Shape memory properties of the Ti$_{36}$Ni$_{49}$Hf$_{15}$ high temperature shape memory alloy


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Abstract

The shape memory properties have been studied in a Ti$_{36}$Ni$_{49}$Hf$_{15}$ high temperature shape memory alloy (SMA) by bending tests. The shape memory effect (SME) of the alloy is closely related to the deformation condition. It shows about 3% completely reversible strain when the TiNiHf alloy is deformed at the room temperature. The shape recovery ratio is constant at 92% when the deformation temperature is below 457 K, then rapidly decreases to zero above 590 K for the specimen deformed to 4.5%. Obvious two-way shape memory effect (TWSME) is obtained in the Ti$_{36}$Ni$_{49}$Hf$_{15}$ alloy aged at 973 K for various hours. As the aging time further increases, the TWSME decreases. Moreover, TWSME in the aged Ti$_{36}$Ni$_{49}$Hf$_{15}$ alloy is unstable and decreases rapidly after several thermal cycles. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ternary Ti–Ni–Hf alloys are newly developed high temperature shape memory alloys (SMAs) and we recognized the potential of these materials for high temperature applications. TiNiHf alloys exhibit better shape memory properties than other TiNiX (X = Pt, Pd, Au, Zr) and NiAl high temperature SMAs with the close martensitic transformation temperature [1–4]. But until now, no systematic studies about the shape memory effect (SME) except for the effect of the Hf content on the SME [5] were reported.

In the present work, the shape recovery properties, the effect of deformation strain and deformation temperature on the one-way SME, and two-way shape memory effect (TWSME) are studied in detail in the Ti$_{36}$Ni$_{49}$Hf$_{15}$ high temperature SMA.

2. Experiment

A Ti$_{36}$Ni$_{49}$Hf$_{15}$ alloy was prepared by consumable arc-melting under an Ar atmosphere in a water-cooled copper crucible of 60 mm in diameter. The
The electrode was a compaction of 99.92 wt.% sponge Ti, 99.95 wt.% electrolytic Ni plate and 99.90 wt.% Hf shot. The ingot was then remelted twice to ensure composition homogeneity by a levitation method under an Ar atmosphere, and the melt was poured into a graphite mold of 35 mm in diameter. After homogenized at 1223 K for 1.5 h, the ingot was hot rolled into a plate of 2.1-mm thickness, 0.45 × 1 × 55 mm³ specimens were cut in the rolling direction, mechanically polished and solution treated at 1173 K for 1 h. The phase transformation temperatures of the solution-treated alloy were determined by differential scanning calorimeter DSC to be $M_s = 421$ K, $M_f = 452$ K, $A_s = 489$ K, $A_f = 504$ K.

The SME was examined by bending tests, as systematically shown in Fig. 1. One end of the strip sample was clipped at the center of the plate. The specimen was first heated to above $A_f$ temperature, then cooled to the selected temperature, subsequently bent to different strains and finally heated to 600 K. The pre-strain is estimated by $\epsilon = h/(d + h)$. The recovery ratio was calculated as $R = (\theta_f - \theta_h)/\theta_d \times 100\%$.

The TWSME was obtained by aging the specimens at 973 K for 5, 10, 20, 40, 80, and 120 h, respectively. The aged specimens are first deformed against the cylindrical rod to a given constant strain at room temperature, then heated to 550 K after unloading and finally the specimen quenched into silicone cooling oil. Subsequently, the specimens were cycled from 293 to 550 K several times. At each cycle, the TWSME was measured by the values of $\theta_{rm}$ ($\theta_{rm} = \theta_m - \theta_h$).

3. Results and discussion

3.1. Deformation strain dependence on the shape recovery ratio

Two typical shape recovery characteristic curves for the specimens bent to 2.5% and 4.5% at the ambient temperature are shown in Fig. 2a and b, respectively. It can be seen that the alloy shows a perfect recovery for the specimen with 2.5% pre-strain and a 91% recovery for the specimen with 4.5% pre-strain. The shape recovery starts at about 490 K, then performs rapidly from 500 to 520 K and reaches a plateau when the temperature is higher than 520 K.

Fig. 2b shows that the variation of the shape recovery ratio $R$ with the deformation strain for the Ti$_{50}$Ni$_{40}$Hf$_{15}$ alloy bent at 293 and 373 K, respectively. It is very clear that the $R$ is strongly dependent on the deformation strain. At 293 K, the speci-
men can completely recover to its original shape, as the deformation strain is less than 3%. With increasing deformation strain, the shape recovery ratio decreases slowly and the maximum recovery ratio simply reaches about 80%, as the total deformation strain is about 6%. The change of $R$ with the deformation strain for the specimen deformed at 373 K is similar to that at 293 K. The only difference is that the completely recoverable strain for the alloy deformed at 373 K decreases to 92% compared with that at 293 K.

The present experimental alloy only shows a completely recoverable strain of 3%, which is obviously smaller than that of 8% in TiNi alloys [6] and a little bigger than that in NiAl alloy [4] and TiPdX (X = Cr, Fe, Ni) alloys [7–9]. In the Ti$_{36}$Ni$_{49}$Hf$_{15$ alloy, the dominant substructure of martensite variant is (001) stacking faults and (001) compound twins [10], which is always considered as a deformation twin in TiNi binary alloys [11,12]. The formation of the (001) compound twin might develop in the slip of $a/2$ on the (001) plane according to Kudoh et al. [13], which indicates that a large amount of irreversible defects might exist in the TiNiHf (001) twinning martensite. These defects in the martensite variant would impede the movement of martensite inter-variants boundaries and twin boundaries during the reorientation of the martensite variant and/or detwinning, which will lead to irreversible plastic deformation and the decrease of the recovery ratio when the deformation strain exceeds 3%.

3.2. Deformation temperature dependence on the shape recovery ratio

Fig. 3 shows the effect of deformation temperature on the shape recovery ratio for the Ti$_{36}$Ni$_{49}$Hf$_{15$ alloy deformed to 4.5%. Obviously, the shape recovery ratio is almost constant and then decreases with the increase in the deformation temperature. Fig. 3 can be divided into three stages according to the different deformation modes, whose shape is very similar to that in the TiNiNb [14] and TiNiPd [15] alloys.

Stage I: below 457 K ($M_s$). The recovery ratio does not change with the increase in the deformation temperature in this temperature range. Its deformation mode is believed to reorient the martensite variant and/or detwinning in the low temperature range (below $M_s$). With an increase in the deformation temperature, the critical stress for dislocation slip decreases rapidly and is lower than that for the reorientation of the martensite variant. Therefore, the irreversible strain induced by deformation remains almost constant, which results in the recovery ratio hardly changing when the specimen is deformed in this stage.

Stage II: 457–590 K (590 K, the $M_s'$ temperature of the Ti$_{36}$Ni$_{49}$Hf$_{15$ alloy [16], at which the critical stress for stress-induced martensite transformation is equal to the yield strength of the parent phase). The specimens were heated to 590 K and then cooled to the selected temperature to ensure that the specimens were completely in an austenite state. In this stage, the shape recovery ratio decreases rapidly as the deformation temperature increases. The deformation mode involves stress-induced martensitic (SIM) transformation. The critical stress for SIM transformation increases with the increase in the deformation temperature, while that for the dislocation slip decreases. As a result, the SIM transformation and the slip deformation occur simultaneously during the process of bending, which leads to the irreversible permanent deformation of the parent phase. Clearly, the decrease of the shape recovery ratio is mainly attributed to the increase in the yield stress of the parent phase and the introduction of the dislocation slip.

Stage III: above 590 K. The shape recovery ratio remains zero in this stage. The deformation mode is
the plastic deformation of the parent phase. Above 590 K, the critical stress for SIM transformation is higher than that for the dislocation slip in the TiNiHf alloy. Therefore, the parent phase is deformed plastically and the strain cannot recover.

3.3. Two-way shape memory property

The TWSMEs are observed in both the solution-treated and the aged TiNiHf alloy. In the solution-treated alloy, the TWSME is very weak (θw = 3–4°) and difficult to be precisely detected, whereas in the aged alloy the TWSME is very obvious, as depicted clearly in Fig.4. The curve of θw, with the aging time for the specimens aged at 973 K, is plotted in Fig. 4a, which demonstrates that the TiNiHf alloy shows a maximum TWSME (θw = 17°) when aged at 973 K for 5 h. With further increase in the aging time, θw decreases and reaches about 9° when the aging time is 120 h.

The TWSME in the aged TiNiHf alloy is found to be unstable. It decreases as the number of the thermal cycles increases. In Fig. 4b, it is evident that θw decreases rapidly in the first several cycles, and then slowly reaches a stable value as the number of cycles increases further. The phenomenon may be explained by a change of the dislocation configuration in the aged specimen [17]. Generally, the TWSME originates from the complex dislocation arrays caused by bending deformation. These dislocations form a stress field that is beneficial to the forward and reverse transformations of preferentially oriented martensites under thermal cycles. In the present alloy, the decrease of the TWSME after several thermal cycles probably lies in the change of dislocation patterns.

4. Conclusions

1. About 3% completely reversible strain is obtained when the TiNiHf alloy is deformed at room temperature. The relatively low shape recovery ratio at different temperatures lies mainly in the high critical stress for reorientation of the martensite variant and/or detwinning and the low critical stress for the dislocation slip.

2. The shape recovery ratio of the TiNiHf alloy remains constant and then decreases with an increase in the deformation strain as the alloy is deformed at 293 and 373 K, respectively.

3. The shape recovery ratio of the TiNiHf alloy remains almost constant when the temperature is below 457 K (Mₐ), then decreases rapidly and finally reaches zero above 590 K (Mₐ'). The different deformation modes should be responsible for the variation of the recovery ratio with the deformation temperature.

Obvious TWSME is observed in the TiNiHf alloy aged at 973 K for different hours. With an increase in the aging time, the TWSME deteriorates. The TWSME is unstable, which decreases while increasing the number of thermal cycles.

References