

High Temperature Shape Memory Effects in Ternary Ti-Ni-X (X=Pd,Zr) Thin Films

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High temperature shape memory thin films have been developed in Ti-Ni-Pd and Ti-Ni-Zr systems. Ti-rich compositions are required in both systems to achieve high temperature shape memory effects. The Ti-rich films include precipitates; i.e. a $Ti_2(Pd,Ni)$ phase with a C_{11b} structure in the Ti-Ni-Pd films, and a ternary $TiNiZr$ phase with an $MgZn_2$ -type Laves phase structure (λ_1) in the Ti-Ni-Zr films. They strengthen the films, but they are likely to lower the recoverable strain and/or to make the film brittle. Heat treatments at low temperatures around the crystallization temperatures of about 750K are effective to improve the characteristics. This article reviews shape memory characteristics of the films such as martensitic transformation temperatures (MTTs) and the recoverable strain (ϵ_R), and mechanical properties such as the critical stress inducing slip deformation (σ_c) and the fracture toughness, with respect to their characteristic microstructures such as sub-micron grain sizes and finely distributed precipitates.

Key words: high temperature shape memory effects, thin films, Ti-Ni-Pd, Ti-Ni-Zr

1. INTRODUCTION

Shape memory thin films (SMA thin films) are considered to be promising candidates for micro-actuators. The sputter-deposited Ti-Ni thin films are well known to exhibit excellent shape memory effects comparable to those of bulk specimens [1]. In order to use them in various operating environments, it is essential to control shape memory characteristics of the films. Most of all, martensitic transformation temperatures (MTTs) are important parameters, which affect the working temperature, stability and response speed. However, the MTTs of the conventional Ti-Ni alloys are essentially restricted under 370K. Therefore, SMA thin films with intrinsically high MTTs are highly demanded.

The present authors have developed sputter-deposited high temperature SMA thin films in the ternary systems of Ti-Ni-Pd [2,3] and Ti-Ni-Zr [4-6]. The Ti-Ni-Pd thin films showed high temperature shape memory effects comparable to those of bulk specimens [2]. The Ti-Ni-Zr alloys have an advantage for practical uses, since they contain no precious metal element. However, they have a serious drawback of their brittleness [7]. It was found that the Ti-Ni-Zr thin films crystallized in an amorphous state exhibited sufficient fracture toughness to realize shape memory effect under tensile loading conditions [4]. In both systems, various heat treatments were attempted in the films with Ti-rich compositions in order to improve their shape memory characteristics and mechanical properties [3,5,6].

This article reviews shape memory characteristics of the films such as MTTs and the recoverable strain (ϵ_R), and mechanical properties such as the critical stress inducing slip deformation (σ_c) and the fracture toughness, emphasizing the characteristic microstructures of the thin films crystallized in amorphous states.

2. FILM DEPOSITION

A carousel type magnetron sputtering apparatus was used for film deposition in this study. The alloys are deposited on glass substrates attached on the side of a cylindrical holder rotating at a certain rate, by sputtering the pure metal targets of alloy contents surrounding the substrate holder. The detail of the sputtering method has been described in our previous papers [3,6]. Here, we would like to emphasize that any given film composition can be obtained by independently varying the D.C. power consumed at each target. It has a benefit in the cases of multi-component systems.

The substrate temperature was kept at 470K during depositions. No further increase in the substrate temperature was observed, and as-deposited films exhibited an amorphous phase. The crystallization temperatures (T_c) measured by differential scanning calorimetry with a heating rate of 10K/min were found to be around 750K for all Ti-Ni-Pd and Ti-Ni-Zr thin films fabricated in the present study. It was also found that the crystallization occurred even at slightly lower temperatures than T_c , when the films were held at the temperatures. It should also be mentioned that the rotation of the substrate holder realizes the homogeneous distribution of the film composition in the horizontal direction.

3. MARTENSITIC TRANSFORMATION TEMPERATURES

The film compositions, annealing conditions, martensitic transformation start (M_s) temperatures and the reverse martensitic transformation finish (A_f) temperatures of the films fabricated in the present study are listed in Table 1. The films annealed at 970K for 1 hour showed the MTTs comparable to those of bulk specimens [7,8]. The MTTs are dependent not only on the amount of the ternary additives, but also on the deviation in the composition from the chemical

Table 1. The thin films fabricated in the present study and their Ms and Af temperatures.

No.	film composition	annealing conditions	Ms	Af
1	Ti _{51.2} (Ni _{21.8} Pd _{27.0})	970K, 1h	458	479
2	"	870K, 1h	441	475
3	"	770K, 1h	418	453
4	Ti _{49.5} (Ni _{22.0} Pd _{28.5})	970K, 1h	481	505
5	Ti _{47.9} (Ni _{22.3} Pd _{29.8})	970K, 1h	344	377
6	Ti _{45.6} (Ni _{28.1} Pd _{26.3})	970K, 1h	—	—
7	(Ti _{35.7} Zr _{14.9})Ni _{49.4}	970K, 1h	400	477
8	(Ti _{35.0} Zr _{15.4})Ni _{49.7}	970K, 1h	414	484
9	"	870K, 1h	367	453
10	"	770K, 1h	343	434
11	(Ti _{33.4} Zr _{14.8})Ni _{51.7}	970K, 1h	—	—

stoichiometry of Ti:(Ni,Pd)=1:1 or (Ti,Zr):Ni=1:1. For an nearly equiatomic (No. 4) and Ti-rich compositions (No. 1, 7 and 8), the additions of above 25at% Pd or 15at% Zr increase As temperature to above 470K. On the other hand, the films with Ni-rich compositions show relatively lower MTT values (No. 5) or no shape memory effect (No. 6 and 11), which is probably due to lower Ms temperatures less than the lower measuring temperature limit of 150K. It was also found that the Ti-Ni-Zr films showed larger temperature hysteresis (70 to 80K) than that of the Ti-Ni-Pd films (20 to 30K).

It can be seen in Table 1 that the MTTs of Ti_{51.2}(Pd_{27.0}Ni_{21.8}) films (No. 1 through 3) and (Ti_{35.0}Zr_{15.4})Ni_{49.7} films (No. 8 through 10) decrease with decreasing annealing temperature. The decrease in the MTTs of these Ti-rich films is associated with the change in the volume fraction, size and distribution of precipitates, which affect the strength of the films. It has been proposed that the increase in a yield stress increases a driving shear stress of the martensitic transformation, which in turn decreases the Ms temperature [9]. It should also be taken into account that the precipitation brings about the change in the composition of the matrix. Very recently, the present authors have quantitatively investigated the relationship between Ms and σ_c in the (Ti_{35.0}Zr_{15.4})Ni_{49.7} thin films annealed under various conditions [6]. It was found that the Ms almost linearly decreased with increasing σ_c , with small scattering due to the compositional change of the matrix caused by the precipitation.

4. MICROSTRUCTURES

Ti-rich or near-equiatomic compositions are required in both systems to achieve high MTTs. The Ti-rich films include precipitates, which strengthen the films, but they are likely to lower ϵ_R and/or to make the film brittle. Heat treatments at low temperatures around Tc are effective to improve the characteristics. It is attributed to characteristic microstructures of the films. Figure 1 shows some examples of the microstructures produced by the low temperature heat treatments: (a) plate-like precipitates inside grains in a Ti_{51.2}(Ni_{21.8}Pd_{27.0}) thin film; (b) and (c) sub-micron grains with or without precipitates in (Ti_{35.0}Zr_{15.4})Ni_{49.7} thin films.

The plate-like precipitate shown in Fig. 1 (a) was

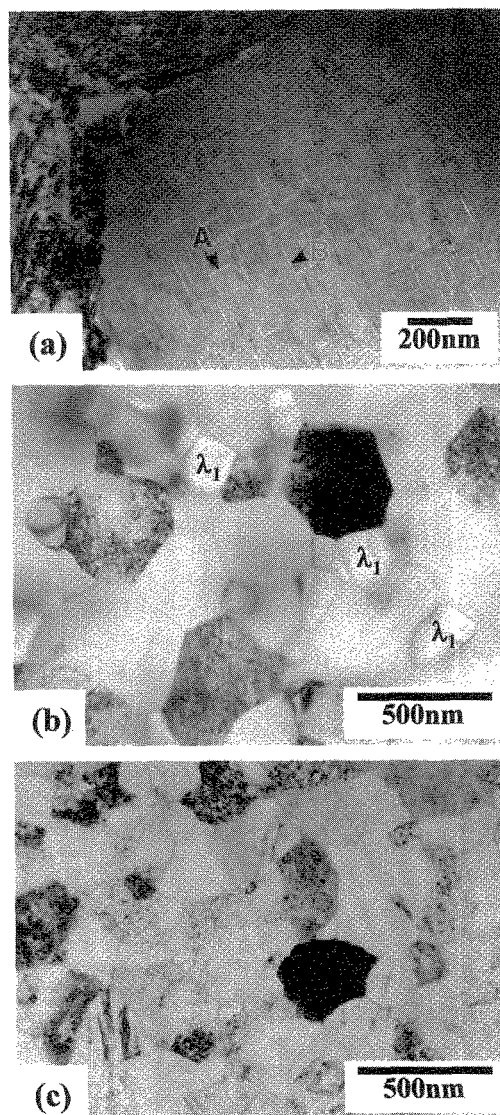


Fig. 1. TEM microstructures of the thin films. (a) Ti_{51.2}(Ni_{21.8}Pd_{27.0}) annealed at 770K for 1 hour (b) (Ti_{35.0}Zr_{15.4})Ni_{49.7} annealed at 970K for 1 hour (c) (Ti_{35.0}Zr_{15.4})Ni_{49.7} annealed at 770K for 5 minutes

identified as a Ti₂(Pd,Ni) phase with a tetragonal MoSi₂-type (C_{11b}) structure [10] (Hereinafter, simply denoted as "Ti₂Pd"). They have the habit plane parallel to the {100} plane of the B2 matrix with the orientation relationship of (001)_{B2}|| (001)_{Ti2Pd} and [100]_{B2}|| [100]_{Ti2Pd}. Two sets of platelets perpendicular to each other, denoted as A and B in Fig. 1 (a), are associated with two kinds of variants with different habit planes.

It should be noted that the crystalline structure and the orientation relationship of the Ti₂Pd are consistent with those of GP zone-like precipitates reported in Ti-Ni-based thin films annealed at low temperatures around Tc [11]. The Ti₂Pd precipitates have also been reported in the Ti₅₄Ni_{36.8}Pd_{9.2} thin film annealed at 770K [12], although the film composition is in two-phase region comprising a Ti(Ni,Pd) phase and a Ti₂(Ni,Pd) phase with Ti₂Ni-type structure [13]. In both cases, the plate-like thin precipitates disappear when the annealing

temperature is elevated, since they are not the thermodynamically stable phases. On the other hand, the increase in annealing temperature simply results in the increase in their size and the change of their distribution in the $\text{Ti}_{51.2}(\text{Ni}_{21.8}\text{Pd}_{27.0})$ thin films. The location of the precipitates changes from inside the $\text{Ti}(\text{Ni},\text{Pd})$ grains to along the grain boundaries with increasing annealing temperature.

The $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ thin film annealed at 970K for 1 hour exhibits a ternary TiNiZr phase with an MgZn_2 -type Laves phase structure (λ_1) at grain boundaries, as shown in Fig. 1 (b). The λ_1 phase disappears as the annealing temperature and/or the annealing time decrease. Fig. 1 (c) shows the TEM microstructure without the λ_1 precipitates in the film annealed at 770K for 5 minutes.

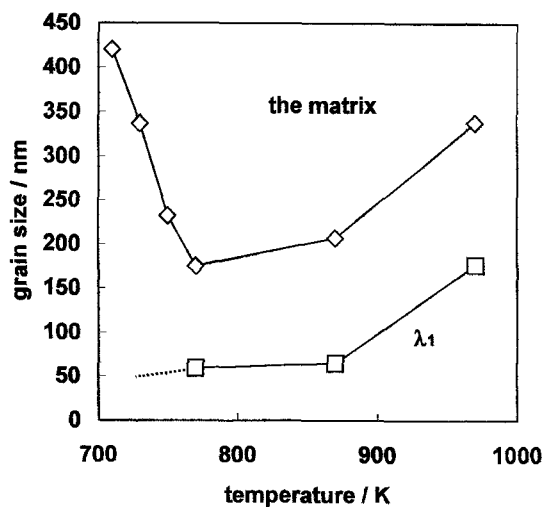


Fig. 2. The grain sizes of the matrix and λ_1 precipitates for the $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ films annealed at various temperatures for 1 hour.

The $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ films exhibited sub-micron grain sizes. It is considered to be not only due to the low diffusion rate of atoms in the solid state, but also due to a pinning effect of grain boundaries by the λ_1 precipitates. Figure 2 shows the grain size of the matrix and the λ_1 particles in the $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ films annealed at various temperatures for 1 hour as a function of the annealing temperature. The figure can be divided into two temperature regions. The grain size steeply decreases with increasing annealing temperature below 770K, while increase with increasing annealing temperature above 770K. It was also found that the volume fraction of the λ_1 phase increases with increasing temperature in the lower temperature region below 770K, while stay almost constant above 770K. Therefore, the evolution of the microstructure can be characterized by the nucleation of λ_1 particles below 770K, while by the growth of the λ_1 grains above 770K. It is considered that the increase in the grain size with decreasing annealing temperature below 770K is attributed to the decrease in the number of the λ_1 precipitates.

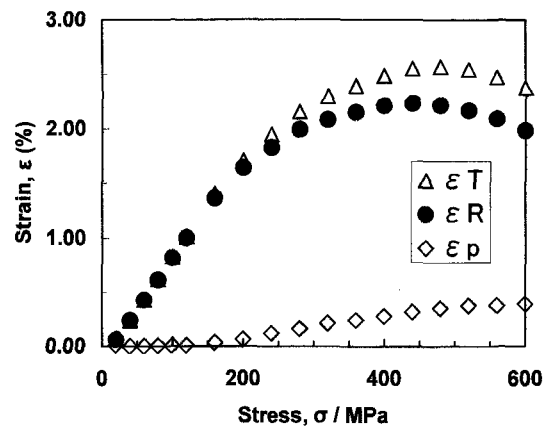


Fig. 3. ϵ_T , ϵ_R and ϵ_p of the $\text{Ti}_{51.2}(\text{Ni}_{21.8}\text{Pd}_{27.0})$ thin film annealed at 870K for 1 hour

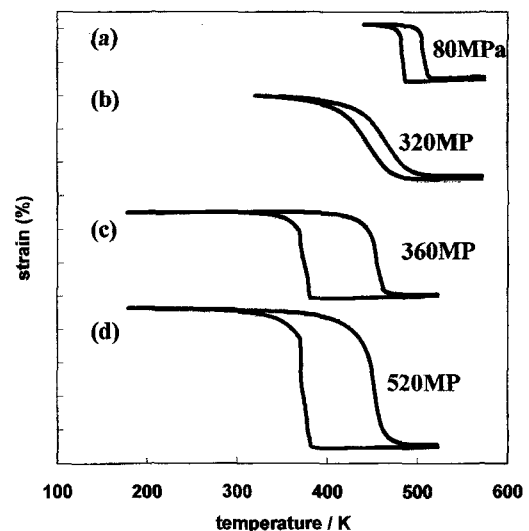


Fig. 4. Strain-temperature curves at the maximum recovery stresses.

- (a) $\text{Ti}_{49.5}(\text{Ni}_{22.0}\text{Pd}_{28.5})$ annealed at 970K for 1 hour
 (b) $\text{Ti}_{51.2}(\text{Ni}_{21.8}\text{Pd}_{27.0})$ annealed at 770K for 1 hour
 (c) $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ annealed at 970K for 1 hour
 (d) $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ annealed at 770K for 5 minutes

5. SHAPE MEMORY CHARACTERISTICS

The shape memory characteristics were evaluated by measuring strain-temperature curves under various constant stresses. The transformation strain (ϵ_T), the recoverable strain (ϵ_R) and the permanent strain (ϵ_p) were obtained from the curves. Figure 3 represents ϵ_T , ϵ_R and ϵ_p as a function of applied stress, for the $\text{Ti}_{51.2}(\text{Ni}_{21.8}\text{Pd}_{27.0})$ thin film annealed at 870K for 1 hour. ϵ_R increases with increasing applied stress. However, ϵ_p also increases with increasing stress, and causes work hardening of the film. As a result, ϵ_R decreases at higher stresses. Consequently, the recoverable strain and recovery stress are limited by the critical stress inducing slip deformation (σ_c). In the present study, σ_c is defined as the stress where ϵ_p reaches 0.1%.

Figure 4 shows some examples of strain-temperature

curves of the films. Each curve is given for their maximum recoverable strain and recovery stress, that is, the strain-temperature curve at the stress just below σ_c . Figures 4 (a) and (b) show the strain-temperature curves of $\text{Ti}_{49.5}(\text{Ni}_{22.0}\text{Pd}_{28.5})$ annealed at 970K for 1 hour and $\text{Ti}_{51.2}(\text{Ni}_{21.8}\text{Pd}_{27.0})$ thin film annealed at 770K for 1 hour, respectively. The former is associated with a single-phase microstructure of Ti(Ni,Pd) without precipitates, while the latter is associated with the microstructure with fine plate-like Ti_2Pd precipitates (Fig. 1 (a)). Figure 4 (c) and (d) show the strain-temperature curves of $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ thin films annealed at 970K for 1 hour and 770K for 5 minutes, respectively. They are associated with the microstructures with or without λ_1 precipitates, as shown in Fig. 1 (b) and (c), respectively. In both cases, evidently, the low temperature heat treatments are effective to increase the recoverable strain and recovery stress utilizing fine distribution of the plate-like precipitates or the sub-micron grain size without precipitates.

6. CRITICAL STRESS FOR INDUCING SLIP DEFORMATION

There are three conceivable factors governing σ_c , i.e. the precipitation strengthening, solution strengthening and grain size effect. The precipitation strengthening is a major factor affecting σ_c in the $\text{Ti}_{51.2}(\text{Pd}_{27.0}\text{Ni}_{21.8})$ films. In particular, the fine distribution of plate-like Ti_2Pd precipitates inside grains significantly strengthens the film. It is probably because of the internal strain field produced along the $\{100\}$ planes of the precipitates, which are coherent with the matrix.

In the $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ films, the grain size also has an important role to improve σ_c . In the previous paper, the present authors discussed the dominant factors affecting σ_c of the $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ films with various grain sizes with or without λ_1 precipitates, prepared by varying the annealing temperature from 770K to 970K, and the annealing time from 5 minutes to 10 hours [6]. The conclusion was that the σ_c was dominantly affected by the grain size for the annealing temperature of 970K, while by the precipitation strengthening for the annealing temperature of 770K. The relationship between σ_c and the grain size (d) could be expressed by the following equation, in analogy with Hall-Petch equation.

$$\sigma_c = \sigma_0' + k_y' d^{-1/2}$$

where σ_0' and k_y' are constants associated with yielding during thermal cycling under constant stresses.

7. FRACTURE TOUGHNESS

It has been known that Ti-Ni-Zr alloys with Ti-rich compositions show brittleness and bad workability, due to brittle precipitates at grain boundaries [7]. In spite of the existence of the brittle λ_1 precipitates at grain boundaries, however, the $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ thin films showed sufficient fracture toughness to undergo tensile loadings. The sub-micron grain sizes of the $(\text{Ti}_{35.0}\text{Zr}_{15.4})\text{Ni}_{49.7}$ films annealed below 970K can contribute the sufficient fracture toughness of the films. It should also be mentioned that the shape of λ_1 precipitates would be associated with the fracture toughness. In bulk specimens, λ_1 precipitates show a

film-like shape covering B2 grains. It is due to the solidification sequence of Ti-rich Ti-Ni-Zr alloys, where the λ_1 phase is finally solidified. The brittle precipitates with the film-like shape covering B2 grains are thought to hinder slip transfer between one grain and another, resulting in brittleness of the whole alloy. On the other hand, thin films crystallized in the amorphous state have never been exposed to such a high temperature that a liquid phase appears in the system. The λ_1 phase nucleates in the non-equilibrium (Ti,Zr)Ni phase containing Ti and Zr in excess, and grows into particles. Therefore, λ_1 precipitates show an agglomerated shape, as shown in Fig. 1 (b), which may be another reason for the sufficient fracture toughness.

The microstructures without λ_1 precipitates produced by heat treatments just above or below T_c (ex. 770K for 5min) are considered to be more effective to improve fracture toughness, as well as σ_c .

8. CONCLUDING REMARKS

The shape memory characteristics and mechanical properties of the Ti-Ni-X (X=Pd,Zr) thin films annealed in amorphous states can be explained by the grain size of the matrix, and the size, shape and distribution of the precipitates. The characteristics were effectively improved by sub-micron grain sizes and finely distributed precipitates in the Ti-rich films produced by the annealing at low temperatures around T_c of about 750K. The MTTs are dependent not only on their chemical compositions, but also on the strength of the films.

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