Phase transition, structure and shape memory effect of $Ni_{47}Ti_{43}Hf_{10}$ alloy*

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Abstract A $Ni_{47}Ti_{43}Hf_{10}$ high temperature shape memory alloy is fabricated. The martensitic transformation temperature (TT) is obtained by differential scanning calorimetry and four-probe electrical resistivity measurements. The effect of thermal cycling is investigated and it is found that the TT tends to be stable quickly, which is of benefit to practical applications. The martensite structure is determined to be B19′ monoclinic by X-ray diffraction and transmission electron microscopy. One-way and two-way (which is seldom reported before) shape memory properties are studied by tensile and bending tests. The cycling number of two-way shape memory effect is tested for more than 20000 times.

Keywords: **$Ni_{47}Ti_{43}Hf_{10}$ alloy, phase transition, structure, two-way shape memory effect.**

In recent years, smart materials have attracted much attention in space and aerospace technology and in a variety of other engineering fields[1]. Shape memory alloys (SMAs) belong to these materials because of their unique ability to remember and recover their original shape with their energetic recovery power and precise shape-temperature-stress response under certain conditions. However, the operating temperature of most currently used SMAs is limited to 373 K by their thermoelastic martensitic transformation. This unfortunately hinders the application of SMAs in high temperature environment. So great efforts have been made to develop high temperature SMAs.

Russell et al.[2] have made a comparison of the fabrication cost for various potential high temperature SMAs and found that Ni-Ti-Hf alloys are the best candidates. Although a lot of studies on NiTiHf alloys have been carried out, there are some conflicting reports on certain issues in the Hf substitution ranging from 6 at. % to 15 at. %[3~7], such as the martensite structure and the phase transition sequence. And the two-way shape memory effect (SME) has seldom been reported.

In this study, a $Ni_{47}Ti_{43}Hf_{10}$ high temperature shape memory alloy has been fabricated and its martensitic transformation, structure and SME are investigated. The thermal cycling stability is checked. Both one-way and two-way SME have been observed in tensile and bending tests. The cycling number of the two-way SME has been tested more than 20000 times in a bending experiment.

1 Experiments

To fabricate the high temperature shape memory alloy with transformation temperature higher than 373 K, a $Ni_{47}Ti_{43}Hf_{10}$ alloy was melted by the floating method in a vacuum cold crucible. To reduce the cost, Ni plates, Ti plates and Hf wires with purity of 99.9% were used as raw materials. After six times of remelting, the ingot was homogenized at 1237 K for 24 h, followed by air cooling without subsequent thermomechanical treatment. Specimens for measurements were prepared by spark cutting and the surface oxide was etched by a chemical solution ($HF:HNO_3:H_2O = 1:2:10$). The phase transformation temperatures were determined by a Rigaku PTC-10A differential scanning calorimeter and four-probe electrical resistivity measurements. The lattice structure of the

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alloy was determined by a Rigaku D/max-ra X-ray diffractometer and a JEOL-2000EX transmission electron microscope. The SME was investigated in tensile and bending experiments.

2 Results and discussion

Fig. 1 shows a typical differential scanning

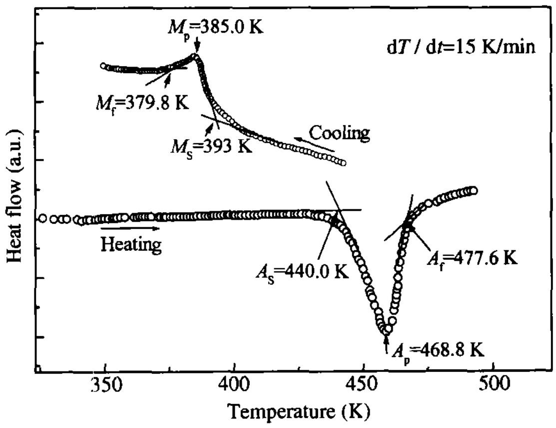

Fig. 1. The first thermal cycle DSC curve of $Ni_{47}Ti_{43}Hf_{10}$ alloy.

calorimetry (DSC) curve of $Ni_{47}Ti_{43}Hf_{10}$ in the first cycle for the forward and reverse transformations. The heating curve shows that the transformation of martensite to the parent phase is endothermic with $A_s = 440.0$ K, $A_f = 477.6$ K and the peak temperature $A_p = 468.8$ K. The cooling curve in Fig. 1, however, shows an exothermic transformation with $M_s = 393.0$ K, $M_f = 379.8$ K and $M_p = 385.0$ K. In many applications, SMAs are subjected to repeated cycling, either by heating and cooling, or by loading and unloading. Therefore, the thermal cycling stability of the shape memory behavior has to be considered. The stabilization of transformation temperature (TT) occurs within the first four cycles. Afterwards, only a small decrease is shown. It is known that thermal cycling effects are caused by defects and internal stress induced during fabrication and subsequent thermomechanical treatment. After sufficient cycling, when the defects are stabilized and the internal stress relaxed, the TT tends to be stabilized. Wu et al.[8] and Besseghini[9] have obtained results similar to our results. However, more cycles were needed to stabilize the TT in their NiTi-Hf alloys, i.e. 50 cycles in Ref. [8] and 20 in Ref. [9] respectively, as compared to only four cycles in the present work. Possibly, this difference lies in the fact that the alloys used in Refs. [8] and [9] underwent thermomechanical treatment and water quenching while no subsequent treatment was given to our $Ni_{47}Ti_{43}Hf_{10}$ alloy, so more cycles were needed to stabilize the defects and to relax the internal stress for their alloys.

Four-probe electrical resistivity measurements verified the TT obtained by DSC. Curve 1 in Fig. 2 is a typical R vs. T relation for the first cycle. From this curve we can obtain the TT's $A_s = 441.2$ K, $A_f = 477.4$ K, $M_s = 394.2$ K and $M_f = 378.3$ K, respectively. They coincide with the TT obtained by DSC method. After the TT being stable, the curve shape is unchanged except that it shifts to lower temperature (Fig. 2, curve 2).

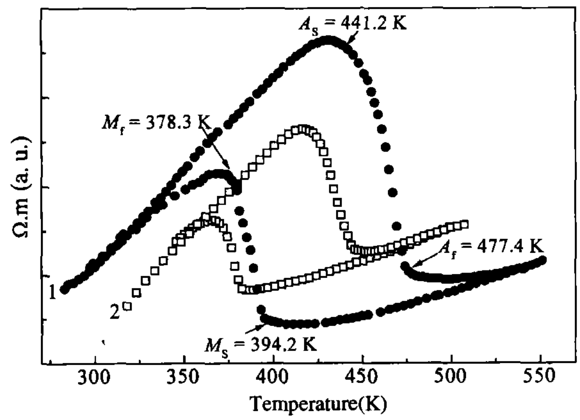

Fig. 2. R vs. T curve of $Ni_{47}Ti_{43}Hf_{10}$ alloy. Curve 1, the first cycle; 2, after TTs have been stable.

The XRD experiments indicate that the structure of the parent phase of the $Ni_{47}Ti_{43}Hf_{10}$ alloy is B2 (CsCl) type with a lattice constant $a = 0.3055$ nm and the transformed structure is B19′ monoclinic with lattice constants $a = 0.2849$ nm, $b = 0.4146$ nm, $c = 0.4669$ nm and $\beta = 98.8°$, respectively. No R-phase was observed. Fig. 3 shows the XRD pattern taken during heating, and the

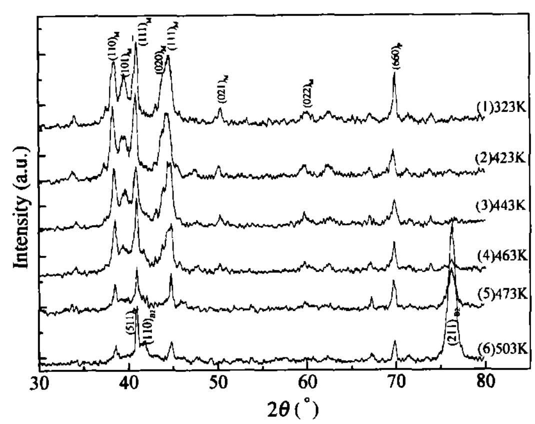

Fig. 3. XRD pattern of $Ni_{47}Ti_{43}Hf_{10}$ alloy during heating.

diffraction peaks of martensite, parent phase and precipitate are marked by subscripts of M, B2 and P, respectively. As the temperature increases, the intensities of martensite peaks decrease and those of B2 increase. The TTs obtained from XRD also coincide with those obtained by DSC. In order to confirm the results of XRD and to determine the structure of the precipitate, TEM observation was carried out at room temperature. Fig. 4 shows the electron micrograph of martensite variants and the corresponding electron diffraction patterns (EDP). It shows a $(11\bar{1})$ type-I twin relationship. Fig. 4(c) is the calculated electron diffraction pattern (EDP) of $(11\bar{1})$ twin using the lattice constants obtained from XRD. Since Fig. 4 (b) and (c) is fitting well, the martensite structure obtained by XRD is confirmed. Fig. 5 shows the TEM results of the precipitate. The precipitate is determined to be an FCC structure with space group of Fd3m and the lattice constant $a_0 = 1.129$ nm. As the structure of the precipitate has been determined, the X-ray diffraction peaks can be calculated and are marked in Fig. 3.

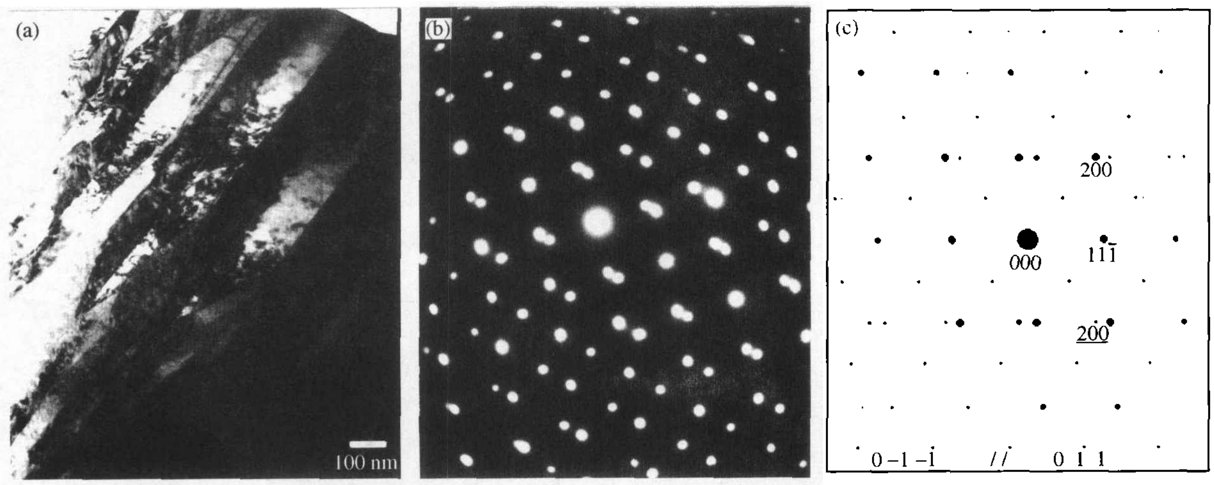

Fig. 4. Electron micrograph of martensite variants (a); the corresponding EDP(b); and calculated EDP of $(11\bar{1})$ twin using the lattice constants obtained by XRD (c).

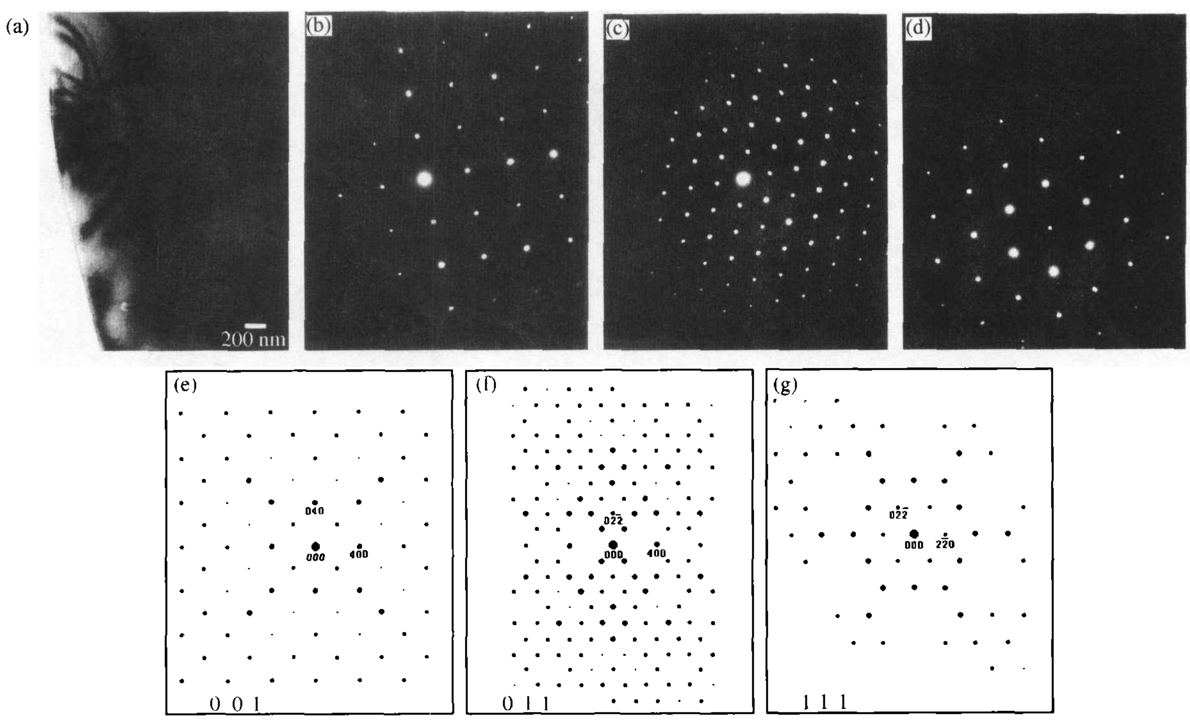

Fig. 5. TEM results of the precipitate. (a) Bright field image; (b) ~ (d) corresponding EDPs; (e) ~ (g) the calculated EDPs corresponding to (b) ~ (d).

Usually tensile tests are used to characterize the shape memory behavior of SMAs, so we performed tensile tests on the $Ni_{47}Ti_{43}Hf_{10}$ alloy by Mi-44 micromachine. When the total tensile strain (ε_t) was 1.5%, the residual strain (ε_r) was 0.4% after unloading and the recovery ratio on heating was 100%. As ε_t increased to 3%, ε_r was 0.7% and recovery ratio was 89%. In such experiment, thermal expansion will affect the shape recovery measurement. To avoid that, a bending method was used (just the same as that used in Ref. [10]). For a $Ni_{47}Ti_{43}Hf_{10}$ alloy piece of 6 cm long and 0.4 mm thick, when the bending strain is 0.13%, the recovery ratio of the one-way SME can reach 100% during heating. For the NiTiHf alloys, two-way SME has been reported only by Meng et al.[10] so far in an aged $Ti_{36}Ni_{49}Hf_{15}$ alloy. But the two-way SME of their alloy is unstable and decreases as the cycling number increases. After being trained appropriately only twice, the two-way SME could be observed in the $Ni_{47}Ti_{43}Hf_{10}$ alloy and the strain of two-way SME (ε_{tw}) was 0.06%. The cycling number of the two-way SME, which is a decisive factor for practical applications, was tested by bending. If the specimen was trained twice, it could cycle more than 3000 times, then ε_{tw} decreased. If it was trained ten times, ε_{tw} was kept at 0.06% after 10000 cycles; while ε_{tw} decreased very slightly after 20000 cycles. This decrease might be attributed to only ten times of training or surface oxidation during the cycles (the sample was heated to a temperature higher than 523 K in this bending experiment). If it was trained more times and the oxidation was avoided, the cycling number of two-way SME might be increased. Obviously, the stability of the two-way SME of the $Ni_{47}Ti_{43}Hf_{10}$ alloy is better than that of the materials previously reported. Although it did not undergo any thermomechanical treatment (except for training), the $Ni_{47}Ti_{43}Hf_{10}$ alloy could manifest very good SME.

Taking account of the long cycling number of the two-way SME and the low fabrication cost (raw materials are of only 99.9% purity without subsequent treatments), the $Ni_{47}Ti_{43}Hf_{10}$ alloy could have a potential commercial value as high temperature SMAs.

3 Conclusion

A $Ni_{47}Ti_{43}Hf_{10}$ high temperature shape memory alloy has been fabricated with transformation temperatures $A_s = 440.0$ K, $A_f = 477.6$ K, $M_s = 393.0$ K and $M_f = 379.8$ K. The thermal cycling behavior has been investigated and the results demonstrate that it has very good thermal cycling stability. Through XRD and TEM observations, the structure of the martensite has been determined to be B19′ monoclinic with lattice constants $a = 0.28485$ nm, $b = 0.4146$ nm, $c = 0.4669$ nm and $\beta = 98.8°$, and that of the precipitate is $a_0 = 1.129$ nm with the space group of Fd3m. One-way and two-way SMEs have been observed in the tensile and bending tests. The cycling number of two-way SME are more than 20000 times.

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