Fabrication and characterization of Ti–Ni shape memory thin film using Ti/Ni multilayer technique

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Abstract

Alloying process and shape memory properties of a Ti/Ni multilayer thin film fabricated by a dual d.c. magnetron sputter–deposition method were investigated, and compared with those of a Ti–Ni amorphous thin film fabricated by an alloy target sputter–deposition method. The multilayer thin film was made by depositing Ti and Ni layers alternately on a SiO2/Si substrate. The Ti and Ni of the Ti/Ni multilayer thin film were crystalline after deposition. Alloying of the Ti/Ni multilayer thin film proceeded in multi steps. Amorphous phase was formed at the interfaces between the Ti and Ni layers by inter-diffusion of the Ti and Ni atoms during heating up to 640 K. Ni-rich Ti–Ni B2 phase was formed during heating up to 710 K. During further heating up to 750 K, the Ni-content of the Ti–Ni B2 phase decreased and Ti2Ni phase was formed. The Ti/Ni multilayer thin film exhibited shape memory effect after heat-treatment at 673 K where Ti–Ni amorphous thin films were not crystallized. The heat-treated Ti/Ni multilayer thin films exhibited the shape memory effect equivalent to that of the heat-treated Ti–Ni amorphous thin films when the heat-treatment temperature was above 873 K.

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Keywords: Shape memory alloy; Ti–Ni; Sputtering; Thin film; Shape memory effect; Multilayer; Alloying process

1. Introduction

Ti–Ni shape memory alloys are considered as the most promising candidates for actuators of MEMS (micro–electro–mechanical systems) because of their large recovery strain and recovery force [1]. In order to apply the Ti–Ni alloys to MEMS, it is required to make them thin down to micron size. Rolling and melt spinning methods are available for making thin plates with thickness larger than 15 μm. However, sputter–deposition methods are available for making thin films with thicknesses less than 10 μm. Ti–Ni thin films fabricated by the sputter–deposition method are expected to be applied in microdevices such as microvalves [2], micropumps [3] and cantilevers [4], since they exhibit an excellent shape memory effect and good mechanical properties. Martensitic transformation start temperature ($M_s$) of the Ti–Ni thin films is strongly affected by the composition [5–8]. Therefore, controlling the composition of a Ti–Ni thin film is very important in order to apply to various purposes. Ti–Ni alloy targets have been used in conventional sputter–deposition methods. The composition of the film is adjusted by placing pure Ti chips on the Ti–Ni alloy target. However, the composition of the Ti–Ni thin film fabricated by this method is difficult to be adjusted precisely, because the composition of the deposited thin film is affected by the surface state of the target. Ti–Ni thin films can be fabricated by Ti/Ni multilayer thin films composed of pure Ti and Ni layers [9]. By using this method, controlling the composition of thin films seems to be easier in comparison with the thin films fabricated by the alloy target method, since the composition of the thin films can be adjusted by setting the sputtering time and sputtering power. Alloying of the Ti/Ni multilayer thin films is necessary for the thin films to exhibit shape memory effect. However, no detailed investigation of the alloying process of the multilayer thin films has been conducted. In this study, the alloying process of Ti/Ni multilayer films was investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Then, shape memory
properties of the alloyed thin films were investigated by thermal cycling tests under constant stresses.

2. Experimental

A Ti/Ni thin film was prepared by a dual-source sputtering system. Fig. 1 shows the dual-source sputtering system used in this study. This system consists of two d.c. magnetron sputtering sources and a SiO₂/Si substrate which is placed on a turn-table in the chamber. Ti and Ni layers were deposited alternately on the substrate by rotating the turn-table until reaching each position corresponding to a Ti or Ni target. The sputtering atmosphere was pure Ar at a pressure of 2.5 × 10⁻⁴ Pa. Typical background pressure before sputtering was lower than 5 × 10⁻⁵ Pa. Pre-sputtering of Ti and Ni targets was carried out prior to the deposition of the multilayer thin film in order to minimize contamination. The Ti and Ni targets were sputtered at d.c. powers of 280 and 60 W, respectively. The sputtering time of each layer was adjusted in order to control the film thickness. The Ti/Ni thin film used in this study was made to obtain Ti–51at%Ni alloy composition by controlling the sputtering time for each layer; i.e. 41 s for Ti and 64 s for Ni. The total number of Ti and Ni layers in the thin film was 100 (Ti: 50, Ni: 50). The thickness of the Ti/Ni multilayer thin film was 3.0 μm. A Ti–Ni amorphous thin film was also fabricated by the conventional sputter-deposition method using a Ti–Ni alloy target for comparison. The compositions of the thin films were determined by an electron probe microanalyzer (EPMA). The compositions of the Ti/Ni multilayer thin film and the amorphous thin film were determined to be Ti–51.3at%Ni and Ti–51.6at%, respectively, after heat-treatment at 1073 K for 3.6 ks. The as-sputtered multilayer thin film was removed from the SiO₂/Si substrate for the DSC measurement. The DSC measurement was performed up to 773 K with a heating rate of 10 K/min to measure the alloying temperature. The film samples were also kept in a quartz tube during the heat-treatment mentioned above, then quenched into water without breaking the tube. The crystal structures and precipitates of the as-sputtered and heat-treated thin films were determined by XRD using Cu Kα radiation. The cross-section of the multilayer thin film was observed by TEM. The cross-section specimens for the TEM observations were prepared by a focused ion beam (FIB) system.

3. Results and discussion

3.1. Alloying process of Ti/Ni multilayer thin film

Fig. 2 shows DSC curves of the as-sputtered Ti/Ni multilayer thin film and the as-sputtered Ti–Ni amorphous thin film upon heating with a heating rate of 10 K/min. A single exothermic peak was observed at 750 K in the DSC curve of the Ti–Ni amorphous thin film. However, in the case of the multilayer thin film, three exothermic peaks were observed at 621, 693 and 745 K, respectively. This indicates that alloying of the Ti/Ni multilayer thin film proceeds in multi steps. Fig. 3 shows the XRD profiles of the as-sputtered Ti–Ni amorphous thin film and the thin film heated up to 750 K. The film was observed in a quartz tube during the heat-treatment mentioned above, then quenched into water without breaking the tube. The crystal structures and precipitates of the as-sputtered and heat-treated thin films were determined by XRD using Cu Kα radiation. The cross-section of the multilayer thin film was observed by TEM. The cross-section specimens for the TEM observations were prepared by a focused ion beam (FIB) system.

![Fig. 1. A dual-source sputtering system.](image1)

![Fig. 2. DSC curves of the as-sputtered multilayer thin film and as-sputtered amorphous thin film.](image2)
temperatures with the same heating rate as in the DSC measurement, and the results are also shown in Fig. 4. The XRD profile obtained from the specimen heated up to 640 K exhibited that the diffraction peak from the Ni became broader. For the specimen heated up to 710 K, a peak corresponding to the Ti–Ni B2 appeared, while the peak from the Ni disappeared and the intensity of the peak corresponding to the Ti decreased. The Ti–Ni B2 is considered as a Ni-rich phase, because the peak from the Ti was still remained while the peak from the Ni disappeared. After further heating up to 750 K, the intensity of the peak from the Ti–Ni B2 increased, while the peak from the Ti disappeared. Peak corresponding to Ti2Ni was also observed in the specimen heated up to 750 K as shown in Fig. 4. It is interesting to note that the \( \{110\}_{B2} \) peak slightly shifted to a lower diffraction angle, indicating that the lattice spacing of the Ti–Ni B2 phase increased by heating from 710 up to 750 K. It was reported in previous researches that the lattice parameter of the Ti–Ni decreased with increasing Ni-content in the Ni-rich region [11]. Thus, the increase of the lattice spacing of the Ti–Ni B2 in the Ti/Ni multilayer thin film indicates that the Ni-content of the Ti–Ni B2 decreased with increasing heating temperature by inter-diffusion of Ti atoms into the Ti–Ni from the residual Ti layers sandwiching the Ti–Ni layer.

Fig. 5 shows bright field images and the corresponding selected area diffraction patterns of the as-sputtered Ti–Ni multilayer thin film and multilayer thin films heated up to 640 and 750 K with a heating rate of 10 K/min. Alternate bright and dark layers were observed in the bright field image of the as-sputtered specimen as shown in Fig. 5(a). Average thicknesses of the bright (Ti) and dark (Ni) layers were about 36 and 24 nm, respectively. The diffraction spots from \( (100)_{Ti}, \ (101)_{Ti}, \ (002)_{Ti} \) and \( (111)_{Ni} \) of Ti and Ni polycrystals were observed in the selected area diffraction pattern (SADP). This indicates that the Ti and Ni were in the crystalline state. The SADP also reveals a strong \( \{001\}_{Ti} \) and \( \{111\}_{Ni} \) fiber textures in the Ti and Ni layers, respectively. For the specimen heated up to 640 K, a reaction layer was observed at each interface between Ti and Ni layers as shown in Fig. 5(b). In addition to the diffraction spots from the Ti and Ni, a diffused halo-ring was observed in the selected area diffraction pattern. This indicates that an amorphous layer was formed in each interfacial region by inter-diffusion of Ti and Ni. Similar solid state amorphization phenomenon between Ti and Ni has been also reported by previous researches [12–20]. Based on the above results, it is considered that the first exothermic peak in a DSC curve is due to the reaction for the solid state amorphization. After further heating up to 750 K, the Ti/Ni multilayer thin film was alloyed completely as shown in Fig. 5(c). Diffraction rings corresponding to \( \{110\}_{B2}, \ \{220\}_{Ti,Ni}, \ \{311\}_{Ti,Ni}, \ \{331\}_{Ti,Ni} \) and \( \{511\}_{Ti,Ni} \) were observed in the diffraction pattern indicating that both the B2 and Ti2Ni phases coexist, which is consistent with the XRD result in Fig. 4. The diffraction ring of \( \{110\}_{B2} \) indicates that the alloyed Ti–Ni B2 has no appreciable preferred orientation although the Ti and Ni layers have a strong fiber texture. It is supposed that the random orientation of the Ti–Ni B2 is due to that it was crystallized from amorphous. The diffraction ring of \( \{110\}_{B2} \) was broad, suggesting that the lattice parameter of the Ti–Ni B2 varied due to the variation in composition. It is due to that the inter-diffusion of Ti and Ni was not satisfied in this specimen.

Fig. 3. XRD profiles of the as-sputtered Ti–Ni amorphous thin film and the Ti–Ni amorphous thin film heated up to 750 K with a heating rate of 10 K/min.

Fig. 4. XRD profiles of an as-sputtered Ti/Ni multilayer and Ti/Ni multilayers heated up to 640, 710 and 750 K with a heating rate of 10 K/min.
Based on the DSC, XRD and TEM results, it is concluded that the alloying of Ti/Ni multilayer thin films proceeded in multi steps; the first DSC peak is due to the solid state amorphization at each interface between Ti and Ni layers, the second DSC peak is due to the formation of the Ti–Ni B2 phase from the amorphous, and the third DSC peak is due to the formation of Ti₂Ni.

### 3.2. Shape memory properties

Thermal cycling tests under various constant stresses were carried out for the Ti–Ni amorphous thin films and Ti/Ni multilayer thin films, which were subjected to heat-treatment at various temperatures between 673 and 973 K for 3.6 ks, in order to evaluate shape memory properties. Fig. 6 shows example of the results thus obtained; i.e. the strain vs. temperature (S–T) relationships for the Ti–Ni amorphous thin film and Ti/Ni multilayer thin film subjected to heat-treatment at 973 K for 3.6 ks. The solid and dashed lines correspond to cooling and heating curves, respectively. \( M_s \) stands for the martensitic transformation start temperature upon cooling. The shape recovery strain induced upon heating due to the reverse martensitic transformation is denoted by \( \varepsilon_A \), while the permanent plastic strain is denoted by \( \varepsilon_p \). The \( M_s \) and \( \varepsilon_A \) of both specimens increased with increasing stress. The Ti/Ni multilayer thin film exhibited the shape memory effect almost equivalent to that of the heat-treated Ti–Ni amorphous thin film. But the fracture stress of the amorphous thin film and multilayer thin film were 700 and 500 MPa, respectively. Furthermore, the \( \varepsilon_p \) of the multilayer thin film was larger than that of the amorphous thin film at the same stress. In order to further investigate the difference of shape memory properties between the films made from the amorphous thin film and the multilayer thin film, the effect of heat-treatment...
temperature on maximum shape recovery strain ($\varepsilon_{A}^{\text{max}}$) was also investigated as follows.

Fig. 7 shows the heat-treatment temperature dependence of $\varepsilon_{A}^{\text{max}}$ of the heat-treated Ti–Ni amorphous thin films and Ti/Ni multilayer thin films heat-treated for 3.6 ks.

Fig. 7 shows the heat-treatment temperature dependence of $\varepsilon_{A}^{\text{max}}$ in both the Ti–Ni amorphous thin film and the Ti/Ni multilayer thin film. The amorphous thin film heat-treated at 673 K for 3.6 ks did not exhibit shape memory effect. This is due to that the Ti–Ni B2 phase was not fully crystallized by the heat-treatment. When heat-treatment temperature was higher than 723 K, the amorphous thin film was fully crystallized and exhibited shape memory effect. The recovery strain increased slightly with increasing heat-treatment temperature. On the other hand, the shape memory effect was observed in the Ti/Ni multilayer thin film heat-treated at 673 K for 3.6 ks. This indicates that the Ti/Ni multilayer thin film exhibited shape memory effect even if heat-treated at a lower temperature where the amorphous thin film was not crystallized. It is considered that the alloying for the multilayer thin film proceeded partially by inter-diffusion of Ti and Ni during heat-treatment at 673 K. This indicates that the formation of the Ti–Ni B2 in the Ti/Ni multilayer thin film occurred at a lower temperature than that in the Ti–Ni amorphous thin film. This result is consistent with the DSC results in Fig. 2. However, the $\varepsilon_{A}^{\text{max}}$ of a Ti/Ni multilayer thin film was only 1.1% for the specimen heat-treated at 673 K for 3.6 ks. The $\varepsilon_{A}^{\text{max}}$ increased with further increasing heat-treatment temperature for the Ti/Ni multilayer thin film. But the Ti/Ni multilayer thin films heat-treated in the temperature range between 773 and 873 K exhibited smaller $\varepsilon_{A}^{\text{max}}$ than the amorphous thin films heat-treated at the same temperatures. The amorphous thin film and the multilayer thin film exhibited a similar value of $\varepsilon_{A}^{\text{max}}$ after the heat-treatment at 973 K for 3.6 ks.

The small recovery strains of the Ti/Ni multilayer thin films heat-treated at lower temperatures were explained by their lower fracture stresses. Fig. 8 shows the heat-treatment temperature dependence of fracture stress ($\sigma_{f}$) for the heat-treated Ti–Ni amorphous thin film and Ti/Ni multilayer thin film. The $\sigma_{f}$ of the Ti/Ni multilayer thin film was lower than that of the Ti–Ni amorphous thin film when heat-treated at the same temperature, especially heat-treated in the temperature range between 673 and 773 K. Thus, the smaller values of $\varepsilon_{A}^{\text{max}}$ of the Ti/Ni multilayer thin films are attributed to the lower $\sigma_{f}$. It is suggested that the lower $\sigma_{f}$ is due to the inhomogeneous composition of Ti–Ni B2. The $\varepsilon_{A}^{\text{max}}$ increased with increasing heat-treatment temperature. It is supposed that this is due to the increase in grain size and the improvement in homogeneity of composition. But further systematic research including microstructural observation is required to clarify the effect of heat-treatment temperature on shape memory properties. Based on the above results, it can be concluded that the multilayer thin films can exhibit excellent shape memory properties equivalent to those of the amorphous thin films fabricated using an alloy target. Further researches on the effects of thickness of multilayers and heat-treatment condition on the microstructural evolution are required to obtain the optimal shape memory properties.

4. Conclusion

In the present study, alloying process and shape memory properties of a Ti/Ni multilayer thin film fabricated by a dual-source sputtering method with pure Ti and Ni targets were investigated, and compared with those of a Ti–Ni amorphous thin film fabricated by a sputtering method with a Ti–Ni target. The following conclusions were obtained.

1. One exothermic peak due to crystallization was observed in the DSC measurement of the as-sputtered
amorphous thin film upon heating, whereas three exothermic peaks were observed in the DSC measurement of the as-sputtered multilayer thin film. The formation of an amorphous phase at each interface between Ti and Ni layers due to inter-diffusion of Ti and Ni atoms occurred during the first DSC peak, and Ti–Ni B2 phase was formed during the second DSC peak. The Ni-content of the Ti–Ni B2 decreased and the Ti2Ni phase was formed by inter-diffusion of Ti atoms into the Ti–Ni B2 from the residual Ti layers during the third DSC peak.

(2) The Ti/Ni multilayer thin films exhibited shape memory effect even if heat-treated at a lower temperature where Ti–Ni amorphous thin films were not crystallized. But the fracture stress of the multilayer thin film was lower than that of the amorphous thin film when heat-treated in the temperature range between 673 and 773 K for 3.6 ks.

(3) The fracture stress of the multilayer thin film increased with increasing heat-treatment temperature. When heat-treated at 873 and 973 K, heat-treated Ti/Ni multilayer thin films exhibited the shape memory effect almost equivalent to that of the heat-treated Ti–Ni amorphous thin films.

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