Influence of Fe Addition on Phase Transformation, Microstructure and Mechanical Property of Equiatomic NiTi Shape Memory Alloy

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Abstract Based on equiatomic nickel and titanium, three kinds of NiTiFe alloys with a nominal chemical composition of $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$, $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$ and $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$ (at.%), respectively, have been designed to investigate the influence of the addition of Fe element on phase transformation, microstructure and mechanical property of equiatomic NiTi shape memory alloy. The microstructures of three kinds of NiTiFe alloys are characterized by the equiaxed grains instead of the dendrites. Consequently, some Ti_2Ni precipitates are found to distribute in the grains interior and at the grain boundaries. The content of Fe element has an important influence on mechanical property of NiTiFe alloy. With increasing content of Fe element, the strength of NiTiFe alloy increases substantially, but the plasticity decreases sharply. It can be concluded that precipitation strengthening and solution strengthening play a significant role in enhancing the strength of NiTiFe alloy. In the case of three NiTiFe alloys, neither martensitic transformation nor reverse transformation can be observed in the range from -150 to 150 °C. On the one hand, the phase transformation temperature is probably out of the scope of the present experimental temperature. On the other hand, the addition of Fe element probably suppresses first-order martensitic transformation or reverse transformation, and consequently the second-order-like phase transformation from an incommensurate stage to a commensurate stage can probably take place.

KEY WORDS: Shape memory alloy; Mechanical property; Microstructure; Phase transformation

1 Introduction

More and more attention has been paid to NiTi shape memory alloy because of its shape memory effect and superelasticity [1, 2]. The phase transformation temperature plays an important role in the engineering application of NiTi shape memory alloy. In general, the phase transformation

temperature of NiTi shape memory alloy is closely related to chemical composition, heat treatment and plastic processing history [3, 4]. In particular, the addition of a third element to the binary NiTi shape memory alloy has a significant influence on the phase transformation temperature [5]. Even the addition of a third element to the binary NiTi shape memory alloy can alter the phase transformation path of NiTi shape memory alloy [6]. For example, the addition of Cu to the binary NiTi shape memory alloy is capable of diminishing the phase transformation temperature hysteresis [7, 8]. However, the substitution of Nb element for Ni element in the binary NiTi shape memory alloy contributes to the enhancement of the phase transformation temperature hysteresis [9, 10]. The addition of Co to the binary NiTi shape memory alloy can change the microstructure as well as the phase transition and thus improve its corrosion resistance [11]. The additions of Pt, Pd, Zr and Hf elements to the

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binary NiTi shape memory alloy are able to enhance the reverse phase transformation temperature, which lays the foundation for developing high-temperature shape memory alloy [12–15]. The substitution of Fe element for Ni element in the binary NiTi shape memory alloy contributes to lowering the martensitic transformation start temperature [16–18]. So far, researchers have been more and more interested in the NiTiFe shape memory alloy. In addition to phase transformation of NiTiFe shape memory alloy, researchers have performed a deep investigation with respect to damping characteristic, fatigue life, deformation behavior and dynamic recrystallization of NiTiFe shape memory alloy [19–22].

In the present study, the addition of Fe element to equiatomic NiTi shape memory alloy was implemented and phase transformation, microstructure and mechanical property of the resultant NiTiFe alloy were investigated.

2 Materials and Methods

Equiatomic Ni₅₀Ti₅₀ (at.%) shape memory alloy and three kinds of NiTiFe alloys, which possess a nominal chemical composition of Ni_{50-x/2}Ti_{50-x/2}Fe_x (at.%) where *x* stands

for 2, 4 and 6, respectively, were designed to investigate the influence of the addition of Fe element on phase transformation, microstructure and mechanical property of equiatomic NiTi shape memory alloy. For the sake of convenience, three kinds of NiTiFe alloys are designated as Ni₄₉Ti₄₉Fe₂, Ni₄₈Ti₄₈Fe₄ and Ni₄₇Ti₄₇Fe₆ in the following context, respectively. Three kinds of NiTiFe alloys were melted by means of vacuum arc melting method. Subsequently, the as-cast Ni₅₀Ti₅₀ and NiTiFe alloys were hold for 12 h at 1000 °C and then were quenched into ice water. Then, the chemical composition of three NiTiFe alloys was examined by energy dispersive spectroscopy (EDS). The results showed that the actual chemical compositions of Ni₄₉Ti₄₉Fe₂, Ni₄₈Ti₄₈Fe₄ and Ni₄₇Ti₄₇Fe₆ alloys correspond to Ni_{48.87}Ti_{49.12}Fe_{2.01}, Ni_{47.89}Ti_{48.20}Fe_{3.91} and Ni_{47.21}Ti_{46.80}Fe_{5.99} (at.%), respectively. The solution-treated Ni₅₀Ti₅₀ and NiTiFe alloy samples with the height of 6 mm and the diameter of 4 mm were cut from the solution-treated NiTiFe alloys ingots by electro-discharge machining (EDM) for compression tests. The compression tests were carried out on the INSTRON-5500R universal material testing machine, where the samples were compressed at the strain rate of 0.001 s⁻¹ and at room temperature.

Fig. 1 DSC curves of Ni₅₀Ti₅₀ and NiTiFe alloys: **a** Ni₅₀Ti₅₀; **b** Ni₄₉Ti₄₉Fe₂; **c** Ni₄₈Ti₄₈Fe₄; **d** Ni₄₇Ti₄₇Fe₆

The phase transformation of the solution-treated Ni₅₀Ti₅₀ and NiTiFe alloys was analyzed by differential scanning calorimetry (DSC). DSC test was performed in the range from -150 to 150 °C at the heating and cooling rates of 10 °C/min.

Microstructures of the solution-treated Ni₅₀Ti₅₀ and NiTiFe alloys were characterized by scanning electron microscopy (SEM, FEI Quanta 200) and transmission electron microscopy (TEM, FEI TECNAI G2 F30, 300 kV). The specimens for SEM observation were etched in a solution of HF:HNO₃:H₂O = 1:2:10. In addition, the phase composition was obtained by X-ray diffraction (XRD, X-pert PRO). Foils for TEM observation were mechanically ground to 70 μm and then thinned by twin-jet polishing in an electrolyte consisting of 6% HClO₄, 34% C₄H₁₀O and 60% CH₃OH by volume fraction.

3 Results

3.1 Phase Transformation of Ni₅₀Ti₅₀ and NiTiFe Alloys

Figure 1 indicates DSC curves of Ni₅₀Ti₅₀, Ni₄₉Ti₄₉Fe₂, Ni₄₈Ti₄₈Fe₄ and Ni₄₇Ti₄₇Fe₆ alloys. It can be found that in the case of heating and cooling in the temperature range from -150 to 150 °C, Ni₅₀Ti₅₀ alloy exhibits the phase transformation, whereas three kinds of NiTiFe alloys do not exhibit any phase transformation.

3.2 SEM Analysis of Ni₅₀Ti₅₀ and NiTiFe Alloys

Figure 2 shows SEM micrographs of Ni₅₀Ti₅₀, Ni₄₉Ti₄₉Fe₂, Ni₄₈Ti₄₈Fe₄ and Ni₄₇Ti₄₇Fe₆ alloys. It can be observed

Fig. 2 SEM micrographs of Ni₅₀Ti₅₀ and NiTiFe alloys: **a** Ni₅₀Ti₅₀; **b** Ni₄₉Ti₄₉Fe₂; **c** Ni₄₈Ti₄₈Fe₄; **d** Ni₄₇Ti₄₇Fe₆

Fig. 3 XRD patterns of $\text{Ni}_{50}\text{Ti}_{50}$ and NiTiFe alloys: **a** $\text{Ni}_{50}\text{Ti}_{50}$; **b** $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$; **c** $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$; **d** $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$

that the dendrites are dominant in the microstructure of $\text{Ni}_{50}\text{Ti}_{50}$ alloy, whereas the microstructures of three kinds of NiTiFe alloys are characterized by the equiaxed grains instead of the dendrites. In the case of three NiTiFe alloys, in particular, some precipitates are distributed in the grains interior and at the grain boundaries.

3.3 XRD Analysis of $\text{Ni}_{50}\text{Ti}_{50}$ and NiTiFe Alloys

Figure 3 illustrates XRD patterns of $\text{Ni}_{50}\text{Ti}_{50}$, $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$, $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$ and $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$ alloys. B2 austenite phase and B19' martensite phase coexist in $\text{Ni}_{50}\text{Ti}_{50}$ alloy, whereas each of three NiTiFe alloys is composed of B2 austenite phase.

3.4 TEM Analysis of $\text{Ni}_{50}\text{Ti}_{50}$ and NiTiFe Alloys

Figure 4 shows TEM micrograph and the corresponding selected area electron diffraction (SAED) pattern of $\text{Ni}_{50}\text{Ti}_{50}$ alloy. B19' martensite phase is dominant in $\text{Ni}_{50}\text{Ti}_{50}$ alloy. Furthermore, plenty of twins are distributed in the martensite matrix. Figures 5, 6 and 7 show TEM micrographs and the corresponding SAED patterns of NiTiFe alloys. Figure 5 shows that $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$ alloy consists of

B2 austenite phase and Ti_2Ni precipitate phase. In particular, Ti_2Ni precipitate phase keeps a certain orientation relationship with B2 austenite matrix, as shown in Fig. 5b. In addition, as for $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$ alloy, Ti_2Ni precipitate phase occurs at the grain boundaries of the B2 austenite matrix (Fig. 6). However, in the case of $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$ alloy, some dislocations appear in the B2 austenite matrix, as shown in Fig. 7. This phenomenon indicates that the increase in the content of Fe element contributes to the unbalanced crystallization of NiTiFe alloy. Furthermore, the Ti_2Ni precipitate phase in the $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$ alloy exhibits an apparently different shape compared with $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$ and $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$ alloys.

3.5 Mechanical Property of $\text{Ni}_{50}\text{Ti}_{50}$ and NiTiFe Alloys

Figure 8 illustrates compressive stress–strain curves of $\text{Ni}_{50}\text{Ti}_{50}$, $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$, $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$ and $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$ alloys. It can be noted that the stress–strain curve of $\text{Ni}_{50}\text{Ti}_{50}$ alloy agrees well with one of NiTi shape memory alloy with martensite phase. In other words, $\text{Ni}_{50}\text{Ti}_{50}$ alloy experiences elastic deformation of martensite, reorientation and detwinning of martensite, elastic deformation of reoriented

Fig. 4 TEM micrographs of $\text{Ni}_{50}\text{Ti}_{50}$ alloy: **a** bright field image; **b** SAED pattern from **a** showing the existence of B19' martensite phase

Fig. 5 TEM micrographs of $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$ alloy: **a** bright field image; **b** SAED pattern from **a** showing Ti_2Ni precipitate in the B2 austenite matrix

Fig. 6 TEM micrographs of $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$ alloy: **a** bright field image showing Ti_2Ni precipitate at the grain boundary of the B2 austenite matrix; **b** SAED pattern of B2 austenite matrix from **a**; **c** SAED pattern of Ti_2Ni precipitate from **a**

Fig. 7 TEM micrographs of $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$ alloy: **a** bright field image showing B2 austenite matrix; **b** SAED pattern of B2 austenite matrix from **a**; **c** bright field image showing the existence of Ti_2Ni precipitate; **d** SAED pattern of Ti_2Ni precipitate from **c**

Fig. 8 Compressive stress–strain curves of $\text{Ni}_{50}\text{Ti}_{50}$ and NiTiFe alloys

and detwinned martensite and plastic deformation of reoriented and detwinned martensite based on dislocation slip. As for three kinds of NiTiFe alloys, the strength

increases but the plasticity decreases with increasing content of Fe element. In addition, in terms of the shape of stress–strain curve, NiTiFe alloys exhibit a substantial distinction from equiatomic NiTi shape memory alloy. In addition, it can be seen from Fig. 9 that $\text{Ni}_{50}\text{Ti}_{50}$ and NiTiFe alloys exhibit a characteristic of brittle fracture. Furthermore, NiTiFe alloys exhibit a more apparent brittle fracture characteristic with increasing content of Fe element.

4 Discussion

It is well known that equiatomic NiTi shape memory alloy generally exhibits one-stage phase transformation in the case of heating and cooling. On the one hand, equiatomic NiTi shape memory alloy is transformed from B2 austenite phase into B19' martensite phase upon cooling. On the other hand, it is transformed from B19' martensite phase into B2 austenite phase upon heating. It has been reported

Fig. 9 Fractographs of Ni₅₀Ti₅₀ and NiTiFe alloys: **a** Ni₅₀Ti₅₀; **b** Ni₄₉Ti₄₉Fe₂; **c** Ni₄₈Ti₄₈Fe₄; **d** Ni₄₇Ti₄₇Fe₆

in the literature that the substitution of Fe for Ni in the NiTi shape memory alloy contributes to lowering the martensitic transformation start temperature M_s . It can generally be accepted that NiTiFe shape memory alloy has frequently been used for shape memory alloy pipe coupling to guarantee the reliability of pipe coupling during service. However, in the present study, the substitution of Fe element for Ni and Ti elements on the basis of equiatomic NiTi shape memory alloy is performed to investigate the influence of Fe on the phase transformation of NiTi shape memory alloy. Unfortunately, no phase transformation can be observed in the case of three NiTiFe alloys, including Ni₄₉Ti₄₉Fe₂, Ni₄₈Ti₄₈Fe₄ and Ni₄₇Ti₄₇Fe₆ alloys. In other words, neither martensitic transformation nor reverse transformation can be found in the case of three NiTiFe alloys. For further clarifying the phase transformation of NiTiFe alloys, it is necessary to obtain the knowledge involved in the case of transformation thermodynamics. In

general, in the case of martensitic transformation, the variation of Gibbs free energy $\Delta G^{P \rightarrow M}$ can be expressed as follows:

$$\Delta G^{P \rightarrow M} = \Delta G_C^{P \rightarrow M} + \Delta G_E^{P \rightarrow M}, \quad (1)$$

where $\Delta G_C^{P \rightarrow M}$ is the variation of chemical free energy, which is the driving force for transformation from austenite to martensite, and $\Delta G_E^{P \rightarrow M}$ is the variation of the elastic strain energy, which is the resistance for transformation from austenite to martensite.

However, in the case of reverse martensitic transformation, the variation of Gibbs free energy $\Delta G^{M \rightarrow P}$ can be expressed as follows:

$$\Delta G^{M \rightarrow P} = \Delta G_C^{M \rightarrow P} + \Delta G_E^{M \rightarrow P}, \quad (2)$$

where $\Delta G_C^{M \rightarrow P}$ is the variation of chemical free energy, which is the chemical driving force for transformation from martensite to austenite, and $\Delta G_E^{M \rightarrow P}$ is the variation of the

elastic strain energy, which is the mechanical driving force for transformation from martensite to austenite.

It can be found from Eq. (1) that it is necessary to enhance the resistance for transformation from austenite to martensite in order to lower the martensitic transformation start temperature M_s . In the same manner, according to Eq. (2), it is necessary to diminish the mechanical driving force for transformation from martensite to austenite so as to enhance the austenitic transformation start temperature A_s . Therefore, the elastic strain energy stored in the martensite phase plays a significant role in the phase transformation of NiTi shape memory alloy [23]. In general, the conventional NiTiFe shape memory alloy is designed by replacing Ni element by Fe element to lower the martensitic transformation start temperature M_s . As for a typical $\text{Ni}_{47}\text{Ti}_{50}\text{Fe}_3$ shape memory alloy, a two-stage transformation can occur in the case of cooling. In particular, R-phase transformation is able to take place prior to the subsequent martensitic transformation [1]. With the decrease in the content of Fe element, $\text{Ni}_{48}\text{Ti}_{50}\text{Fe}_2$ shape memory alloy exhibits the two-stage transformation in the case of heating and cooling. The two-stage transformation corresponds to the transformation from B2 austenite to R-phase and then the transformation from R-phase to B19' martensite in the case of cooling, while two-stage transformation corresponds to the transformation from B19' martensite to R-phase and then the transformation from R-phase to B2 austenite in the case of heating [24]. With the increase in the content of Fe element, when the content of Fe element is equal to or more than 6% by atomic fraction, no phase transformation can be observed in the case of heating and cooling. The phenomenon is attributed to the proposition that NiTiFe shape memory alloy exhibits the second-order-like phase transformation from an incommensurate stage to a commensurate stage instead of first-order phase transformation containing R-phase transformation [25, 26]. In the case of three NiTiFe alloys, including $\text{Ni}_{49}\text{Ti}_{49}\text{Fe}_2$, $\text{Ni}_{48}\text{Ti}_{48}\text{Fe}_4$ and $\text{Ni}_{47}\text{Ti}_{47}\text{Fe}_6$, the substitution of Fe element for Ni and Ti elements on the basis of equiatomic NiTi shape memory alloy probably suppresses the occurrence of the first-order phase transformation. In other words, neither martensitic transformation nor reverse transformation can be observed in the temperature range from -150 to 150 °C. On the one hand, the phase transformation temperature is probably out of the scope of the present experimental temperature. On the other hand, the addition of Fe element seems to suppress first-order martensitic transformation or reverse transformation, and consequently the second-order-like phase transformation from an incommensurate stage to a commensurate stage can probably take place.

5 Conclusions

1. The microstructures of three kinds of NiTiFe alloys are characterized by the equiaxed grains instead of the dendrites. Three NiTiFe alloys are composed of B2 austenite matrix and Ti_2Ni precipitate phases. In addition, Ti_2Ni precipitates are distributed in the grains interior and at the grain boundaries.
2. The content of Fe element has an important influence on mechanical properties of NiTiFe alloys. The strength of NiTiFe alloys increases substantially with increasing content of Fe element. However, the plasticity of NiTiFe alloys decreases sharply with increasing content of Fe element. It can be concluded that precipitation strengthening and solution strengthening play a significant role in enhancing the strength of NiTiFe alloys.
3. In the case of three NiTiFe alloys, neither martensitic transformation nor reverse transformation can be observed in the range from -150 to 150 °C. On the one hand, the phase transformation temperature is probably out of the scope of the present experimental temperature. On the other hand, the addition of Fe element seems to suppress first-order martensitic transformation or reverse transformation, and consequently the second-order-like phase transformation from an incommensurate stage to a commensurate stage can probably take place.

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