Phase transformation and precipitation in aged Ti–Ni–Hf high-temperature shape memory alloys

X.L. Meng*, W. Cai, Y.F. Zheng, L.C. Zhao

Department of Materials Physics and Chemistry, School of Materials Science and Technology, Harbin Institute of Technology, Harbin 150001, China

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Abstract

More attention has been paid to ternary Ti–Ni–Hf high-temperature shape memory alloys (SMAs) due to their high phase transformation temperatures, good thermal stability and low cost. However, the Ti–Ni–Hf alloys have been found to have low ductility and only about 3% shape memory effect and these have hampered their applications. It is well known that there are three methods to improve the shape memory properties of high-temperature SMAs: (a) cold rolling + annealing; (b) adding another element to the alloy; (c) aging. These methods are not suitable to improve the properties of Ti–Ni–Hf alloys. In this paper, a method of conditioning Ni-rich Ti–Ni–Hf alloys as high-temperature SMAs by aging is presented. For Ni-rich Ti$_{80-x}$Ni$_x$Hf$_{20}$ alloys (numbers indicate at.%) the phase transformation temperatures are on average increased by more than 100 K by aging at 823 K for 2 h. Especially for those alloys with Ni contents less than 50.6 at.%, the martensitic transformation start temperatures (Ms) are higher than 473 K after aging. Transmission electron microscopy shows the presence of (Ti + Hf)$_3$Ni$_4$ precipitates after aging. Compared with the precipitation of Ti$_3$Ni$_4$ particles in Ni-rich Ti–Ni alloys, the precipitation of (Ti + Hf)$_3$Ni$_4$ particles in Ni-rich Ti–Ni–Hf alloys needs higher temperatures and longer times.

Keywords: High-temperature shape memory alloy; Ti–Ni–Hf alloy; Phase transformation; Precipitation

1. Introduction

Recently, a lot of shape memory alloys (SMAs) with high martensitic transformation temperatures have been investigated to meet the requirements of high-temperature applications [1–4]. Among them, Ti–Ni–Hf alloys have received special attention mainly due to the relative low price and excellent mechanical process properties. However, the shape memory effect (SME) of Ti–Ni–Hf alloy is only about 3% because the strength of the matrix is low. Otsuka and Ren [5] presented three methods to strengthen the matrix of TiNi-based high-temperature SMAs: (1) thermo-mechanical treatment (cold working followed by suitable annealing), (2) addition of quaternary element and (3) precipitation hardening. Up to now, the Ni content of Ti–Ni–Hf alloy is usually lower than 50 at.%. The Ti–Ni–Hf alloys with Ni content more than 50 at.% cannot be used as high-temperature SMAs because the martensitic transformation temperature would decrease sharply with increasing Ni content.

For Ti-rich Ti–Ni–Hf alloys, the first method is not suitable because of the brittleness. Moreover, it has been reported that the other methods did not improve the SME in Ti–Ni–Hf alloys [6,7].

It is well known that in the binary Ni-rich Ti–Ni alloys, the martensitic transformation temperatures and SME can be increased by the precipitation of Ti$_3$Ni$_4$ [8,9]. So we try to use Ni-rich Ti–Ni–Hf alloy as a high-temperature SMA through precipitation. On the one side, the martensitic transformation temperature would be increased if Ti$_3$Ni$_4$ type particles precipitate in the Ni-rich Ti–Ni–Hf alloys. On the other side, the matrix would be strengthened by precipitation.

In the present paper, the phase transformation behavior and the precipitation in Ni-rich Ti–Ni–Hf alloy have been investigated by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM).

2. Experimental

Ti$_{29.4}$Ni$_{50.8}$Hf$_{20}$ and Ti$_{29.2}$Ni$_{50.4}$Hf$_{20}$ alloys (numbers indicate at.%) have been prepared by arc melting the elements (≥99.9% purity) in a water-cooled copper crucible under an
Ar atmosphere (average button weight is about 100 g). The ingots were re-melted for six times and then homogenized at 1273 K for 4 h followed by air-cooling. These ingots were solution-treated at 1173 K for 1 h in vacuum and then quenched into the ice water. Plate samples were cut from the ingot with a thickness of 1 mm. Subsequently, some samples were aged at 823 K for 0.5, 1, 2, 5 and 30 h, respectively. The DSC measurements were performed using a PERKIN ELMER DSC7 calorimeter. The heating and cooling rates were 15 K/min and the temperature range is from 293 to 623 K. TEM specimens were mechanically polished to 50 μm in thickness and then electrochemically polished using an electrolyte of 20% H₂SO₄ and 80% methanol at 253 K. TEM observations were performed using a Philips CM-12 electron microscope operated at 175 kV.

3. Results and discussion

Fig. 1 shows the DSC curves of the solution-treated and aged Ti₂₉.₄Ni₅₀.₆Hf₂₀ and Ti₂₉.₂Ni₅₀.₈Hf₂₀ alloys. For the solution-treated Ti₂₉.₄Ni₅₀.₆Hf₂₀ alloy, a B₂ ↔ B₁₉′ transformation occurs during cooling and heating processes, respectively. Its Ms is only 352 K so that the solution-treated Ti₂₉.₄Ni₅₀.₆Hf₂₀ alloy cannot be used as high-temperature SMA. For the solution-treated Ti₂₉.₂Ni₅₀.₈Hf₂₀ alloy, the particulate transformation temperatures (PTTs) cannot be detected in the present experiment, which suggests its PPTs are lower than room temperature. After aging, it is seen that the PPTs of both Ti₂₉.₄Ni₅₀.₆Hf₂₀ and Ti₂₉.₂Ni₅₀.₈Hf₂₀ alloys are increased remarkably. When the Ti₂₉.₄Ni₅₀.₆Hf₂₀ alloy is aged at 823 K for 2 h, the PPTs increase more than 100 K in average. For the aged Ti₂₉.₄Ni₅₀.₆Hf₂₀ alloy, there are three characteristic features that change with aging: (1) the type of transformation changes from one step to two steps, (2) the width of the overall transformation temperature range changes from small to large, (3) there are obvious shifts in peak positions.

The effect of aging time on the PPTs in the Ti₂₉.₄Ni₅₀.₆Hf₂₀ alloy aged at 823 K is illustrated in Fig. 2. At the beginning of aging, the PPTs increase rapidly with increasing the aging time. When the aging time is more than 5 h, the PPTs change slightly with further increasing the aging time. As indicated by DSC measurements, the precipitation process may occur in the Ni-rich Ti–Ni–Hf alloys during aging at 823 K. This has been proven by the following TEM observations.

Fig. 1. DSC curves of Ni-rich Ti–Ni–Hf alloys: (a) 1173 K/1 h solution-treated Ti₂₉.₄Ni₅₀.₆Hf₂₀ alloy; (b) 823 K/2 h aged Ti₂₉.₂Ni₅₀.₈Hf₂₀ alloy; (c) 823 K/2 h aged Ti₂₉.₂Ni₅₀.₈Hf₂₀ alloy.
Fig. 2. Effect of aging time on PTTs in Ti29.4Ni50.6Hf20 alloy aged at 823 K.

Fig. 3(a) shows the TEM bright-field image of precipitates in the Ti29.2Ni50.8Hf20 alloy aged at 823 K for 5 h. Lenticular particles of a second phase are revealed. Fig. 3(b) shows the associated diffraction patterns from the precipitates. Both diffraction patterns show the characteristic precipitate spots of Ti3Ni4 type particles that subdivide the reciprocal distance associated with (213)B2 into seven intervals [8]. The diffraction patterns and EDX results obtained in the present study identify the precipitates as the (Ti+Hf)3Ni4 type.

TEM images of precipitates of (Ti+Hf)3Ni4 in Ti29.4Ni50.6Hf20 alloy aged at 823 K for different times are shown in Fig. 4. When the aging time is 1 h, some spherical particles with the size of about 10 nm are observed as shown in Fig. 4(a). With prolonging the aging time to 2 h, most particles grow to lenticular-like. Further increasing the aging time, the precipitates coarsen clearly. When the aging time is over 30 h, the size of the precipitates is more than 100 nm.

It is well known that in Ni-rich Ti–Ni alloys, the Ti3Ni4 particles fully precipitate in a temperature range from 673 to 773 K after a short time (less than 0.5 h). However, for the Ni-rich Ti–Ni–Hf alloy, the precipitation of (Ti+Hf)3Ni4 particles needs higher temperature and longer time than in Ni-rich Ti–Ni alloys. This is an important feature of precipitation of (Ti+Hf)3Ni4 particles in Ni-rich Ti–Ni–Hf alloy.

It is deduced that the diffusion of Hf and Ti in the matrix
is more difficult in the Ni-rich Ti–Ni–Hf alloy than the diffusion of Ti in Ti–Ni. A higher activation energy for precipitation of (Ti + Hf)₃Ni₄ would result in a slow rate of precipitation.

According to the results reported above, it is possible to use aged Ni-rich Ti–Ni–Hf alloy as high-temperature SMAs. For the Ti–Ni–Hf alloy with Ni concentration of about 50.6 at.%, the PTTs can be maintained at a relatively high level (above 423 K) after proper aging. The main disadvantage of Ti–Ni–Hf alloy is the lower strength of the matrix [10], which leads to a small recoverable strain. However, there is no doubt that the precipitation of (Ti + Hf)₃Ni₄ particles would strengthen the matrix. In addition, the amount of (Ti, Hf)₂Ni particles, which deteriorates the mechanical properties of the Ti–Ni–Hf alloy, decrease due to the higher Ni concentration in the present alloys. As a result, it can be forecasted that the mechanical properties and SME would be improved in Ni-rich Ti–Ni–Hf alloys after aging. Further work is being carried out by the authors of the present work.

4. Conclusions

(i) It is feasible to use Ni-rich Ti–Ni–Hf alloys as high-temperature SMAs after aging.

(ii) The PTTs of Ni-rich Ti–Ni–Hf alloys are significantly increased after aging. For Ti₂₉.₄Ni₅₀.₆Hf₂₀ alloy aged at 823 K, the PTTs increase rapidly with increasing the aging time at the beginning of the aging and then change slowly for aging time larger than 2 h.

(iii) (Ti + Hf)₃Ni₄ particles precipitate in the Ni-rich Ti–Ni–Hf alloys during aging at 823 K. With prolonging the aging time, the (Ti + Hf)₃Ni₄ particles change gradually from spherical-like to lenticular-like and then coarsen.

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References
