Two-way shape memory effect of a TiNiHf high temperature shape memory alloy


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Abstract

The two-way shape memory effect in a Ti₃₆Ni₄₉Hf₁₅ high temperature shape memory alloy (SMA) has been systematically studied by bending tests. In the TiNiHf alloy, the martensite deformation is an effective method to get two-way shape memory effect even with a small deformation strain. When the TiNiHf alloy is deformed at a full martensite state, the deformation mechanism is the martensite orientation accompanied by the dislocation slip. The experimental results indicated that the internal stress field formed by the bending deformation is in the directions of the preferentially oriented martensite variants formed during the bending deformation. Upon cooling the preferentially oriented martensite variants form under such an oriented stress field, which should be responsible for the generation of the two-way shape memory effect. Proper training process and aging benefit the formation of the oriented stress field, resulting in the improvement of the two-way shape memory effect. When the training strain is 7.1% and the training temperature is room temperature, a two-way shape memory strain of 0.88% is obtained in the Ti₃₆Ni₄₉Hf₁₅ alloy. This value is the maximum two-way shape memory strain in the TiNi-based high temperature SMAs so far. In comparison with the TiNi alloy, the TiNiHf high temperature SMA shows the two-way shape memory effect with the relative poor stability due to the lower strength of martensite.

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1. Introduction

Two-way shape memory effect means the shape memory alloys (SMAs) are able to “remember” a geometrical shape at high temperature (above \( A_f \)) and another shape at low temperature (below \( M_f \)), and during the repeated heating and cooling the SMAs change its shape between these two shapes without the help of the external stress. It is well known that in near-equiatomic TiNi SMAs a two-way shape memory effect can be obtained commonly through certain thermomechanical treatments (so-called training), which mainly include shape memory training [1], stress-induced martensitic transformation training (pseudoplastic training) [2] and thermal cycling training under a constant stress [3,4]. These three methods all involve phase transformations between the parent phase and martensite. Commonly, an anisotropic dislocation structure is introduced into the parent phase matrix through training. This dislocation structure creates an anisotropic stress field, which benefits the formation of preferentially oriented martensite variants adopting the training procedure, thus resulting in a macroscopic shape change during subsequent thermal transformation cycles [5].

TiNiHf alloys are considered to be attractive candidates for SMAs used at high temperatures due to its high transformation temperatures, excellent workability and lower cost compared with the other high temperature SMAs [6]. Its constitutional phases [7], microstructure and substructure [8,9], transformation behaviors [10], mechanical properties and shape memory effect [11], and precipitation behaviors during aging [12–14] have been studied. However, except our previous works [15], seldom results about its two-way shape memory effect are reported. Dissimilar to TiNi alloys, a small two-way shape memory effect in the aged TiNiHf alloys can be obtained directly by the deformation of the martensite without training [12,15]. Its detailed mechanism is not clear so far. The finding of the two-way shape memory effect in the TiNiHf high temperature SMA plays an important role to accelerate its practical applications.

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The Ti36Ni49Hf15 alloy was prepared by the consumable arc-melting in an argon atmosphere using 99.92 wt.% sponge Ti, 99.95 wt.% Ni plate and 99.90 wt.% Hf shot. The ingot was then remelted twice to ensure the composition homogeneity by a levitation method in an argon atmosphere, and the melt was poured into a graphite mold of 35 mm in diameter. After homogenizing at 1223 K for 1.5 h, the ingot was hot-rolled into plates of 2.1 mm thickness. 1 mm × 0.5 mm × 50 mm specimens cut along the direction parallel to the rolling surface were solid solution-treated at 1273 K for 1 h in vacuum and then quenched into water. The phase transformation temperatures of as-treated specimen were determined by the differential scanning calorimeter (DSC) to be \(M_f = 421\) K, \(M_s = 452\) K, \(A_f = 489\) K, \(A_s = 504\) K, as shown in Fig. 1. \(M_f, M_s, A_f, A_s\) denote martensitic transformation start temperature, martensitic transformation finish temperature, reverse martensitic transformation start and finish temperatures, respectively. Some specimens were aged at 973 K for 5, 10, 20, 40, 90, 120 h in vacuum and then quenched into the silicon cooling oil, respectively.

The measurement of the two-way shape memory effect was done by bending tests, as illustrated in Fig. 2. One training cycle includes: (1) the specimen was bent against the cylindrical rod to the deformation position at the required temperatures, (2) the specimen was unloaded, and the specimen sprung back to the spring back position, (3) the specimen was heated up to 600 K to recover to the heating position, (4) and then the specimen was cooled down to the room temperature, corresponding to the cooling position shown in Fig. 2. The specimens were trained by repeating the steps from (1) to (4). During the training process, we define the bending deformation strain in the first cycle as training strain, and the bending temperature of the martensite as training temperature. The bending deformation strain is estimated by \(\epsilon_d = d/(d + 2R)\). The deformation strains in this paper are 2, 3.3. 4.5, 5.7 and 7.1%, respectively. The shape recovery strain caused by heating after deformation in the first cycle is calculated by \(\epsilon_r = (180 - \theta_c)/(180 - \theta_f)\). The two-way shape memory strain is measured by value \(\epsilon_{tw} = (\theta_f - \theta_c)/(180 - \theta_f)\). The permanent strain is \(\epsilon_p = \theta_c/(180 - \theta_f)\). In addition, some specimens that have obtained two-way shape memory effect are thermal cycled between 300 and 600 K in order to study the stability of the two-way shape memory effect of the present alloy.

### 3. Results and discussion

#### 3.1. Two-way shape memory effect induced only by martensite deformation

In the Ti36Ni49Hf15 alloy, the two-way shape memory effect can be obtained easily by the deformation of the martensite. Fig. 3 shows the variation of the strain with the temperature for the Ti36Ni49Hf15 specimens deformed to the different strains. It can be seen that the recovery of the deformation started from the very beginning of the heating process with increasing temperature. When the specimens were heated to a certain temperature above \(A_f\), the shape recovery finished. Moreover, the shape recovery finish temperature increases with increasing deformation strain, indicating that deformation leads to the increase of the reverse martensitic transformation temperatures of the present alloy [17]. From these curves shown in Fig. 3, it is observed that the shape recovery finish temperature of the specimen deformed to 7.1% is higher than that of the specimen deformed to 2% for about 12 K. This implies that the stabilization of the martensite is induced by deformation.

Fig. 4 shows the recovery strain \(\epsilon_{ren}\) as a function of the bending deformation strain in the deformed Ti36Ni49Hf15
alloy. Meanwhile, the variation of the shape recovery ratio ($r_{sr}$) with the bending deformation strain is also plotted in Fig. 4 for comparison. With increasing the bending deformation strain, the recovery strain increases, while the corresponding shape recovery ratio decreases rapidly. This is similar to the previous results [18].

The variation of the two-way shape memory strain ($\varepsilon_{tw}$) and the residual permanent strain ($\varepsilon_p$) with the bending deformation strain is shown in Fig. 5. Clearly, the two-way shape memory strain almost increases linearly with increasing deformation strain. It is seen that for the experimental alloy the shape cannot be recovered completely upon heating even when the deformation strain is only 2%. The corresponding permanent strain is about 0.194%. It is suggested that when the TiNiHf high temperature SMA is deformed at full martensite state, the slip of dislocations is introduced accompanied by the reorientation of the martensite. When the deformation strain is 7.1%, the two-way shape memory strain reaches a maximum of 0.45%. This value is smaller than that obtained in the TiNi binary alloy by the constant-stress training [19] or constraint aging [20]. For the solid solution-treated TiNi alloy, its stress-curve shows a stress plateau with the corresponding straining of about 7% when the alloy is deformed at full martensite state. The corresponding martensite deformation mechanism is mainly the reorientation of the martensite variants. However, for the Ti$_{36}$Ni$_{49}$Hf$_{15}$ alloy, no obvious stress plateau is observed in the stress-strain curves, which are characterized by the strong work hardening and continuous yielding. The deformation mechanism of martensite in the TiNiHf alloy is the reorientation of martensite variants accompanied by the slip of dislocations [15]. In addition, some dislocations are also introduced to compensate the mismatch of the preferentially oriented martensite variants in the neighboring grains. All the dislocations create an oriented stress field, which induces the two-way shape memory effect.

It should be noted that for the present alloy, the two-way shape memory effect could be obtained by even 2% deformation strain as shown in Fig. 3. Although the two-way shape memory strain is only 0.034%, its corresponding angle change during the bending test is about 3°, which can be precisely detected. For the near-equiatomic TiNi alloy the reorientation of martensite variants occurs when it is deformed to 2% at full martensite state and the two-way shape memory effect could not be induced by such a small deformation strain. Whereas for the present alloy the critical stress for the martensite reorientation is almost equal to that for the dislocation slip [11]. The dislocations are introduced easily by the martensite deformation to create an internal stress field, which induces a two-way shape memory effect. The larger the deformation strain is, the stronger the stress field is. This explains that the two-way shape memory strain increases remarkably with increasing the deformation strain.

### 3.2. Two-way shape memory effect induced by training

The effect of the number of training cycles on the two-way shape memory strain for the specimens with the different training strains is shown in Fig. 6. It is seen that the two-way
Fig. 6. Effect of the number of training cycles on the two-way shape memory strain of the Ti₃₆Ni₄₉Hf₁₅ alloy with different training strains.

Fig. 7. Effect of training strain on the two-way shape memory strain.

Fig. 8. Effect of the number of training cycles on the two-way shape memory strain for the Ti₃₆Ni₄₉Hf₁₅ alloy with different training temperatures.

Fig. 9. Effect of training temperature on the two-way shape memory strain.

The two-way shape memory strain increases rapidly in the first 5–8 training cycles and then almost does not change with further increasing the cycle number. This result indicates that at the onset of training procedure the dislocations are introduced continuously to create an oriented stress field, which is gradually strengthened. Further increasing the number of training cycles, the stress field created by the beginning several cycles would suppress the introduction of more dislocations during the subsequent training processes. Thus, the two-way shape memory strain becomes stable rapidly after the beginning several training cycles. Fig. 7 shows the relation curve between the two-way shape memory strain and the training strain for the Ti₃₆Ni₄₉Hf₁₅ alloy after 30 training cycles. Compared Fig. 7 and Fig. 5, it is found that for the Ti₃₆Ni₄₉Hf₁₅ alloy specimens with the same deformation strain, the two-way shape memory strain obtained by 30 training cycles is about twice more than that obtained only by martensite deformation. When the training strain is 7.1%, the two-way shape memory strain reaches 0.88% after 30 training cycles. Although the value is very poor in comparison with that in TiNi binary alloys, it is the maximum two-way shape memory strain obtained in the TiNiHf high temperature SMAs so far.

During the training process, the deformation temperature of martensite also affects the two-way shape memory effect seriously. Fig. 8 shows the number of the training cycles dependence of the two-way shape memory strain of the Ti₃₆Ni₄₉Hf₁₅ alloy specimens with the variant training temperatures when the training strain is 7.1%. The shape of the curves is similar to that shown in Fig. 6. It is seen that the two-way shape memory strain obtained by 30 training cycles decreases when the training temperature increases. Fig. 9 depicts the effect of the training temperature on the two-way shape memory strain in the Ti₃₆Ni₄₉Hf₁₅ alloy in the first training cycle. When the training temperature is below 457 K (near Mₛ), the two-way shape memory strain obtained in the first training cycle almost keeps constant, irrespective of the change of the deformation temperature. While when the training temperature is over 457 K, the two-way shape memory strain in the first training cycle drops down with the training temperature increasing and reaches zero.
at about 600 K. For the Ti_{36}Ni_{49}Hf_{15} alloy after 30 training cycles, the two-way shape memory strain decreases continuously when the training temperature increases from 293 to 630 K. This indicates that the serious dislocation slip is accumulated gradually by each training cycle when the training temperature is high enough. The critical stresses for both the dislocation slip and the martensite reorientation of the Ti_{36}Ni_{49}Hf_{15} alloy decrease when the deformation temperature increases [11]. It is suggested that the dislocations slip is very easy to be introduced when the TiNiHf alloy is deformed at high temperature (near $M_s$). The higher the training temperature is, the larger the amount of dislocations introduced during training is. The dislocations introduced with a higher training temperature would damage the repeated movement of the boundaries between the parent phase and the martensite to some extent. Therefore, its two-way shape memory strain decreases continuously with increasing the training temperature. A better two-way shape memory effect of Ti_{36}Ni_{49}Hf_{15} alloy must be obtained when the training temperature is far lower than $M_s$.

3.3. Effect of aging on two-way shape memory effect

In the present study, we try to get the better two-way shape memory effect in the aged Ti_{36}Ni_{49}Hf_{15} alloy. The two-way shape memory effect is obtained directly by deformation at room temperature without training in the aged Ti_{36}Ni_{49}Hf_{15} alloy. Fig. 10 shows the effect of aging time on the two-way shape memory strain of the Ti_{36}Ni_{49}Hf_{15} alloy aged at 973 K with a deformation strain of 4.5%. It is found that for the Ti_{36}Ni_{49}Hf_{15} alloy aged at 973 K for 5 h, its two-way shape memory strain is about 0.44%, which is about twice than that in the solid solution-treated specimen with the same bending deformation strain as shown in Fig. 3. Further increasing the aging time the two-way shape memory strain decreases continuously with increasing the training temperature. A better two-way shape memory effect of Ti_{36}Ni_{49}Hf_{15} alloy must be obtained when the training temperature is far lower than $M_s$.

3.4. Stability of two-way shape memory effect

Thermal stability of the two-way shape memory effect of the TiNiHf high temperature SMA is an important issue on its way to practical applications because under many conditions TiNiHf alloy will be subjected to many cycles by repeated heating and cooling. Fig. 11 compared the stabilities of three two-way shape memory effects obtained by only martensite deformation, 30 training cycles and aging + martensite deformation in the Ti_{36}Ni_{49}Hf_{15} alloy with the deformation strain of 4.5%, respectively. It can be seen that the two-way shape memory strain decreases rapidly in the first several thermal cycles and then becomes stable with further increasing the number of thermal cycles. According to the results above, it can be deduced that the dislocations introduced by the thermal cycling relax the stress field formed by the martensite deformation or the training process, leading to the difficulty to form the preferentially oriented martensite variants and the decrease of the two-way shape memory effect. After the initial several thermal cycles, the dislocations introduced by the thermal cycles interact with the oriented stress field formed by the deformation to create a stable dislocation configuration resulting in the stabilization of the two-way shape memory effect. In addition, it is observed that after 30 thermal cycles the two-way shape memory strain obtained by 30 training cycles is slightly larger than that obtained by the other two methods, indicating that the stress filed induced by training is more stable. Hence, in the Ti_{36}Ni_{49}Hf_{15} alloy a relative large, stable two-way shape memory effect can be got by proper training process.
3.5. Mechanism of two-way shape memory effect in TiNiHf alloy

Two-way shape memory effect is not the nature of the TiNi-based alloy. There are two options on the mechanisms of the two-way shape memory effect until now. One is that the two-way shape memory effect is derived from the residual martensite variants in the parent phase after training [21]. Those residual martensite variants do not transform to parent phase even when the temperature is over \( A_f \). Upon cooling, the residual martensite variants grow and affect the other variants to form the preferentially oriented martensite variants resulting in the two-way shape memory effect. However, increasing the heating temperature far above \( A_f \) to make the residual martensite variants transform to parent phase completely, the two-way shape memory effect does not vanish indicating that the residual martensite variants is not the main reason for the two-way shape memory effect. The other is that two-way shape memory effect is due to the effect of dislocations introduced by training [22]. It is analyzed that the energy of the dislocations is lowest in the martensite variants after training than that in the other type variants. So upon cooling, the martensite variants with the same orientation with the variants after training would form preferentially. Thus the two-way shape memory effect is observed.

In the TiNiHf high temperature SMAs the two-way shape memory effect mainly arises from the stress field created by the dislocations introduced by deformation or training process. This stress field is created in the directions of the preferentially oriented martensite variants formed during the deformation or training process. Thus the preferentially oriented martensite variants would form upon cooling and then recover upon heating. On the one hand, the dislocations introduced by martensite deformation/training process contribute to the formation of the oriented stress field. On the other hand, those dislocations prohibit the movement of the boundaries between the parent phase and martensite to some extent. For example, for the Ti\(_{36}\)Ni\(_{49}\)Hf\(_{15}\) alloy specimen with a high training temperature, the two-way shape memory strain decrease due to the serious dislocation slip. However, as a kind of high temperature SMA, TiNiHf ternary alloy has its own two characteristics about the two-way shape memory effect compared with TiNi alloys:

1) Two-way shape memory effect is easy to induce in the Ti\(_{36}\)Ni\(_{49}\)Hf\(_{15}\) alloy, but its value is small. As mentioned above, it can be got even when the deformation strain is only 2%. Fig. 12 shows the schematic diagram of the stress–strain curves of TiNiHF and TiNi SMAs at full martensite state. For the TiNi alloy, when it is deformed to a deformation strain less than about 7% (within the plateau stage shown in Fig. 12), the corresponding deformation mechanism is the reorientation of the martensite variants. Upon heating, the deformation almost completely recovers. Whereas for the TiNiHf alloy, its stress–strain curve does not show a stress plateau and can be divided into three stages corresponding to different deformation mechanims, as indicated in Fig. 12: the initial elastic deformation of thermal martensite (stage I), the reorientation of the martensite variants with dislocation slip (stage II), plastic deformation of martensite (stage III). It is quite different from that for TiNi alloy that in the stage II the reorientation of martensite and dislocation slip coexist for the TiNiHf alloy. This can be supported by that a permanent deformation of 0.194% was measured even in the specimen with deformation of a small deformation strain of 2% shown in Fig. 4. Therefore, the stress field easily induces the two-way shape memory effect. However, two-way shape memory strain in the experimental alloy is small compared with that obtained in the TiNi alloy by the conventional training methods. The maximum two-way shape memory strain obtained in the present work is only 0.88%, while with the same training method about 3% two-way shape memory strain can be obtained in the aged Ti–51.0 at.% Ni alloy aged at 773 K for 1 h [23]. It is suggested that the dislocation slip also damages the two-way shape memory effect to some extent due to its obstruction to the movement of the boundaries between the parent phase and martensite. The increase in the two-way shape memory strain with increasing the bending deformation strain is closely related to the extent of the dislocation slip.

2) The stabilization of the two-way shape memory effect of the Ti\(_{36}\)Ni\(_{49}\)Hf\(_{15}\) alloy is worse than that of the TiNi alloys. It is shown in Fig. 11 that the two-way shape memory strain decreases to 0.2% after 30 thermal cycles, corresponding to the 46.5% of the initial value before the thermal cycling. However, in the Ti–51.0 at.% Ni alloy aged at 773 K for 1 h, its two-way shape memory strain obtained by the shape memory training with 8% training strain decreases slightly from 2.86 to 2.73% after 100 thermal cycles [23]. The poor stability of the two-way shape memory effect in the Ti\(_{36}\)Ni\(_{49}\)Hf\(_{15}\) alloy is attributed to the introduction of the dislocations during the thermal cycling that relax the original oriented stress.
field. TEM observation has found that the substructure of the martensite of Ti36Ni49Hf15 alloy is mainly (001) compound twins [9]. In accordance to the theory of Kudo et al. [24], the slip of a/2 on (001) is involved during the formation of the (001) compound twin. As a result, it is understandable that a lot of dislocations are introduced during the repeated phase transformations. These dislocations destroy the original dislocation configuration created by martensite deformation or training process and deteriorate the two-way shape memory effect of the Ti36Ni49Hf15 alloy. According to the above discussion, the easy introduction of the dislocation slip should be responsible for the easy creation and the instability of the two-way shape memory effect in the Ti36Ni49Hf15 alloy. The experimental results indicate that the internal stress field is created by the dislocation slip is directional. Hence the preferentially oriented martensite variants are formed in the directions of the internal stress field upon cooling. In the subsequent thermal transformation cycles, the newly generated dislocations change the oriented stress field leading to the decrease of the two-way shape memory effect. So any methods that can prohibit the slip of the dislocations in the matrix would benefit the increase of the two-way shape memory effect and the improvement of its stability. Adding the fourth element (such as Cu [25], Re [26], etc.) into the TiNiHf alloy, proper heat-mechanical treatment and aging maybe the other effective methods to achieve this, which study is being undergone by the present authors.

4. Conclusions

The martensite deformation is an effective method to introduce a two-way shape memory effect in the TiNiHf alloy. The two-way shape memory strain increases with increasing deformation strain. When the TiNiHf alloy is deformed at full martensite state, the martensite reorientation process is accompanied by the dislocation slip. The oriented stress field formed by the dislocation slip is considered to be responsible for the generation of two-way shape memory effect.

Training process and aging increase the two-way shape memory effect of the Ti36Ni49Hf15 high temperature SMA. This is attributed to that the training and aging are beneficial to the formation of the oriented stress field. The two-way shape memory strain decrease continuously when increasing the deformation temperature during training.

The stability of the two-way shape memory effect in the Ti36Ni49Hf15 high temperature SMA is poor due to its lower strength of martensite. During the thermal phase transformation cycles, the dislocations are easy to be introduced and damage the orientated stress field.

References