Effect of Pd content on crystallization and shape memory properties of Ti–Ni–Pd thin films

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The Pd content dependence of the crystallization process of Ti–Ni–(19.1–35.3)Pd (at. %) thin films fabricated by a sputter-deposition method was investigated. Ti–Ni–(19.1–26.1)Pd (at. %) as-deposited thin films were found to be amorphous, whereas Ti–Ni–(29.1–35.3)Pd (at. %) thin films were crystalline in the as-deposited condition. Both the crystallization temperature and activation energy for the crystallization of the amorphous thin films decrease with increasing Pd content. The shape memory effect was confirmed in the \textit{in situ} crystallized thin film. The finer grain size in the \textit{in situ} crystallized thin film results in a higher critical stress for slip and a smaller recovery strain when compared with the thin film crystallized by post annealing.

\textbf{Keywords:} shape memory alloy; thin film; martensitic phase transformation; crystallization; sputtering

1. Introduction

Ti–Ni thin film shape memory alloys have attracted significant attention as potential candidates for microactuator materials in micro-electro-mechanical system (MEMS) because of their large recoverable strain and high recovery force [1–4]. Many types of devices utilizing Ti–Ni thin films have been developed and exploited, such as microgrippers, microvalves, micropumps and microactuators [5–15].

Microactuators utilizing Ti–Ni thin films have a limitation in their actuation speed because they are operated by temperature variation. It was reported that the displacement of a microactuator utilizing the B2-B19\textsuperscript{′} transformation of binary Ti–Ni films decreased with increasing working frequency and no effective displacement was detected at over 50 Hz [16]. It is necessary to reduce the time for the martensitic transformation during cooling in order to increase actuation speed. It has been suggested that two different methods are available to decrease the time for the martensitic transformation: (1) reducing the hysteresis of the transformation and (2) increasing transformation temperature [14,15,17]. A narrow transformation hysteresis allows a shape memory actuator to operate by a smaller temperature variation. It has been suggested that utilizing the B2–R or B2–B19 transformation in a microactuator is effective to decrease the hysteresis of the transformation [14]. Increasing transformation temperature is another effective way because cooling speed can
be raised by increasing the temperature difference between the transformation and room temperatures. Consequently, microactuators utilizing Ti–Ni–Pd films are one of the most promising solutions since the addition of Pd not only decreases the hysteresis but also increases transformation temperature [18–21].

Ti–Ni thin films are typically prepared by a sputtering method and they are deposited in an amorphous form if the substrate is not deliberately heated during deposition; thus crystallization heat treatment (usually above 700 K) is required for the shape memory effect [3]. The microstructure and shape memory properties are strongly dependent on the post heat treatment conditions [3,22–25]. In addition, during the crystallization heat treatment an interfacial reaction between the thin film and substrate occurs and the properties of the interface affect the actuation properties [26–30]. Tomozawa et al. [31] investigated the effect of crystallization temperature on the microstructure and actuation behavior of Ti–Ni–Cu thin films deposited on a SiO$_2$/Si substrate. They reported that the reaction layer was formed between the Ti–Ni–Cu thin film and SiO$_2$ layer of substrate during crystallization heat treatment, and its thickness increased with increasing crystallization temperature. They also mentioned that the growth of the reaction layer resulted in the reduction of the SiO$_2$ layer thickness which led to the decrease in the displacement of the microactuator.

Shape memory thin films without post heat treatment may provide another opportunity for innovative applications. It is expected that the higher transformation temperature of Ti–Ni–Pd actuators will extend their functional capabilities and fields of application, such as automobile, aircraft, chemical plant and power-generation systems where a higher actuation temperature is required.

2. Experimental procedure

In this study, the Pd content dependence of the crystallization process of Ti–Ni–(19.1–35.3)Pd (at. %) thin films was investigated by differential scanning calorimetry (DSC) and X-ray diffractometry (XRD). The crystallization temperature and activation energy for the crystallization of the amorphous thin films were investigated. The shape memory properties of two types of thin films, i.e. the thin film crystallized by post annealing and in situ crystallized thin film, were investigated by thermal cycling tests under various stresses. The results are discussed with respect to the microstructure of the thin films. The detailed experimental procedure was as follows.

Ti–Ni–Pd thin films with various Pd contents from 19.1 to 35.3 at. % were deposited onto Cu foil substrates using a radiofrequency magnetron sputtering apparatus. The sputter deposition parameters were set as follows: power = 500 W, time = 1 h, Ar pressure = 0.56 Pa and base pressure less than $2 \times 10^{-5}$ Pa. The thickness of the thin films was about 6 μm. Two types of targets, such as Ti–30Ni–20Pd (at. %) and Ti–30Ni (at. %), were used depending on the desired composition. The compositions of the thin films were adjusted by changing the number of pure Ti, Ni and Pd chips placed on the targets. After deposition the Cu foil substrate was dissolved in a solution of 70% HNO$_3$ and 30% H$_2$O by volume to extract the thin film. The composition of the thin films was determined by electron probe microanalysis (EPMA). The ratio of Ti/(Ni+Pd) was controlled not to be less than 1 since the transformation temperature drastically decreases with decreasing Ti in Ti-poor compositions. Hereafter, the thin films are termed according to the amount of Pd content.

The crystal structure of as-deposited thin films was determined by XRD using a Cu K$_{α}$ radiation at room temperature. DSC measurements were performed with a heating rate of 10 K/min in order to measure transformation temperatures or crystallization temperature. For amorphous thin films, DSC measurements at various heating rates of 5–30 K/min were carried out in order to investigate the activation energy for crystallization.
The shape memory properties were investigated by thermal cycling tests (heating and cooling rate of 10 K/min) under various stresses. The test was conducted in a helium gas atmosphere in order to prevent oxidation and improve the thermal conductivity. The dimensions of the specimens were 5 mm in gauge length, 1 mm in width and 6 μm in thickness. The internal structures of the thin films were investigated by using a transmission electron microscope (TEM) at room temperature (RT) and 573 K. The samples for TEM were prepared by electrolytic polishing using a twin-jet polishing apparatus.

3. Results and discussion

3.1. Crystallization behavior of Ti–Ni–Pd thin films

Figure 1 shows XRD profiles of as-deposited Ti–Ni–(19.1–35.3)Pd (at. %) thin films obtained at RT. The peaks corresponding to Cu and Si were, respectively, from the specimen holder and the Si powder used as an in situ standard. An amorphous mound was observed at $2\theta = 35 \sim 45^\circ$ in the Ti–Ni–19.1Pd and Ti–Ni–26.1Pd specimens, indicating that the as-deposited thin films are of amorphous nature. This is consistent with other Ti–Ni-based thin films such as Ti–Ni [32] and Ti–Ni–Zr [33]. On the other hand, all peaks except Cu and Si were identified as the B19 phase in the XRD profiles of the Ti–Ni–Pd thin films with a higher Pd content, i.e. Ti–Ni–29.1Pd, Ti–Ni–31.4Pd and Ti–Ni–35.3Pd, implying that these thin films were deposited directly into the crystalline state.

Figure 2 shows DSC curves of as-deposited Ti–Ni–(19.1–35.3)Pd thin films upon heating with a heating rate of 10 K/min. For the Ti–Ni–19.1Pd and Ti–Ni–26.1Pd specimens,
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Heating rate: 10K/min

| Pd Content | Peak Temperature |
|------------|-----------------|
| 19.1 at. % | 758 K           |
| 29.1 at. % | 744 K           |
| 35.3 at. % | 562 K           |

Figure 2. DSC curves of as-deposited Ti–Ni–(19.1–35.3)Pd (at. %) thin films upon heating up to 800 K.

an exothermic peak is seen at 758 K and 744 K, respectively, which is due to the crystallization of the amorphous phase. Similar DSC curves with an exothermic peak upon heating were also reported in other Ti–Ni base thin films which are amorphous in as-deposited state [32–35]. No exothermic peak upon heating was observed in the DSC curves of the as-deposited Ti–Ni–(29.1–35.3)Pd thin films, on the other hand, an endothermic peak was observed. The endothermic peak corresponds to the reverse martensitic transformation since the as-deposited Ti–Ni–(29.1–35.3)Pd thin films are of martensite phase at RT.

Figure 2. DSC curves of as-deposited Ti–Ni–(19.1–35.3)Pd (at. %) thin films upon heating up to 800 K.

The peak temperature, $A^*$, of the Ti–Ni–Pd thin films is plotted as a function of Pd content in Figure 3. The Pd content dependence of $A^*$ in Ti–49.5Ni–Pd bulk specimens solution treated at 1173 K is also shown in Figure 3 for comparison. It can be seen that $A^*$ decreases with addition of 10 at. % Pd, then increases by further increasing Pd content from 10 at. % to 30 at. % for the Ti–49.5Ni–(10–30)Pd bulk specimens. This is consistent with previous reports; the addition of about 10 at. % Pd changes the martensite structure from B19' to B19 and the change of martensite structure causes the transformation temperature to decrease. The transformation temperature of B2–B19 transformation increases with increasing Pd content.

For the crystalline films in the as-deposited state, a similar Pd content dependence was observed; however, the values of $A^*$ of the thin films are somewhat lower than those of bulk specimens when comparing similar Pd content specimens. It is supposed that the lower values of $A^*$ of the thin films are due to the smaller grain size of them.

Figure 4 shows the Pd content dependence of crystallization peak temperature, i.e. the exothermic peak temperature, of as-deposited Ti–Ni–Pd thin films. The crystallization peak temperature slightly increased with increasing Pd content up to 19.1 at. %, then decreased markedly with further increasing Pd content up to 26.1 at. %. As mentioned above, the thin films with Pd content of 29.1 at. % and more were deposited directly into the crystalline state.
Figure 3. The Pd content dependence of the peak temperature of the reverse transformation in as-deposited Ti–Ni–Pd thin films and Ti–49.5Ni–Pd bulk specimens solution treated at 1173 K.

Figure 4. The Pd content dependence of the temperature at the maximum of the crystallization peak in as-deposited Ti–Ni–Pd thin films.

The activation energies of crystallization of Ti–Ni–(19.1–25.5)Pd were evaluated by the Kissinger method [36], according to

\[
\ln\left(\frac{\alpha}{T_p^2}\right) = C - \frac{Q}{RT_p},
\]

where \(\alpha\) is heating rate, \(T_p\) is the peak temperature for crystallization, \(R\) is the gas constant and \(C\) is a constant. Figure 5 shows DSC curves for the as-deposited Ti–Ni–19.1Pd thin
film specimens measured at various heating rates of 5–30 K/min. It can be seen that the exothermic peak for crystallization is shifted to a higher temperature with increasing heating rate. Similar DSC measurements were conducted for Ti–Ni–23.6Pd and Ti–Ni–25.5Pd thin film specimens.

Figure 6 shows \( \ln(\alpha / T_p^2) \) versus \( 1/T_p \) curves of three films. From the slope of the linear relation, the activation energies for crystallization were calculated and the results are plotted as a function of Pd content in Figure 7. The activation energies for crystallization

![DSC curves](image)

Figure 5. DSC curves of the as-deposited Ti–Ni–19.1Pd thin film specimens measured at heating rates of 5, 10, 20 and 30 K/min.

![ln(\(\alpha / T_p^2\)) versus \(1/T_p\)](image)

Figure 6. The plots of \( \ln(\alpha / T_p^2) \) versus \( 1/T_p \) for the Ti–Ni–19.1Pd, Ti–Ni–23.6Pd and Ti–Ni–25.5Pd thin films.
for Ti–Ni–19.1Pd, Ti–Ni–23.6Pd and Ti–Ni–25.5Pd were determined to be 352 kJ/mol, 321 kJ/mol and 293 kJ/mol, respectively, indicating that the activation energy for crystallization decreases with increasing Pd content. From Figures 6 and 7, it is reasonable to consider that the stability of amorphous structure becomes lower as the Pd content of the thin film increases. As a result, it is suggested that the low stability of amorphous structure led to the crystallization during deposition in the Ti–Ni–Pd thin films with Pd contents of 29.1 at. % and above.

3.2. Shape memory effect of Ti–Ni–Pd thin films

Shape memory properties of the as-deposited Ti–Ni–29.1Pd thin film were evaluated via strain–temperature relationships measured during thermal cycling under various constant stresses, as shown in Figure 8a. The test was performed in such a way that the magnitude of the applied stress was increased stepwise by 50 MPa in each thermal cycle, using the same specimen throughout the test. The solid and dashed lines indicate cooling and heating processes, respectively. For comparison, a similar thermal cycling test was carried out using a Ti–Ni–22.1Pd thin film crystallized by heat treatment at 973 K for 3.6 ks and the results are shown in Figure 8b. Ti–Ni–Pd thin films with Pd content of 26.1 at. % and less were amorphous in the as-deposited state, thus crystallization heat treatment was required to reveal the shape memory effect.

The elongation and contraction of the specimen during cooling and heating confirms the shape memory effect of the as-deposited thin film. Symbols $M_s$, $M_f$, $A_s$ and $A_f$ are abbreviations of the temperatures for martensitic transformation start, its finish, reverse transformation start and its finish, respectively. The transformation temperatures increased with increasing applied stress in accordance with the Clausius–Clapeyron relationship: $d\sigma/dT = -\Delta H/T\varepsilon$, where $\sigma$ is the applied stress, $\varepsilon$ is the transformation strain, $\Delta H$ is the enthalpy of transformation per unit volume and $T$ is the transformation temperature. By extrapolating the relationship, $M_s$, $M_f$, $A_s$ and $A_f$ at zero stress were
determined to be 483, 450, 482 and 508 K for Ti–Ni–29.1Pd and 383, 362, 398 and 422 K for Ti–Ni–22.1Pd specimens, respectively. This result is consistent with the intrinsic Pd content dependence of transformation temperatures in Ti–Ni–Pd alloys shown in Figure 3.

For both specimens, the recovery strain $\varepsilon_a$ increased with increasing applied stress, however the increase in the applied stress caused incomplete shape memory effect because the plastic strain $\varepsilon_p$ also increased with increasing applied stress. Figure 9 shows the dependence of $\varepsilon_a$ and $\varepsilon_p$ on applied stress for both specimens. In the Ti–Ni–22.1Pd specimen, $\varepsilon_a$ increased linearly with increasing stress in lower stresses, then it started to decline from

Figure 8. Strain–temperature curves of (a) an as-deposited Ti–Ni–29.1Pd film and (b) a Ti–Ni–22.1Pd thin film crystallized by heat treatment at 973 K for 3.6 ks.

Figure 9. Dependence of recovery strain and plastic strain on stress in the as-deposited Ti–Ni–29.1Pd film and Ti–Ni–22.1Pd thin film crystallized by heat treatment at 973 K for 3.6 ks.
the linear relationship at 200 MPa until reaching a maximum at 300 MPa. The value of $\varepsilon_a$ decreased slightly with further increasing stress. The maximum $\varepsilon_a$ was measured to be 2.9% in the Ti–Ni–22.1Pd specimen. The plastic strain $\varepsilon_p$ also increased with increasing applied stress: $\varepsilon_p$ slightly increased with increasing stress at lower stresses and it started to increase remarkably at 200 MPa. It is noted that the stress at which $\varepsilon_p$ increased considerably is corresponding to the stress where $\varepsilon_a$ started to decline from the linear relationship, implying that inducing of plastic strain caused the decreased stability of shape memory effect. In this study, the critical stress for slip $\sigma_s$ was defined as the stress under which $\varepsilon_p$ of 0.2% is introduced in the specimen, $\sigma_s$ being 180 MPa for the Ti–Ni–22.1Pd specimen.

On the other hand, $\varepsilon_a$ increased almost linearly with increasing stress until 400 MPa without saturation until fracture for the Ti–Ni–29.1Pd specimen. It is noted that the slope of $\varepsilon_a$ against applied stress in the Ti–Ni–29.1Pd specimen is lower than that in the Ti–Ni–22.1Pd specimen. The maximum $\varepsilon_a$ and $\sigma_s$ were measured to be 1.6% and 380 MPa in the Ti–Ni–29.1Pd specimen. In order to investigate the reason for the higher value of $\sigma_s$ in Ti–Ni–29.1Pd specimen, the microstructure was investigated using TEM.

Figures 10a and 10b show a bright field TEM micrograph and the corresponding diffraction pattern of the Ti–Ni–29.1Pd as-sputtered thin film observed at RT. A typical twinned martensite structure was observed at RT. No second phase was observed and the diffraction rings can be indexed on the basis of B19, as shown in Figure 10b. On the other hand, the bright field TEM micrograph observed at 573 K (above $A_f$) exhibits B2 grains with an average size of 120 nm (Figure 10c). The corresponding selected area diffraction

![Figure 10. Bright field micrographs and selected area diffraction patterns of the as-deposited Ti–Ni–29.1Pd film where (a) and (b) were obtained at RT and (c) and (d) were obtained at 573 K.](image)
pattern can be indexed by only the B2 phase, as shown in Figure 10d; partial Debye rings were indexed as (100), (110), (200), (211) and (220) planes of a B2 structure. It is also confirmed that no precipitation was formed during in situ crystallization.

For comparison, the bright field TEM micrograph of Ti–Ni–22.1Pd thin film which was crystallized at 973 K for 3.6 ks is shown in Figure 11. TEM observation was carried out at 573 K for a better comparison of grain size of B2 phase. The selected area diffraction pattern was taken from the grain with dark contrast in the micrograph. It can be seen that the Ti–Ni–22.1Pd thin film contains no precipitations. The grain size of the Ti–Ni–22.1Pd specimen was measured to be about 530 nm, which is four times larger than that of the as-deposited Ti–Ni–29.1Pd specimen. As mentioned above, no secondary phase was observed in both specimens. Thus it is supposed that the high value of $\sigma_s$ is due to the small grain size of the as-deposited Ti–Ni–29.1Pd specimen.

The smaller grain size in the thin film crystallized in situ was also confirmed in Ti–Ni binary alloy [37]. It is considered that the difference of grain size between two specimens is due to the different crystallization processes. It has been confirmed that the crystallization of Ti–Ni amorphous thin films is governed by the conventional nucleation and growth process; thus the grain size of crystalline phase depends on the crystallization temperature and time [38,39]. After finishing crystallization, the grain size further increases due to the grain coarsening or Ostwald ripening. Lee et al. [39] investigated the crystallization kinetics of Ti–Ni amorphous thin films with in situ TEM. They reported that the average crystallized grain size was determined by the ratio of the growth rate and the steady-state nucleation rate: it decreased from 1500 nm to 800 nm with increasing temperature from 738 K to 788 K. The grain size of 530 nm of the Ti–Ni–22.1Pd thin film after the heat treatment at 973 K seems reasonable when considering the higher heat treatment temperature. On the other hand, it is believed that in situ crystallization at relatively low temperature suppressed the grain growth in the Ti–Ni–29.1Pd specimen.
4. Conclusions

In this study, the Pd content dependence of the crystallization process and shape memory properties of Ti–Ni–(19.1–35.3)Pd (at. %) thin films was investigated.

1. The as-deposited Ti–Ni–Pd thin films with Pd contents of 26.1 at. % and less were of amorphous nature, whereas those with Pd contents of 29.1 at. % and above were crystalline in the as-deposited condition.

2. The crystallization temperature and activation energy for the crystallization decreased with decreasing Pd content in the Ti–Ni–(19.1–25.5)Pd thin films.

3. The crystalline films exhibited the reverse martensitic transformation upon heating where the transformation temperature increased with increasing Pd content.

4. The shape memory effect was confirmed in the as-deposited Ti–Ni–29.1Pd thin film by thermal cycling under various stresses. The as-deposited Ti–Ni–29.1Pd thin film exhibited a higher critical stress for slip and a smaller recovery strain when compared with the Ti–Ni–22.1Pd thin film which was crystallized by post heat treatment at 973 K. The higher critical stress for slip and smaller recovery strain in the in situ crystallized specimen is due to the smaller grain size.

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