy. The above results demonstrate the potential application of titanium oxide to improve for enhancing of RCs for realization of superior electric storage capacitor.

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Table 1. Thirteen kinds of electrolytes and anodic oxidization conditions for anodic oxidization of amorphous Ti-15at%Ni-15at%Si alloys

Fig. 1 Current-time curves during anodization at 30 V and 278 K for 3.6 ks in ten kinds of electrolyte solutions.

Fig. 2 Current-time curves during anodization at 30 V and 278 K for 3.6 ks in 0.4 M H₂SO₄, 0.8 M (NH₄)₂SO₄, 0.8 M(NH₄)₂SO₄-0.005 wt%NH₄F, 0.8 M(NH₄)₂SO₄-0.05 wt%NH₄F, 0.8 M(NH₄)₂SO₄-1wt%NH₄ClO₄.

Fig. 3 SEM images of titanium oxide surfaces of anodically oxidized specimens obtained for 0.8 M (NH₄)₂SO₄(a), 0.8 M(NH₄)₂SO₄-0.005 wt%NH₄F(b), 0.8 M(NH₄)₂SO₄-0.05 wt%NH₄F(c), 0.8 M(NH₄)₂SO₄-1wt%NH₄ClO₄ (d) at 30 V.

Fig. 4 SEM images of titanium oxide surfaces anodically oxidized specimens obtained at 5 V for 3.6 ks in 0.8 M(NH₄)₂SO₄-0.005 wt%NH₄F solution.

Fig. 5 Applied voltage dependences on pore size and electric resistance (a), pore size dependences on C_p and C_s (b), RCs (c), and cross section (d) of titanium oxide layer of anodically oxidized specimens obtained for 0.8 M(NH₄)₂SO₄-0.005 wt%NH₄F solution.

Table 1. Thirteen kinds of electrolytes and anodic oxidization conditions for anodic oxidization of amorphous Ti-15at%Ni-15at%Si alloys

Electrolytes	Anodic oxidized conditions
0.4 M H ₂ SO ₄	at 30V and 278 K, for 3.6 ks
0.8 M (NH ₄) ₂ SO ₄	at 30V and 278 K, for 3.6 ks
0.1 M Na ₂ S ₂ O ₃	at 30V and 278 K, for 3.6 ks
0.1 M NaOH	at 30V and 278 K, for 3.6 ks
0.4 M H ₃ PO ₄	at 30V and 278 K, for 3.6 ks
0.4 M CH ₃ COOH	at 30V and 278 K, for 3.6 ks
0.4 M NH ₃	at 30V and 278 K, for 3.6 ks
0.8 M CH ₃ COOC ₂ H ₅	at 30V and 278 K, for 3.6 ks
0.3 M CH ₃ COONH ₄	at 30V and 278 K, for 3.6 ks
0.1 M H ₂ CrO ₄	at 30V and 278 K, for 3.6 ks
0.8 M (NH ₄) ₂ SO ₄ -0.005wt%NH ₄ F	at 5V, 10V, 15V, 20V, 25V, 30V, and 278 K for 3.6 ks
0.8 M (NH ₄) ₂ SO ₄ -0.05wt%NH ₄ F	at 30V and 278 K, for 3.6 ks
0.8 M (NH ₄) ₂ SO ₄ -1wt%NH ₄ ClO ₄	at 30V and 278 K, for 3.6 ks

Figure 1

Figure 2

Figure 3

(a)

(b)

(c)

(d)

Figure 4

Figure 5

(a)

(b)

(c)

(d)