Two-Stage Martensitic Transformation in Thermal-Cycled $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ Shape Memory Alloy

Tsai-Jung Ho^{*1}, Shyi-Kaan Wu^{*2} and Keng-Hua Lin^{*1}

Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan, R. O. China

Thermal-cycled $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ alloy exhibits $\text{B2} \leftrightarrow \text{B19'}$ martensitic transformation and two DSC transformation peaks appear after 10 thermal cycles. Transformation temperatures rapidly decrease during the early cycles. XRD tests reveal that both transformation peaks are associated with $\text{B2} \leftrightarrow \text{B19'}$ transformation. TEM observations indicate that as-homogenized B19' martensite mainly consists of internal $(011)_{\text{M}}$ type II twins. However, they are gradually replaced by internal $(001)_{\text{M}}$ compound twins with increasing the thermal cycles. This feature accounts for these two transformation peaks are associated with $\text{B2} \leftrightarrow \text{B19'}$ transformation with two different internal twinning modes. The microstructural evolution of B19' martensite is ascribed to the dislocations induced by thermal-cycling as they can promote the formation of thin internal $(001)_{\text{M}}$ compound twins. [doi:10.2320/matertrans.M2009235]

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1. Introduction

TiNi-based shape memory alloys (SMAs) are the most noticeable SMAs due to their superior properties in shape memory effect, pseudoelasticity and damping capacity. However, the working temperature of these alloys is limited to ambient temperature owing to their relatively low transformation temperatures. The addition of a third element (e.g. Au, Pt, Pd, Zr and Hf) in TiNi-based SMAs to replace Ni or Ti could elevate the transformation temperature to several hundred degrees centigrade. These high temperature SMAs can be applied to where higher working temperature is needed. TiNiHf ternary alloys are the promising high temperature SMAs with the merits of having high transformation temperatures and relatively lower cost than TiNiAu and TiNiPd SMAs. Extensive researches were made to reveal the transformation behavior and microstructure of TiNiHf SMAs. It has been found that these alloys would transform from B2 (cubic parent phase) to B19' (monoclinic martensite) structure upon cooling.¹⁾ The morphology and substructure of martensite in deformed TiNiHf alloys and the stress induced martensite (SIM) in undeformed TiNiHf alloys have also been studied.²⁻⁴⁾

Transformation behavior of Ti-rich TiNiHf SMAs under thermo-mechanical treatments such as aging and thermal cycling has been investigated.^{5,6)} It has been reported that the martensitic transformation of TiNiHf alloys becomes two-stage after thermal cycling.⁷⁾ However, the reason for the occurrence of two-stage martensitic transformation is still not clarified. In this paper, Ti-rich $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ SMA (abbreviated as TiNiHf10 SMA) is selected to study due to its moderate transformation temperature. The aim of this study is to understand the microstructure evolution of TiNiHf10 B19' martensite during thermal cycling and the associated effect on the two-stage martensitic transformation.

2. Experimental Procedures

$\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ (in at%) ingot was prepared from 99.8 mass% Ti, 99.9 mass% Ni and 99.9 mass% Hf by vacuum arc-remelting (VAR) with Ti getter in a water-cooled copper crucible. The ingot was remelted 6 times and homogenized at 1000°C for 24 h in vacuum and then cooled in the furnace. The as-homogenized ingot was cut into $1.5\text{ mm} \times 1.5\text{ mm} \times 1.5\text{ mm}$, and $5.5\text{ mm} \times 7.5\text{ mm} \times 0.8\text{ mm}$ specimens for testing with differential scanning calorimetry (DSC) and X-ray diffraction (XRD), respectively. The transformation temperature and martensite structure of as-homogenized and thermal-cycled specimens were determined by DSC (TA Q10 DSC) and XRD (Shimadzu XRD-6000) with scanning temperature between 0°C and 250°C . The heating/cooling rate of DSC experiment was $10^{\circ}\text{C}/\text{min}$. The specimen for thermal cycling test was sealed in a quartz tube under vacuum and then carried out in the temperature range of 250°C salt bath and liquid nitrogen with the cycling number $N = 1 \sim 100$ times. The XRD apparatus was equipped with a hot stage and $\text{CuK}\alpha$ radiation was used (40 kV applied voltage and 30 mA current). The specimens for XRD test were first heated up to 250°C and then cooled down to the set experimental temperature. The transmission electron microscope (TEM) specimens were cut from thermal-cycled ($N = 1, 10$ and 100) specimens and mechanically polished to a thin foil of $90\text{ }\mu\text{m}$ thickness, then electropolished by twin-jet with an electrolyte of 10% H_2SO_4 and 90% CH_3OH in volume at -30°C . Microstructural observation was carried out on a JOEL 2000EX TEM with double tilt holder and 200 kV operating voltage.

3. Results and Discussion

3.1 Thermal cycling effect on transformation behavior of $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ alloy

The effect of thermal cycling on the transformation behavior and microstructure of TiNiHf10 alloy was investigated by DSC, XRD, and TEM. Figure 1 shows the DSC

^{*1}Graduate Student, National Taiwan University

^{*2}Corresponding author, E-mail: skw@ntu.edu.tw

Fig. 1 DSC curves of transformation behavior of TiNiHf10 alloy with $N = 1 \sim 100$ thermal cycles.

Fig. 2 The DSC partial cycling test of $N = 10$ thermal cycled TiNiHf10 alloy.

curves of M^* and A^* peak temperatures of the forward and reverse martensitic transformations for the specimens thermal-cycled for $N = 1 \sim 100$. From Fig. 1, one can find that the M^* peak separates into two peaks, M^*_1 and M^*_2 , for $N = 10 \sim 50$. The results implicate that two-stage transformation can be induced by thermal cycling treatment. The correspondence of the forward martensitic transformation peaks (M^*) to their reverse transformation peaks (A^*) have been determined by the DSC partial cycling test, as shown in Fig. 2. The specimen for the DSC partial cycling test was thermal-cycled for $N = 10$ to induce the two-stage martensitic transformation. As shown in Fig. 2, M^*_1 and M^*_2 peaks correspond to A^*_1 and A^*_2 respectively. In Fig. 3, the variation of transformation peak temperatures, M^*_1 , M^*_2 ,

Fig. 3 The variation of transformation temperatures versus the thermal cycles (N).

A^*_1 and A^*_2 versus N is shown. The transformation peak temperatures of M^*_1 and A^*_1 decrease rapidly for about 30°C in the early cycling stage ($1 \sim 20$ cycles) and keep almost constant with further cycling. The decrease of transformation temperatures is attributed to the dislocations induced by thermal cycling,⁸⁾ and these dislocations would impede the occurrence of martensitic transformation. Figure 1 implicates that the number of dislocations induced in the alloy is getting higher with the increasing number of thermal cycling in the first 20 cycles. The reason why two transformation peaks can be induced by thermal-cycling, as shown in Fig. 1, will be discussed in the following.

3.2 XRD tests on martensitic transformation of thermal-cycled $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ alloy

Airoldi *et al.*⁹⁾ reported that thermal cycling treatment would induce the R phase in binary TiNi-based alloys. In order to clarify the structural evolution of thermal-cycled TiNiHf10 alloy during martensitic transformation, XRD tests at various temperatures are conducted. Figures 4(a), 4(b), and 4(c) show the XRD results of the specimens before ($N = 1$) and after ($N = 10$ and $N = 100$) thermal cycling, respectively. Compared to DSC curves shown in Fig. 1, XRD results also indicate that the alloy with or without thermal cycling contains mainly B2 phase at 250°C . Upon cooling, when the martensitic transformation starts, the intensity of B2 phase decreases and that of $\text{B}19'$ phase increases. The alloy becomes a full $\text{B}19'$ structure when the martensitic transformation finished and no other phase can be found. However, Fig. 1 indicate that the $N = 10$ specimen sustains two-stage martensitic transformation. This explicates that the first (M^*_1) and second (M^*_2) stages of martensitic transformation upon cooling in $N = 10$ specimen are both B2 to $\text{B}19'$ transformation. Here, M^*_1 is defined as the peak temperature of $\text{B}2 \rightarrow \text{B}19'_1$ transformation and M^*_2 represents that of $\text{B}2 \rightarrow \text{B}19'_2$ transformation.

3.3 Microstructural evolution of $\text{B}19'$ martensite in thermal-cycled $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ alloy

Figures 5, 6 and 7 show TEM observations of $\text{B}19'$ martensite at room temperature in TiNiHf10 alloy with $N = 1, 10$, and 100 , respectively. From bright field images of

Fig. 4 The evolutions of X-ray diffraction profile in the thermal-cycled TiNiHf_{10} alloy on cooling (a) $N = 1$, (b) $N = 10$, and (c) $N = 100$.

Figs. 5(a), 6(a), 6(c), and 7(a), one can find that all TiNiHf_{10} specimens contain banded-like martensite variants (banded variants) with internal twins of different configuration. The TiNiHf_{10} specimen with $N = 1$ contains banded variants composed of block-like internal twins. Specimens with $N = 10$ and 100 are also composed of banded variants, but the internal twins inside the variants are far thinner than those in $N = 1$ alloy. In order to distinguish the twinning modes of adjacent martensite variants and those of internal twins in the variants, selected area diffraction patterns (SADPs) and dark field images by TEM are used to reveal the twinning

relations. Figure 5(b) is the SADP of Fig. 5(a) with zone axis $[\bar{2}11]_{A,B} // [\bar{2}11]_C$. Compared with the diffraction pattern shown in Fig. 1(b) of the work of Zheng *et al.*,¹⁰ Fig. 5(b) is recognized as $(011)_M$ type I and $\langle 011 \rangle$ type II twins, i.e., A/B is $(011)_M$ type I twin and A/C is $\langle 011 \rangle_M$ type II twin. Diffraction spots A, B and C come from banded variants A, B and internal twins C, as labeled in Figs. 5(c) and 5(d). Figures 5(c) and 5(d) show that banded variants A and B of Fig. 5(a) have the $(011)_M$ type I twin relation. Thus the internal twins C with the banded variants A and B, as shown in Fig. 5(d), have the $\langle 011 \rangle_M$ type II twin relation. Figures 6(b) and 6(d) show the SADPs of Figs. 6(a) and 6(c), respectively. Figures 5(b) and 6(b) are SADPs along the same $[\bar{2}11]_M$ zone axis. However, Fig. 5(b) shows two twinning modes of $(011)_M$ type I twin and $\langle 011 \rangle_M$ type II twin, but only one twinning mode of $(011)_M$ type I twin can be observed in Fig. 6(b). This indicates that the amount of $\langle 011 \rangle_M$ type II twins decreases in banded variants after $N = 10$. Figure 6(c) also shows the bright field image of $N = 10$ specimen. In Fig. 6(c), instead of block-like $\langle 011 \rangle$ type II internal twins observed in Fig. 5, very thin plates of internal twins in banded variants are shown. Figure 6(d) is the SADP of Fig. 6(c) with $[010]_M$ zone axis and it shows a $(001)_M$ compound twin. From Fig. 6, the B19' martensite of TiNiHf_{10} alloy with $N = 10$ contains banded variants of $(011)_M$ type I twins with their internal twins of $(001)_M$ compound twins. The results of Fig. 7 also indicate that $N = 100$ cycled alloy has the same internal twins relation as $N = 10$ one. In Fig. 7, the banded variants are still related with $(011)_M$ type I twins, but almost all banded variants contain internally thin plates of $(001)_M$ compound twins, instead of $\langle 011 \rangle_M$ type II twins. Obviously, the formation of internal thin $(001)_M$ compound twins is closely related to the thermal-cycling treatment. Upon increasing the N number, the more the thin $(001)_M$ compound twins occur, the less the block-like $\langle 011 \rangle_M$ type II twins retain, but the banded variants still remain $(011)_M$ type I twins.

3.4 Formation mechanism of thin $(001)_M$ compound twins in thermal-cycled $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ alloy

Nishida *et al.*¹¹ investigated the formation sequences and mechanisms of various twinning modes during $B2 \rightarrow B19'$ transformation in $\text{Ti}_{50}\text{Ni}_{50}$ SMA. Since there is no elastic strain at the beginning of martensitic transformation, the martensite variants consisting of $\langle 011 \rangle_M$ Type II twins as a lattice invariant shear firstly appear. In order to minimize the transformation strain, these variants are accommodated to each other. However, this accommodation process may cause the elastic interactions between variants. Therefore, they proposed that the $(100)_M$ and $(001)_M$ compound twins may be introduced to reduce the elastic strain, in which $(001)_M$ compound twins are often observed at the position where the elastic strain is the most accumulative, such as the position with internal defects. The thermal-cycled TiNi -based SMAs can induce the internal defects of dislocations,⁸ and thus the $(001)_M$ compound twins can be produced to release the elastic strain during martensitic transformation. Meanwhile, Dalle *et al.* observed the appearance of thin $(001)_M$ compound twins in $\text{Ti}_{42.2}\text{Ni}_{49.8}\text{Hf}_8$ alloy with 10% tensile deformation.⁶ They made a proposition of the

Fig. 5 The microstructural observations of martensite at room temperature in TiNiHf10 alloy with $N = 1$. (a) bright-field image, (b) SADP corresponding to banded variants A and B of (a), which indicates A/B is $\langle 011 \rangle_M$ type I twin and A/C is $\langle 011 \rangle_M$ type II, (c) and (d) dark field images corresponding to banded variants A and B in (b). The internal twins C in banded variants A and B are also shown in (c) and (d), respectively.

formation of thin $\langle 001 \rangle_M$ compound twins based on the predictive atomic model from Kudoh *et al.*¹²⁾ in which $\langle 001 \rangle_M$ compound twins are easily produced by the dissociation of dislocations with a Burgers vector $\mathbf{a}/2$ on $\langle 001 \rangle_M$ plane in 10% deformed $\text{Ti}_{42.2}\text{Ni}_{49.8}\text{Hf}_8$ alloy.

As mentioned above, thermal-cycled TiNi-based SMAs can induce dislocations to depress their transformation temperatures.⁸⁾ Obviously, the more the number of thermal cycles, the more the dislocations are induced. Thus, the more the $\langle 001 \rangle_M$ compound twins are produced in thermal-cycled specimens, as TEM observations shown in Figs. 5~7.

3.5 Discussion on the two-stage martensitic transformation of thermal-cycled $\text{Ti}_{40.5}\text{Ni}_{49.5}\text{Hf}_{10}$ alloy

The TiNiHf10 alloy with $N = 1$ exhibits $\text{B2} \leftrightarrow \text{B19}'$ martensitic transformation, but thermal-cycled ($N = 10$) one shows $\text{B2} \leftrightarrow \text{B19}'_1$ and $\text{B2} \leftrightarrow \text{B19}'_2$ two transformation peaks. These two transformation peaks gradually merge into one broad peak from $N = 10$ to $N = 100$. Experimental results demonstrate that the evolution of martensitic transformation is associated with the change of martensite microstructure. The TEM observations show that the martensite morphology of TiNiHf10 alloy possesses banded-like martensite variants with internal twins, and each variant is also twin-related to the adjacent one. The banded variants in

all specimens, including $N = 1 \sim 100$, are all $\langle 011 \rangle_M$ type I twin-related, but the internal twins in the variants gradually changes from $\langle 011 \rangle_M$ type II twins to $\langle 001 \rangle_M$ compound twins from $N = 1$ to $N = 10$. In other words, banded variants of TiNiHf10 alloy with $N = 1$ mainly possess $\langle 011 \rangle_M$ type II internal twins, and the amount of $\langle 011 \rangle_M$ type II internal twins decreases and that of $\langle 001 \rangle_M$ compound internal twins increases during thermal-cycling. With thermal cycles up to 100 times, almost all banded variants contain $\langle 001 \rangle_M$ internal compound twins, instead of $\langle 011 \rangle_M$ type II twins. The evolution of internal twinning modes also comes along with the change in the martensite morphology from block-like internal twins to fine plate-like internal twins.

We suggest that the two transformation peaks induced by thermal cycling, as shown in Fig. 1, are related to two internal twinning modes, i.e., $\langle 011 \rangle_M$ type II twins and $\langle 001 \rangle_M$ compound twins. Due to the lower magnitudes of twinning shear,^{13,14)} transformation shape strain shear, twin plane interfacial energy and nucleation strain energy of $\langle 001 \rangle_M$ compound twins,¹⁴⁾ the transformation of $\text{B2} \rightarrow \text{B19}'$ with variants consisting of $\langle 001 \rangle_M$ compound twins is proposed to be easier to form at higher temperature than that of $\text{B2} \rightarrow \text{B19}'$ with variants consisting of $\langle 011 \rangle_M$ type II twins. This indicates that, in Fig. 1, M^*_1 peak appearing at lower temperature represents the martensitic transformation

Fig. 6 The microstructural observations of martensite at room temperature in TiNiHf_{10} alloy with $N = 10$. (a) and (c) bright-field images, (b) SADP of (a) which is $(011)_M$ type I twin-related, (d) SADP of (c) which is $(001)_M$ compound twin-related.

Fig. 7 The microstructural observations of martensite at room temperature in TiNiHf_{10} alloy with $N = 100$. (a) bright-field image, (b) SADP corresponding to (a) which is $(001)_M$ compound twins.

of B2 to $B19'_1$ with variants consisting of $\langle 011 \rangle_M$ type II twins, and M^*_2 peak ($B2 \rightarrow B19'_2$) appearing at higher temperature is the martensitic transformation with variants consisting of $(001)_M$ compound twins. Obviously, M^*_1 temperature is depressed significantly by the early thermal-cycling. Upon increasing the N number from 10 to 100, more thin $(001)_M$ compound twins occur in the alloy, instead of the block-like $\langle 011 \rangle_M$ type II twins.

4. Conclusion

Thermal-cycled TiNiHf_{10} alloy can induce dislocations and depress the transformation temperature and after 10 thermal cycles, two DSC transformation peaks appear. XRD tests reveal that both transformation peaks are associated with B2 to $B19'$ transformation. The evolution of transformation behavior and the corresponding martensite micro-

structure with $N = 1 \sim 100$ are investigated by TEM observations. Experimental results show that TiNiHf10 alloy with $N = 1$ exhibits $B2 \leftrightarrow B19'$ transformation in which the $B19'$ martensite is mainly associated with banded-like martensite variants consisting of $\langle 011 \rangle_M$ type II internal twins. TiNiHf10 alloy with $N = 10$ exhibits two martensitic transformation peaks of $B2 \leftrightarrow B19'_1$ and $B2 \leftrightarrow B19'_2$ which correspond to banded martensite variants composed of internal $\langle 011 \rangle_M$ type II twins and internal $(001)_M$ compound twins, respectively. For TiNiHf10 alloy with $N = 10 \sim 100$, upon increasing the N number, the more the $(001)_M$ compound twins occur and the less the $\langle 011 \rangle_M$ type II twins retain. The dislocations induced by thermal-cycling are suggested that they can promote the formation of internal thin $(001)_M$ compound twins.

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