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Ti-Pd-Ni high temperature shape memory thin films formed with carousel type magnetron sputtering apparatus

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Abstract: High temperature shape memory thin films of Ti-Pd-Ni were formed with a carousel type magnetron sputtering apparatus. Four kinds of films with different compositions (a Ti-rich, a near stoichiometric, and two (Pd, Ni)-rich films) were prepared by independently applying D.C. powers to each pure metal target. The near stoichiometric sample with a composition of $Ti_{49.5}Pd_{28.5}Ni_{22.0}$ was found to consist mainly of a Ti (Pd, Ni) phase, and showed a shape memory effect at about 500K with a recoverable transformation strain of 2.9% and a plastic strain of 0.3% at 160MPa. The Ti-rich film with a composition of $Ti_{51.2}Pd_{27.0}Ni_{21.8}$ was found to contain a $TiPd_2$ type second phase, and showed a shape memory effect at about 490K with a smaller recoverable transformation strain of 1.5% and a smaller plastic strain of 0.05% than those of the near stoichiometric film. One of the (Pd, Ni)-rich films with a composition of $Ti_{47.9}Pd_{29.8}Ni_{22.3}$ was found to possess both B2 and B19 phases at ambient temperature, and showed a shape memory effect at 360K with a recoverable transformation strain of 2.5% almost as large as the near stoichiometric film, and showed a plastic strain of 0.05% as small as that of the Ti-rich film.

1.INTRODUCTION

Shape memory thin films are expected to be used as microactuators such as micropumps and microvalves because of their advantages such as large deformation and strong recovery force. Particularly, sputter-deposited thin films of Ti-Ni are promising candidates[1-3], since they exhibit perfect shape memory effects comparable to those in bulk specimens of Ti-Ni[4] and have sufficient ductility[5]; besides, these films can be easily integrated into micromachining process. In addition, the shape memory characteristics are strongly affected by heat-treatment, alloy composition and sputtering conditions. It has been reported that Ti-rich Ti-Ni thin films annealed under proper conditions show good ductility unlike bulk specimens[6].

Recently, shape memory thin films with higher transformation temperatures have been demanded for higher actuation responses and for higher temperature applications. Since the improvement of film characteristics by precipitation hardening reduces transformation temperatures of films, the development of materials with intrinsically high transformation temperatures is important. From this viewpoint, Ti-Pd-Ni alloys are desirable, because the transformation temperatures in these alloys can be successively varied from ambient temperature up to above 700K by replacing Ni with Pd[7, 8]. Miyazaki et al. have reported that a Ti-26.4Ni-21.8Pd (at%) thin film shows a high temperature shape memory effect at about 385K[9, 10]. Quandt et al. have prepared TiNi, $Ti(Ni_{0.8}Pd_{0.2})$, $Ti(Ni_{0.4}Pd_{0.6})$, and TiPd thin films and measured transformation temperatures by DSC measurement, succeeding in changing transformation temperatures from ambient temperature to around 700K[11].

In this study, the dependence of the shape memory characteristics of Ti-Pd-Ni thin films on film composition, especially Ti/(Pd, Ni) ratio, was investigated. In such multicomponent systems, however, there are few satisfactory methods of controlling the film composition. We succeeded in overcoming this problem with a carousel type magnetron sputtering apparatus. The film composition can be controlled by independently applying the electrical power to each pure metal target. Four kinds of Ti-Pd-Ni shape memory thin films with different compositions were formed. It was investigated whether these films show high temperature shape memory effects or not. Furthermore, the dependence of the shape memory characteristics on the film composition is discussed.

2.EXPERIMENTAL

Fig. 1 shows the carousel type magnetron sputtering apparatus used in this study. Six glass substrates were placed on the sides of a cylindrical substrate holder. The substrate holder was rotated at 60rpm, and Ti, Pd and Ni targets were independently sputtered with different D.C. powers. D.C power at the Ti target was fixed at 800W, and those consumed at the Pd and Ni targets were varied from 70 to 89W, and from 133 to 183W, respectively, in order to control the film composition. The other conditions were as follows: substrate temperature, 473K; Ar gas pressure, 0.3Pa (base pressure, 2.1×10^{-5}Pa); deposition time: 2 hours.

After sputtering, films were removed from glass substrates. The film composition was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Table 1 shows film compositions and film thicknesses under four combinations of D.C. powers consumed at each metal target. A Ti-rich ($Ti_{51.2}Pd_{27.0}Ni_{21.8}$), a near stoichiometric($Ti_{49.5}Pd_{28.5}Ni_{22.0}$), and two (Pd, Ni)-rich ($Ti_{47.9}Pd_{29.8}Ni_{22.3}$, $Ti_{45.6}Pd_{26.3}Ni_{28.1}$) films were obtained. Hereinafter, the symbols of "Ti51", "Ti50", "Ti48", and "Ti46" are used, respectively.

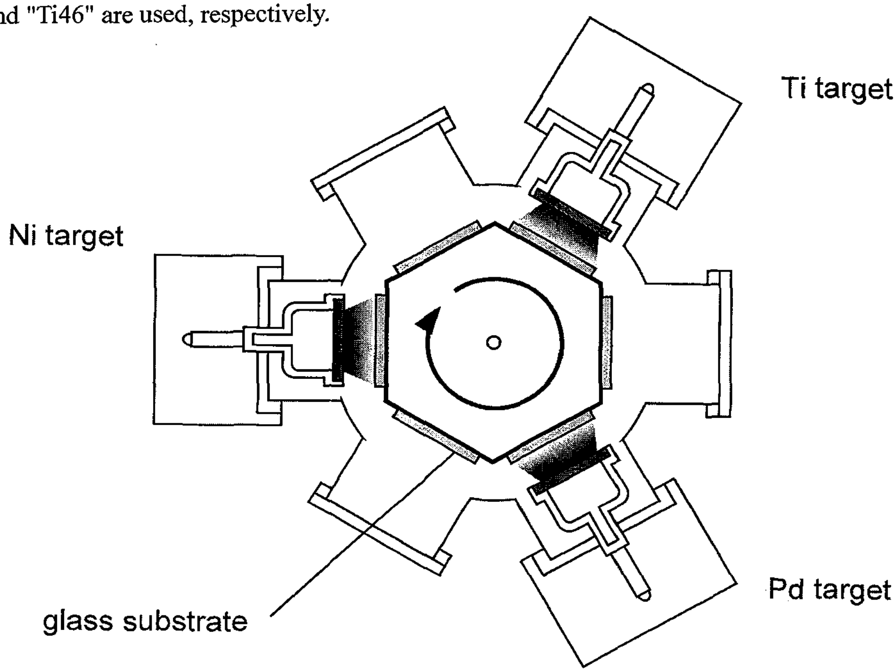

Fig. 1. Carousel type magnetron sputtering apperatus

Table 1. D.C. powers, film compositions and film thicknesses

Sample name	D.C. powers (W)	Film composition	Film thichness (μm)
Ti51	Ti: 800; Pd: 70; Ni: 133	$Ti_{51.2}Pd_{27.0}Ni_{21.8}$	7.0
Ti50	Ti: 800; Pd: 79; Ni: 148	$Ti_{49.5}Pd_{28.5}Ni_{22.0}$	7.8
Ti48	Ti: 800; Pd: 89; Ni: 157	$Ti_{47.9}Pd_{29.8}Ni_{22.3}$	8.2
Ti46	Ti: 800; Pd: 70; Ni: 183	$Ti_{45.6}Pd_{26.3}Ni_{28.1}$	8.1

In order to produce crystallization of Ti(Pd, Ni), they were annealed at 973K for 1 hour in a vacuum, and quenched with Ar gas. The phase formed in the films were identified by X-ray diffraction. The shape memory behavior of these films was measured with a thermomechanical tester. The size of the sample was $1 \times 5mm^2$ (gauge portion) and the thickness was from 7.0 to 8.2 μm. The samples was loaded at a high temperature, and then cooled at the rate of -10K/min and heated back at the rate of 10K/min. A series of strain-temperature measurements under various stresses was carried out with one sample by varying the stress from 20 to 160MPa in steps of 20MPa.

3.RESULTS AND DISCUSSION

3.1 X-ray diffraction

Figure 2 shows X-ray diffraction patterns of as-sputtered thin films, indicating that they are almost amorphous. After annealing at 973K for 1 hour, the films were crystallized as shown in Fig. 3. The near stoichiometric sample (Ti50) was found to consist mainly of a B19 type (Orthorhombic) martensite phase. Sivokha et al. have reported that the martensitic transformations in $Ti_{50}Pd_xNi_{50-x}$ ($0 \leqq x \leqq 50$) system occur via B2(cubic)→R(Rhombohedral) →B19'(Monoclinic) for lower Pd content(x=1.0, 2.8), and via B2→ B19→B19' for immediate Pd content(x=7.4, 11.4, 13.5). Furthermore, for higher Pd content($x \geqq 15.7$), only B2→B19 has been observed, since the transformation temperature from B19 to B19' is pretty low (less than 77K at least)[12]. The martensitic transformation from B2 to B19 is considered to have finished above ambient temperature in Ti50. There appear three other small peaks. However, they have not been identified yet.

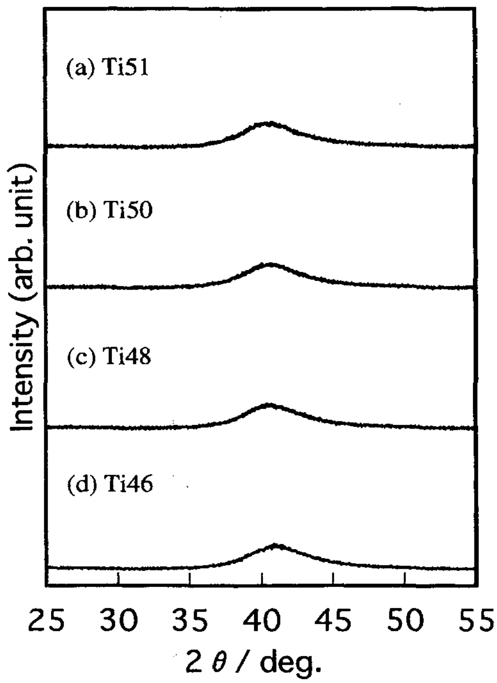

Fig 2. X-ray diffraction paterns of as-sputtered Ti-Pd-Ni thin films.

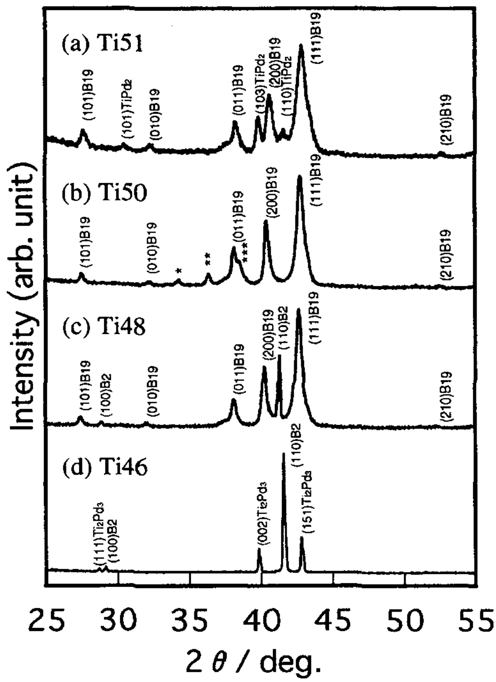

Fig 3. X-ray diffraction paterns of Ti-Pd-Ni thin films annealed at 973K for 1 hous. (*, **, ***: not identified)

The Ti-rich sample (Ti51) shows peaks from a $TiPd_2$ type second phase besides B19. The solid solution curve of Ti(Pd, Ni) is considered to lie between Ti contents of 49.5 and 51.2at% at 973K. One of (Pd, Ni)-rich sample (Ti48) shows both of peaks from B19 and those from B2. This means that the martensitic transformation has started above ambient temperature, but has not finished in this sample at ambient temperature. The other (Pd, Ni)-rich sample (Ti46) shows peaks from B2, indicating that the martensitic transformation start temperature is below ambient temperature. Ti46 also shows the existence of a Ti_2Pd_3 type second phase.

As a result, we succeeded in preparation of Ti(Pd, Ni) thin films with different Ti/(Pd, Ni) ratios with the carousel type magnetron sputtering apparatus.

3.2 Shape Memory behavior

Figure 4 shows strain-temperature curves of Ti-Pd-Ni thin films annealed at 973K for 1 hour. They were measured under three different stresses, 40, 80, and 160MPa. Shape memory effects corresponding to the martensitic transformations from B2 to B19 were observed in Ti51, Ti50, and Ti48. Ti46 shows no shape memory effect in the temperature range from 150K to 523K.

The martensitic transformation start and finish temperatures, and reverse martensitic transformation start and finish temperatures (hereinafter denoted as O_s, O_f, AO_s and AO_f, respectively) were determined from strain-temperature curves, as shown in Fig. 4. The temperature hysteresis is defined as a difference between O_s and AO_f. The recoverable transformation strain, ε_A and the plastic strain, ε_p were also obtained from Fig. 4

Ti50 shows shape memory effects in the highest temperature range among the samples. The mostly perfect shape memory effect is shown at 40MPa. O_s, O_f, AO_s and AO_f points are 483K, 477K, 499K, and 508K at 40MPa, respectively. They slightly increase with increasing stress. The temperature hysteresis is about 20K, in accord with the values reported in the previous work[10]. This value is smaller than those of Ti-Ni thin films of about 30K. This is an advantage for the practical uses as microactuators, since smaller temperature hysteresis produces higher response. This has been usually explained by the smaller lattice deformation at B2→B19 transformation than that at B2 → B19' transformation. The recoverable transformation strain is 0.7% at 40MPa. They increase to 2.9% with increasing

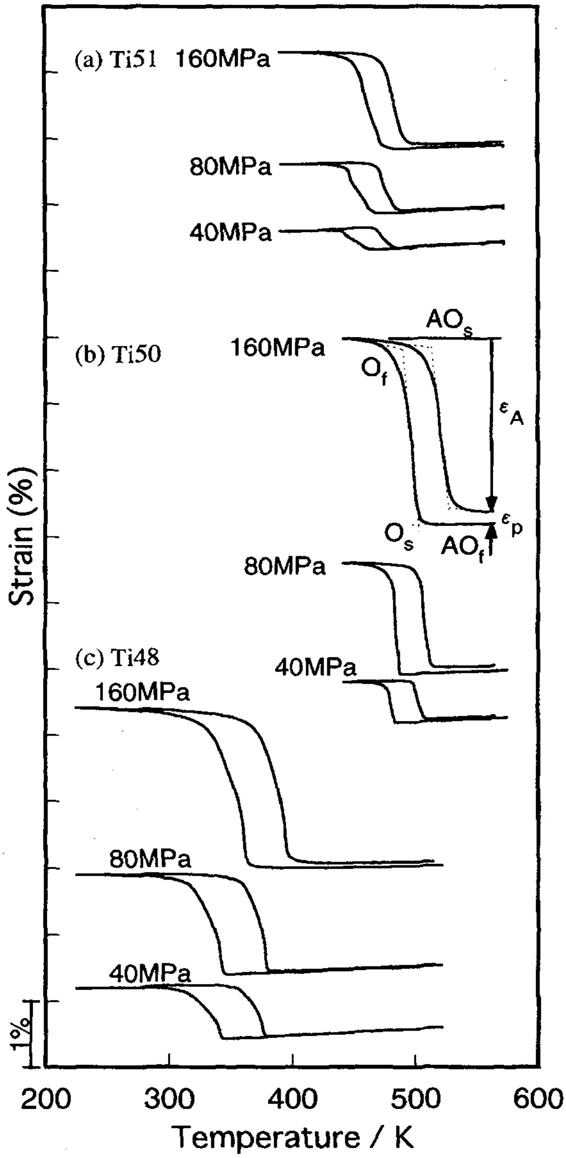

Fig. 4. Strain-temperature curves under various stresses of Ti-Pd-Ni thin films annealed at 973K for 1 hour.

stress to 160MPa. However, the plastic strain also increases to 0.3% with increasing loading stress to 160MPa. Consequently, Ti50 does not show a perfect shape memory effect any longer.

The transformation temperatures of Ti51 are somewhat lower than those of Ti50. O_s, O_f, AO_s and AO_f points at 40MPa are 462K, 441K, 468K, and 483K, respectively. This sample exhibits smaller elongation than Ti50. The recoverable transformation strain is 0.4% at 40MPa, and is limited within 1.5% even at 160MPa. The plastic strain is also small, and is limited within 0.05% even at 160MPa. Consequently, this sample shows a perfect shape memory up to 80MPa. The hardness of this sample is considered to be owing to precipitation hardening caused by a $TiPd_2$ second phase.

O_s, O_f, AO_s and AO_f points of Ti48 at 40MPa are 343K, 310K, 355K, and 376K, respectively. It is noteworthy that this sample shows not only the plastic strains almost as small as that of Ti51, but also the deformation as large as Ti50. The recoverable transformation strain and the plastic strain at 160MPa are 2.5% and 0.05%, respectively. This sample exhibits a perfect shape memory effect with a recoverable transformation strain of 1.6% at the O_s point of 345K at 80MPa. This is the optimum condition in the present article. However, the temperature hysteresis of this sample is about 30K, unexpectedly, which is larger than those of Ti50 and Ti51. Some kinds of microstructures might concern the shape memory characteristics of this (Pd, Ni)-rich sample, though there appears no new phase in the X-ray diffraction as shown in Fig. 3.

Transformation temperatures of samples obtained from the strain-temperature curves can be explained by the results of X-ray diffraction satisfactorily. Transformation temperatures are also affected by Pd content substituting Ni as well as Ti/(Pd, Ni) ratio. Shimizu et al. have measured the transformation temperatures by DSC measurements in plasma melted $Ti_{50-x}Pd_{30}Ni_{20+x}$ ($0 \leqq x \leqq 50$) alloys, and concluded that they increase from about 300K to about 500K with increasing Ti content from 48.5 to 50.2 at%, and stay almost same (slightly decrease) with increasing Ti content from 50.2 to 50.6at%[13]. Transformation temperatures of Ti51, Ti50 and Ti48 are nearly coincident with these values. In addition, those of Ti51 show further decreases probably because of precipitation hardening by a $TiPd_2$ type second phase. Transformation temperatures of Ti46 are far less than those of the other samples, not only because Ti content is smaller, but also because Pd content is smaller than those of the others. Furthermore, a Ti_2Pd_3 type second phase may cause further decrease owing to precipitation hardening.

As a result, high temperature shape memory characteristics of Ti-Pd-Ni thin films were found to be controlled by varying film composition, especially Ti/(Pd, Ni) ratio. In order to clarify the effect of the microstructure on the shape memory characteristics, the detailed microscopic observations are under way.

4. CONCLUSION

A Ti-rich ($Ti_{51.2}Pd_{27.0}Ni_{21.8}$), a near stoichiometric ($Ti_{49.5}Pd_{28.5}Ni_{22.0}$), and two (Pd, Ni)-rich ($Ti_{47.9}Pd_{29.8}Ni_{22.3}$, $Ti_{45.6}Pd_{26.3}Ni_{28.1}$) thin films were formed with a carousel type magnetron sputtering apparatus, and the shape memory characteristics of the films annealed at 973K for 1h were investigated. The results obtained in the present article are as follows.

(1) Ti-Pd-Ni shape memory thin films can be formed with a carousel type magnetron sputtering apparatus. We succeeded in controlling the film composition.

(2) The near stoichiometric sample was found to consist mainly of a Ti (Pd, Ni) phase, and showed a shape memory effect at about 500K with a recoverable transformation strain of 2.9% and a plastic strain of 0.3% at 160MPa.

(3) The Ti-rich sample was found to contain a $TiPd_2$ type second phase, and showed a shape memory effect at about 490K with a smaller recoverable transformation strain of 1.5% and a smaller plastic strain of about 0.05% than those of Ti50 at 160MPa.

(4) One of (Pd, Ni)-rich sample with the composition of $Ti_{47.9}Pd_{29.8}Ni_{22.3}$ was found to possess both B2 and B19 phases at ambient temperature, and showed a shape memory effect at 360K with a recoverable transformation strain of 2.5% almost as large as Ti50 and a plastic strain of about 0.05%

as small as that of Ti50 at 160MPa.

(5) The other (Pd, Ni)- rich sample with the composition of $Ti_{45.6}Pd_{26.3}Ni_{28.1}$ was found to contain a Ti_2Pd_3 type second phase, and showed no shape memory effect above 150K.

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