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Short communication

Pd–Ni–P metallic glass film fabricated by electroless alloy plating

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ABSTRACT

In the present study a Pd–Ni–P film has been fabricated by electroless alloy plating. The fabricated Pd–Ni–P film was found to be a metallic glass on the basis of two features, namely, an amorphous structure and a glass transition followed by crystallization during heating. The thermal stability of the supercooled liquid region, however, was lower than that of bulk Pd–Ni–P metallic glass. And unlike the conventional metallic glasses, the fabricated Pd–Ni–P film did not have a uniform microstructure. The non-uniform microstructure of this film resulted from the inhomogeneous distribution of the free volume accompanying the electroless alloy plating reaction.

1. Introduction

In recent years, various bulk metallic glasses have been obtained by conventional casting techniques at a quenching rate of less than 100 K/s [1]. The unique properties of these materials in comparison with crystalline materials, particularly their high strength, high corrosion resistance, and good soft magnetic properties [1], have prompted many researchers to study them in more detail, in both fundamental and application research.

When applied to micro-machines or micro-electro mechanical systems (MEMS), materials are generally expected to have good formability and to be free from size effects. Unlike conventional amorphous materials, metallic glasses have a supercooled liquid region between the glass transition and crystallization temperatures. The viscous flow of this supercooled liquid region can be used to remove internal stress, or to easily fabricate micro components. The amorphous structure of metallic glasses offers still another advantage, as it ensures that the metallic glasses remain isotropic even when specimen sizes decrease to a micro- or nano-meter order. Thus, metallic glasses show great promise as materials for micro-machines or MEMS [2–4].

Thin films of metallic glass can be fabricated by sputtering [5–9]. Sputtering is expensive, however, and the films fabricated by sputtering tend to have abundant voids or defects. In view of the significant effects of these defects on the mechanical properties of micro-sized materials, another method to fabricate metallic glass films clearly needs to be developed. It was from this viewpoint that we turned our attention to an electroless plating technique as a method for fabrication. Electroless plating can fabricate uniform thin films with few voids and defects, works at a low process temperature, and can be used to plate films on non-conductive materials. Few studies, however, have investigated the fabrication of metallic glass films by electroless plating.

Pd–Ni–P alloy, one of the most popular metallic glasses, includes a metalloid element P [1,10]. In electroless plating, the plated film forms via an oxidation–reduction reaction of hypophosphorous acid. For this reason, we regard the Pd–Ni–P alloy as the optimal material for fabricating metallic glass films by electroless plating. In this study we developed a method for fabricating Pd–Ni–P metallic glass films by electroless alloy plating and examined the thermal properties and microstructure of fabricated films.

2. Experimental procedure

The substrates were films of pure Cu (99.99 mass%) and Al (99.5 mass%) with 10×20 mm^2. The Al substrate was used only for measurement by differential scanning calorimetry (DSC). Each substrate was washed with acetone and rinsed in ion-exchange water before the following pretreatment. The grease was removed from the substrate specimens by successive dipping in a 10% NaOH solution and a 10% HCl solution, followed by rinsing in ion-exchange water. The samples were immersed in activator solution (Okuno Chemical Industries; chemical compositions shown in Table 1) at 303 K, then rinsed in ion-exchange water. This pretreatment was applied to all substrates regardless of the conditions of the electroless alloy plating reaction.

The electroless alloy plating solution was a mixture of Pd and Ni–P electroless plating solutions (Okuno Chemical Industries;

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Table 1
Chemical compositions (mass%) of the activator solution, Pd electroless plating solution, and Ni–P electroless plating solution, respectively

Activator solution	Hydrogen chloride: 18% Ion-exchange water: 81.96%	Palladium chloride: 0.04%
Pd electroless plating solution	Palladium chloride: 0.28% Sodium formate: 1.8%	Ethylenediamine: 0.23% Ion-exchange water: 97.69%
Ni–P electroless plating solution	Nickel chloride: 9% Complexing agent: 12%	Sodium hypophosphite: 12% Ion-exchange water: 67%

chemical compositions shown in Table 1). The electroless alloy plating was conducted with various Pd/Ni–P mixtures at temperatures within a range from 303 to 333 K. The average thickness of the fabricated films was about 250 nm.

The composition of the fabricated film was measured by a scanning electron microscopy (Hitachi: S-4300SE) equipped for energy dispersive X-ray spectroscopy. An accelerating voltage of 20 kV with collecting time of more than 120 s was applied. The structural analysis of the fabricated film was conducted by X-ray diffraction (XRD, Rigaku: Ultima IV) with Cu Kα radiation at a glancing angle of 1°. The microstructure of the films was also observed by a transmission electron microscopy (TEM, Philips: CM200, 200 kV). Thin foil specimens for the TEM observation were prepared by ion milling (Technoorg-Linda: Ion Beam Thinning Unit Type IV3). The ion milling was performed from the Cu substrate side only, in order to permit observation of the microstructure of the fabricated Pd–Ni–P film. To confirm the glass transition and crystallization of the fabricated film, the heat flow was measured by DSC (Ulvac-Riko: DSC-9400) at a heating rate of 20 K/min in an Ar atmosphere after dissolution of the Al substrate with a 10% NaOH solution.

3. Results and discussion

3.1. Electroless alloy plating reaction of Pd–Ni–P

Fig. 1(a) and (b) shows the relationship between the composition of the fabricated film and the plating temperature ((a) mixture with 75 ml Pd and 25 ml Ni–P solutions, (b) mixture with 50 ml Pd and 50 ml Ni–P solutions). Fig. 1(c) shows the relationship between the composition of the fabricated film and the mixture ratio of the plating solution at 313 K. Under all conditions of the present study, an increase in the plating temperature or in the mixture ratio of the Ni–P solution leads to an increase in the Ni content of fabricated film and a decrease in the Pd content. On the other hand, the P content of the fabricated film remains almost constant. These results indicate that the composition of fabricated Pd–Ni–P film can be easily controlled by adjusting the mixture ratio or the plating temperature.

Because metallic glasses are formed with limited compositions, the alloy composition is a very important parameter for their fabrication. Pd–Ni–P alloy becomes bulk metallic glasses within composition ranges of Pd = 25–60 at.% and P = 20 ± 5 at.%, and $Pd_{40}Ni_{40}P_{20}$ (at.%) has the highest glass-forming ability [11]. Based on the results shown in Fig. 1, the optimal plating condition for fabricating the $Pd_{40}Ni_{40}P_{20}$ (at.%) film is a mixture with 75 ml Pd and 25 ml Ni–P solutions at a plating temperature of 313 K.

Fig. 2 shows the XRD pattern of a Pd–Ni–P film with a composition of $Pd_{42}Ni_{33}P_{25}$ (at.%) fabricated under this plating condition. The peaks of the Cu substrate are sharp (at 43 and 50°), but more importantly, the XRD pattern exhibits a broad halo peak at around 40°. On this basis, we can conclude that the fabricated Pd–Ni–P film has an amorphous structure.

3.2. Thermal properties of the Pd–Ni–P film

To confirm the glass-forming ability of fabricated Pd–Ni–P film, the heat flow was measured by DSC at a heating rate of 20 K/min. As shown in Fig. 3, the Pd–Ni–P film ($Pd_{32}Ni_{46}P_{22}$ (at.%)) exhibits an endothermic peak followed by an exothermic peak, corresponding to the glass transition and crystallization, respectively (T_g = 593 K, T_x = 641 K, ΔT_x = 48 K). This DSC analysis demonstrates that the fabricated Pd–Ni–P film is a metallic glass itself. Compared with the bulk Pd–Ni–P metallic glasses formed by water quenching with B_2O_3 flux treatment (T_g = 583 K, T_x = 673 K, ΔT_x = 90 K in $Pd_{30}Ni_{40}P_{20}$ (at.%) and T_g = 576 K, T_x = 678 K, ΔT_x = 102 K in $Pd_{40}Ni_{40}P_{20}$ (at.%)) [11], however, the crystallization temperature of the fabricated Pd–Ni–P film shifts to a lower level in spite of the almost identical glass transition temperature. On this basis, we can assume that the thermal stability of the supercooled liquid is low for the fabricated Pd–Ni–P film. According to earlier reports, atomic diffusion controls the

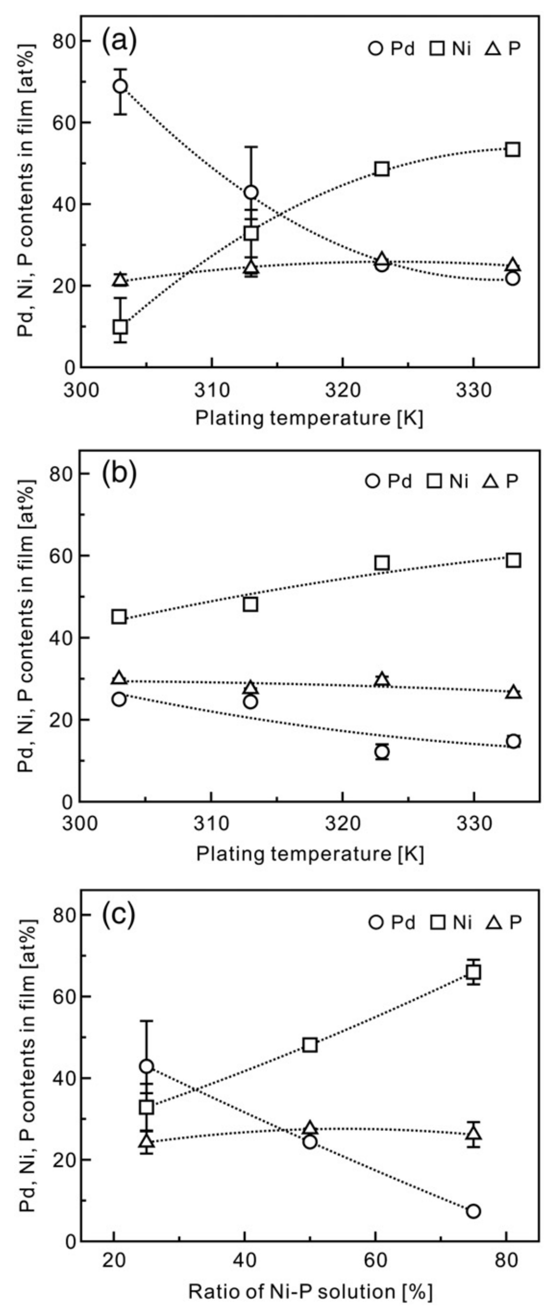

Fig. 1. (a), (b) Relationship between the composition of the fabricated Pd–Ni–P film and plating temperature ((a) mixture with 75 ml Pd and 25 ml Ni–P solutions, (b) mixture with 50 ml Pd and 50 ml Ni–P solutions); (c) relationship between the composition and mixture ratio of the plating solutions at a plating temperature of 313 K.