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Effect of Y addition on microstructure and martensitic transformation of a Ni-rich Ti–Ni shape memory alloy

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Abstract In the present work, 1 at% Y was added to Ti-50.7at%Ni alloy to prepare Ti-50.2Ni-1Y alloy and the effects of rare earth Y addition on the microstructure and martensitic transformation behavior of Ti-50.7at%Ni alloy was investigated by optical microscope, scanning electronic microscope (SEM) X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The results show the microstructure of Ti-50.2Ni-1Y alloy is different with that of Ti-50.7at.%Ni alloy, and its microstructure consists of B19′martensite and the Y-rich phase, which may be YNi phase. One-step martensitic transformation occurs in Ti-50.2Ni-1Y ternary alloy. The phase transformation temperatures increase rapidly with Y addition, and the increase of Ms is about 85°C.

Near equal-atomic Ti–Ni shape memory alloys (SMAs) are technologically important materials with outstanding shape memory effect (SME) and superelasticity. Up to now, the applications of Ti–Ni SMAs have spread many fields such as aerospace, aviation and medical field. Moreover, there is a need for shape memory alloys with high transformation temperatures for many industrial applications. It is well-known that the adding a small quantity of the third and the fourth transition metal elements such as Fe, Hf, Zr and Pd etc to Ti–Ni alloy has remarkable effect on the martensitic transformation starting temperature of Ti–Ni binary alloys (Ms), which can be increased or decreased in a large proportion [1–5]. Especially many transitional elements from the very begging (Hf and Zr) or from the end (Cu, Pd, Pt and Au) of each transition metal series often result in the increase of the martensitic transformation temperatures. Some rare earth elements have been added to Cu–Zn–Al SMAs, Fe–Mn–Si SMAs, Ni–Al alloys, Ni–Mn–Ga alloys and Ti–Ni alloys [6–9], and the researches indicate that rare earth addition can increase martensitic transformation temperatures and improve the mechanical properties. When heavy rare earth element Y is added to Ti–Ni ribbons, the Ms firstly decreases with Y content is less than 0.6 at%, and then increases with Y content increasing [10]. However, there are few researches about the effect of Y addition on the microstructure and martensitic transformation behavior of Ti–Ni binary alloy until now. The aim of this paper is to add 1 at% Y to Ti–50.7Ni alloy and study the effect of Y addition on the microstructure and martensitic transformation of Ti–50.7Ni alloy, which will be of benefit to developing high temperature shape memory alloys.

The experimental alloys were prepared by a non-consumable arc-melting furnace under an argon atmosphere using a water-cooled copper crucible. Firstly the pre-alloy with nominal composition Ti–50.7Ni is prepared by melting 200 g raw materials from 99.97 mass% sponge Ti, 99.7 mass% electrolytic Ni and then the ingot was divided into two parts, Y (99.95 mass%) was added to one part of the pre-alloy to prepare the ternary alloy with nominal composition Ti–50.2Ni–1Y. The arc melting was repeated six times to ensure the uniformity of composition, and a pure titanium ingot was melted as an oxygen getter. The specimens were spark-cut from the ingots and solution-treated at 900 °C for an hour in vacuum quartz capsules followed by quenched into water with breaking the capsules. Following the above procedure, samples were

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mechanically light polished, and then etched in a solution consisting of HF, HNO_3 and H_2O, 1:2:10 by volume.

The phase transformation temperatures of Ti–50.7Ni and Ti–50.2Ni–1Y alloys were determined by differential scanning calorimeter (DSC) using Perkin-Elmer Diamond calorimeter. The temperature range of heating and cooling investigated is from –100 °C to 150 °C with scanning rate 20 °C/min. Tangent lines in the DSC curve were made to determine the phase transformation temperatures. The morphology of the second phases was observed through CamScan MX2600FE equipped with energy dispersive X-ray spectrum (EDS) made by Oxford. The analysis of the phases in Ti–50.2Ni–1Y was applied using a Rigaku D/max-rb rotating anode X-ray diffractometer with a graphite monochromator and CuKα radiation, λ = 0.15418 nm.

In order to observe the microstructure and the distribution of rare earth Y in Ti–50.2Ni–1Y alloy, the back scattering electron images are carried out as shown in Fig. 1. It can be seen that in the binary Ti–Ni alloy, there is no second phases existing in the matrix. However, there are two different areas in the Ti–50.2Ni–1Y alloy (as seen in Fig. 1b), the gray area (the matrix) and the white phases, which is different from that of Ti–50.7Ni alloys. The white phases exhibit different morphology with different place, rod along the grain boundaries and spherical inside the grains. Because the scattering amplitude of the back scattering electron is proportional to the atomic number of the individual element, the content of Y in the white phase is higher than that in the matrix. Moreover, the content of Ti in the white phase is less than that of Y and Ni as shown in Fig. 1b. The compositions of white particles and the matrix of the experimental alloys measured by EDS qualitative analysis are listed in Table 1. It can be seen that only 0.14 at% Yttrium is detected in the matrix, which means the solid solubility of Y in Ti–Ni alloy is very low, moreover, the composition of the matrix is changed from Ni-rich to Ti-rich by Y addition. In the white phase, the ratio of Ti:Ni:Y is about 4:11:10, and the ratio of Ni:Y is about 1.

Figure 2 displays the room temperature X-ray diffraction pattern of Ti–50.2Ni–1Y alloy solution treated at 900 °C. Several martensite diffraction peaks appear, i.e., $(020)_M$, $(1\bar{1}1)_M$, $(002)_M$, and $(111)_M$ peaks, which indicate the Ti- is 50.2Ni–1Y alloy in martensite state at room temperature and the lattice type of martensite is B19′, the same as that of binary Ti–Ni alloy. Besides the characteristic peaks corresponding to B19′ martensite, the peaks at 41.15°, 42.21° and 52.49° may be related to Y-rich phase discussed above. There is no binary compound existing in the assessed Ti–Y binary phase diagram [11], and the assessed Y–Ni phase diagram by Massalski et al. [11] is based on Beaudry et al. [12] and Domagala et al. [13]. Ten intermetallic compounds were reported as Y_3Ni, Y_3Ni_2, YNi, YNi_2, YNi_3, Y_2Ni_7, YNi_4, YNi_5, Y_2Ni_{17} and YNi_9 in

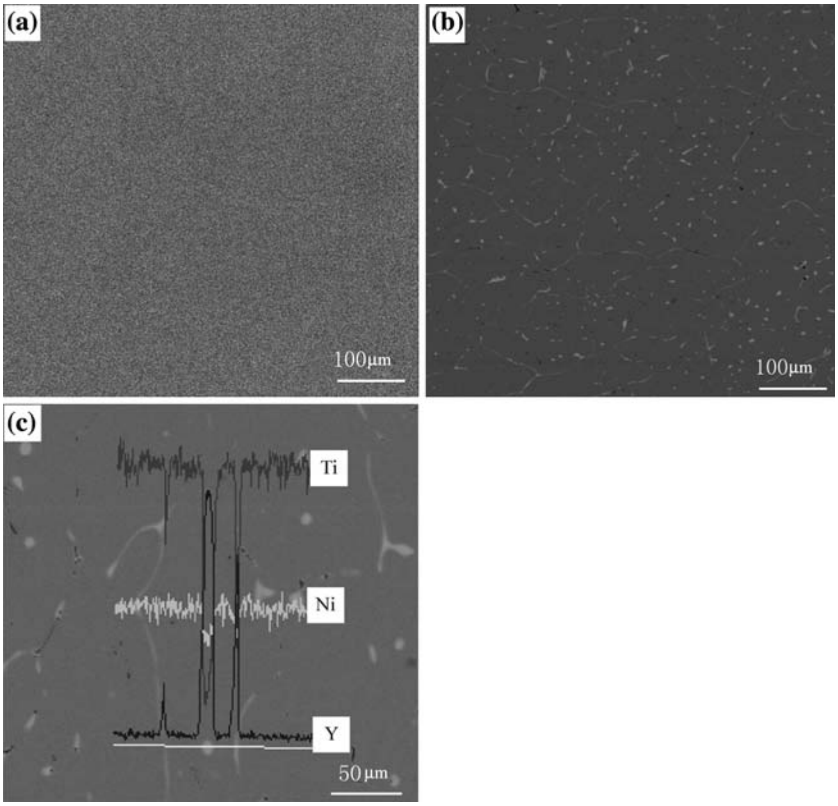

Fig. 1 The SEM image of Ti–Ni–Y alloys. (**a**) The morphology of Ti–50.7Ni alloy, (**b**) the morphology of white phases, (**c**) line-scanning of Ti, Ni and Y element in Ti–50.2Ni–1Y alloy

Table 1 The compositions of the matrix and white phase in $Ti_{48.8}Ni_{50.2}Y_1$ alloys

Alloy	Phase	Ti (at%)	Ni (at%)	Y (at%)
Ti–50.7Ni	The matrix	49.54	50.46	–
Ti–50.2Ni–1Y alloy	The matrix	50.83	49.03	0.14
	The white phase	16.15	44.37	39.48

the Y–Ni phase diagram. In Table 1, the Ni:Y ratio is ~1 in the white phase of Ti–50.2Ni–1Y alloy. Judged from the composition, the white phase may be YNi intermatallic compound with Ti solubilized. Zhuang et al. [14] has studied the 773 K isothermal section of Y–Ni–Ti ternary system, only YNi phase exists in the three-phase region of ($TiNi + Ti_2Ni + YNi$) and ($TiNi + TiNi_3 + YNi$). Moreover, Wang et al. [15] think the unknown phase observed in $Ti_{65}Ni_{25}Y_{10}$ alloy may be YNi or YNi_3 phase. According to their results, the white phase in Ti–50.2Ni–1Y alloy should be YNi phase.

Figure 3 shows the DSC curves of Ti–50.7Ni and Ti–50.2Ni–1Y alloys. It can be seen that only one peak due to B2 ↔ B19′ is observed during the heating and the cooling process of both experimental alloys, which indicates that there is one-step martensitic transformation occurred in Ti–50.2Ni–1Y alloy. This means Y addition does not change the type of martensitic transformation. The martensitic transformation temperatures of both alloys are listed in Table 2, and the martensitic transformation temperatures increase rapidly with Yttrium addition. It is apparently that Ti–50.2Ni–1Y alloy is under martensite state, which is in agreement with the result of X-ray experiment. Compared with the martensitic transformation starting temperature (Ms) of both alloys, the increase of Ms temperature is about 85 °C. It is well known that the ratio of Ti/Ni in the matrix has important influence on the martensitic transformation temperatures of Ti–Ni alloys, i.e., the Ms temperature decreases about 10 °C when the content of Ni in the matrix increase 0.1 at%. The ratio of Ti/Ni in the matrix of Ti–50.7Ni and Ti–50.2Ni–1Y alloys is 0.982 and 1.036, respectively. As discussed above, the increase of martensitic transformation should attribute to two facts: one is the change of the ratio of Ti/Ni in the matrix resulted from adding Y, the other is rare earth Y has an effect on increasing the phase transformation temperatures intrinsically.

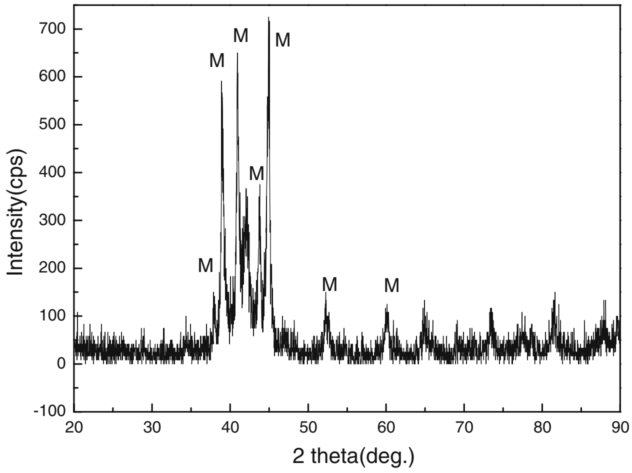

Fig. 2 X-ray diffraction pattern of Ti–50.2Ni–1Y alloy at room temperature

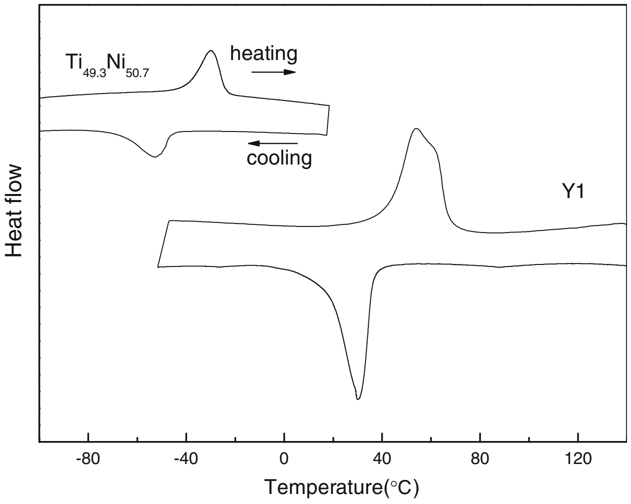

Fig. 3 DSC curves of experimental alloys

Table 2 The phase transformation temperatures of experimental alloys

Alloy	Ms (°C)	Mf (°C)	As (°C)	Af (°C)
Ti–50.7Ni	–47	–66	–38	–24
Ti–50.2Ni–1Y alloy	36	18	43	67

The effects of Y addition on the microstructure and martensitic transformation of Ti–50.7Ni alloy is investigated by SEM, XRD and DSC. The results show that the microstructure of Ti–50.7Ni alloy is different with that of Ti–50.2Ni–1Y alloy, and the microstructure of the ternary alloy is made up of B19′ martensite and the Y-rich phase, which may be YNi phase. Y addition does not change the martensitic transformation behavior, one-step martensitic transformation is observed in Ti–50.2Ni–1Y alloy. The martensitic transformation temperatures increase obviously with Y addition, and the increase of Ms is about 85 °C.

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