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Influence of heat treatments on phase composite and mechanical properties of $Ni_{47}Ti_{44}Nb_9$ alloy①

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Abstract: The influence of heat treatments on the phase composite and mechanical properties of $Ni_{47}Ti_{44}Nb_9$ alloy were investigated by using XRD, SEM, TEM and EDX. The results show that a diffusional transformation takes place when the alloy is heated over 850 ℃ for a long time, and a new precipitation $(Ni, Nb)_3Ti$ with an hcp structure can be found. The formation of the precipitation leads to an increment of microhardness and reduction in elongation.

Key words: Ni-Ti-Nb alloy; heat treatment; precipitation; $(Ni, Nb)_3Ti$
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1 INTRODUCTION

NiTi-based shape memory alloys are the most important commercial shape memory materials. In Ni-rich NiTi alloys, some precipitates such as $Ni_{14}Ti_{11}$, Ni_3Ti_2 and Ni_3Ti can be observed during aging[1, 2], which can improve the superelasticity of alloys[3].

In many cases the alloying or thermomechanical treatments are used in order to change the temperature range of SME manifestation. Ternary addition of niobium to NiTi was reported to significantly widen the thermal hysteresis of the martensite transformation[4]. As an typical example, $Ni_{47}Ti_{44}Nb_9$ exhibited excellent superelasticity in a wide temperature range after annealling at 400 ℃[5], no appreciable aging effect on its microstructure appeared when it was aged at 300-600 ℃ for 0.5-10 h[6, 7], while Kundzhua et al[9, 10] discovered the formation of an X-phase during annealling of Ni46Ti50Nb4 alloy. Yang and Hao[11, 12] studied the phase equilibria of the Ni-Ti-Nb ternary system at 700 and 800 ℃, and discovered at least 4 ternary compounds in this system.

Anyway, still up to now, the diffusional phase transformation in NiTiNb alloys has not been sufficiently studied although this kind of study would be of interest from both the practical and the scientific point of view.

Thus, the aim of this work is to investigate the influence of heat treatments on phase composite and mechanical properties in $Ni_{47}Ti_{44}Nb_9$ alloy.

2 EXPERIMENTAL

The experimental alloy $Ni_{47}Ti_{44}Nb_9$ was prepared by melting sponge titanium, electrolytic nickel and pure niobium with a cold crucible in magnetic suspension furnace under a controlled protective argon followed by quenching into an iron mould. Mass loss during the melting was negligible. The resulting ingot was hot forged and rolled at 850 ℃ to about 3mm thickness. The rolled specimens were annealed at 450, 550, 650, 750, 850 and 950 ℃ for 5 h in evacuated quartz tubes, respectively.

XRD was performed in a Rigaku diffractometer, employing the Cu K_α radiation, the diffraction intensity was recorded in the range of 30 to 120° (2θ) with a scanning rate of about 0.02(°)/s

The microstructure features in selected specimens were studied by SEM and TEM. The samples for SEM investigation were polished and etched in a mixed solution of 10% HF, 40% HNO_3, and 50% H_2O. All TEM observations were performed on a JEM-2010 operated at 120 keV. The X-ray spectra were obtained from EDS system of JEM-2010 by using K-rations and the thin-film correction method.

The mechanical property of the specimens was measured by performing stress-strain tests using an Instron testing machine, and the microhardness was employed in a microvikers hardness tester using a 0.1 N load on mechanically polished and etched sam-

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ples. The indentation load was sufficiently small so that the Vikers impression was completely contained within the Nb-rich phase and the matrix. For each specimen, the average hardness value was obtained from the average of at least six test readings.

3 RESULTS AND DISCUSSION

3.1 XRD analysis

The crystal structure of every phase in Ni_{47}-Ti_{44} Nb_9 alloy at room temperature was analyzed by XRD. Fig. 1(a) shows the typical XRD-line profiles of the as-cast alloy. As normal Ni-Ti-Nb system, the line profiles are fitted well for the two cubic structure phase, i.e., the B2 structure and the β-Nb structure.

The diffraction spectrum of the experimental alloy annealing at 850 ℃ for 5 h is shown in Fig. 1(c). Some of these Bragg peaks were identified to be B2 structure, however, the other peaks cann't correspond to β-Nb structure, it is suggested that there exists precipitate after annealing at 850 ℃ for 5 h. This precipitate can be identified to be hcp structure with a = 0.512 2 nm and c = 0.837 6 nm(c/a = 1.63). According to Ref.[6], the rich-Nb phase cannot disappear in the alloy annealed above 850 ℃ for long time, the fact mentioned above means that the volume fraction of Nb-rich phase in $Ni_{47}Ti_{44}Nb_9$ alloy has changed during long time treatment at 850 ℃ although the B2-type ordered matrix phase keeps almost unchanged.

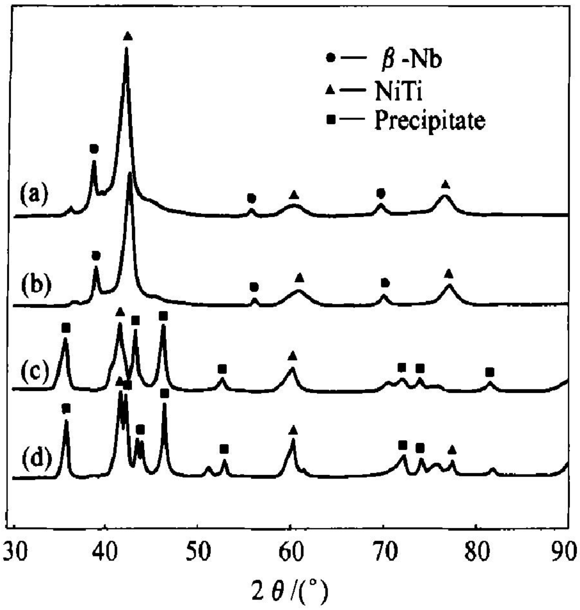

Fig. 1 X-ray diffraction patterns of experimental alloys annealed at different temperatures
(a) —As-cast; (b) —850 ℃ for 0.5 h; (c) —850 ℃ for 5 h; (d) —950 ℃ for 5 h

XRD observation shows that there is no precipitate in $Ni_{47}Ti_{44}Nb_9$ alloy aged below 850 ℃(Fig1(b)), and this is consistent with previous result[6, 7]. There also exist the Bragg peaks of the precipitate on XRD spectrum of the alloy annealed at 950 ℃ for 5 h (Fig. 1(d)). This means that the solution line of Ni_{47} $Ti_{44}Nb_9$ alloy is above 950 ℃.

There exists Ni_3Ti precipitate in Ti-52% Ni alloy annealed at 750-850 ℃, but there is no aging effect at 825 ℃[1, 2]. Therefore it can be concluded that the precipitation temperature is raised. So it is speculated that the presence of niobium inhibits the occurrence of precipitating.

3.2 Microstructure

Fig. 2 shows the SEM micrographs for the $Ni_{47}Ti_{44}Nb_9$ alloy under the as-cast condition and after annealing at 850 ℃ for 5 h. It can be seen from Fig. 2(a) that the as-cast alloy at room temperature consists of three phases: the matrix, the Nb-rich and the $(Ti, Nb)_2Ni$ phase, which was described in detail in Ref.[13]. In the annealed alloy, as shown in Fig. 2(b), we can see that there are new precipitates, corresponding to the Bragg peaks identified as hcp structure in Fig. 1. From this micrograph it can also be found that the precipitating reaction occurs in the areas of original β-Nb particles, while there exist no precipitates in the NiTi matrix. So it can be deduced that the precipitating reaction origins from the interface between the NiTi matrix and the β-Nb particle.

In order to make a further proof, a TEM observation was performed. Fig. 3 shows a typical bright-field image observed at room temperature in $Ni_{47}Ti_{44}$ Nb_9 alloy annealed at 850 ℃ for 5 h. It can be seen that there are at least three phases in the alloy, the difference between them can be recognized easily from the TEM images by bright or dark contrast.

The average quantitative analysis results with EDS spectrum for every phase are presented in Table 1. In order to avoid the overlapping absorption from the matrix phase, all EDX spectra were taken from the corresponding phase at the edge of the hole in thin foil specimens as shown in Fig. 3. Comparing the three results, it is found that the phase labeled A is Nb-rich phase containing some amount of Ni and Ti, the matrix is Ti-rich phase (Ni/Ti = 0.93) with a little Nb. This result differs from that of the matrix of the as-cast alloy, which is Ni-rich[12]. It clearly indicates that the change of the composition of the matrix during long time heat treatment, EDX spectrum taken from area B shows that the composition formula of precipitate containing Ni, Ti and Nb can be written as $(Ni, Nb)_3Ti$ according to the ratio of Ni, Ti and Nb. Fig. 4 shows the electron diffraction patterns taken from area B in Fig. 3. It is clear that the precipitation phase is different from β-Nb, not only in composition but also in structure. All the diffrac-

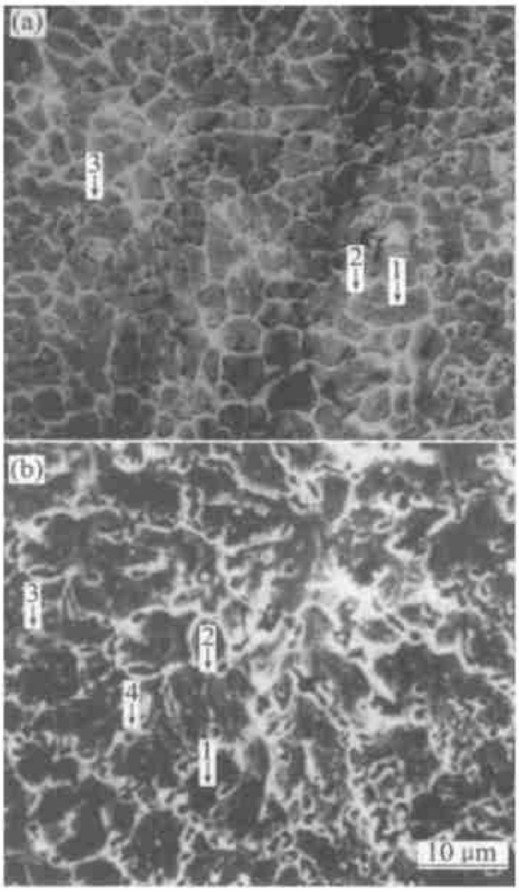

Fig. 2 SEM micrographs of $Ni_{47}Ti_{44}Nb_9$ alloys
(1 —NiTi matrix; 2 —Nb-rich phase;
3 —$(Ti, Nb)_2Ni$; 4 —$(Ni, Nb)_3Ti$)
(a) —As-cast;
(b) —Annealed at 850 ℃ for 5 h

Table 1 TEM/EDX analysis for matrix and precipitates *A*, *B* indicated in Fig. 3 (mole fraction, %)

Position	Ni	Ti	Nb
Matrix	45.0	48.3	6.7
A	4.5	7.5	88.0
B	35.8	24.7	41.5

tion patterns from $(Ni, Nb)_3Ti$ can be indexed by assuming hcp structure with the following parameters: $a = 0.5122$ nm and $c = 0.8376$ nm.

From Fig. 3 we can also confirm the above deduction: there is no eutectic reaction in this system and there are at least three phases including the equilibrium $(Ni, Nb)_3Ti$ in the $Ni_{47}Ti_{44}Nb_9$ alloy annealed at 850 ℃ for 5 h. The reaction is an interface reaction between the NiTi matrix and the β-Nb phase, and $(Ni, Nb)_3Ti$ occupies the original β-Nb site. Therefore, the apparent complicated atomic shuffling in the $(Ni, Nb)_3Ti$ precipitates is likely to originate from complex shuffles in the matrix and the β-Nb particles. This precipitating mechanism is now under study and will be reported in due course. It also means that the nickel concentration of the matrix decreases from the supersaturated state and to reach equilibrium with the $(Ni, Nb)_3Ti$ because the matrix is now Ti-rich phase (atomic ratio of Ni to Ti as 0.93) instead of Ni-rich one.

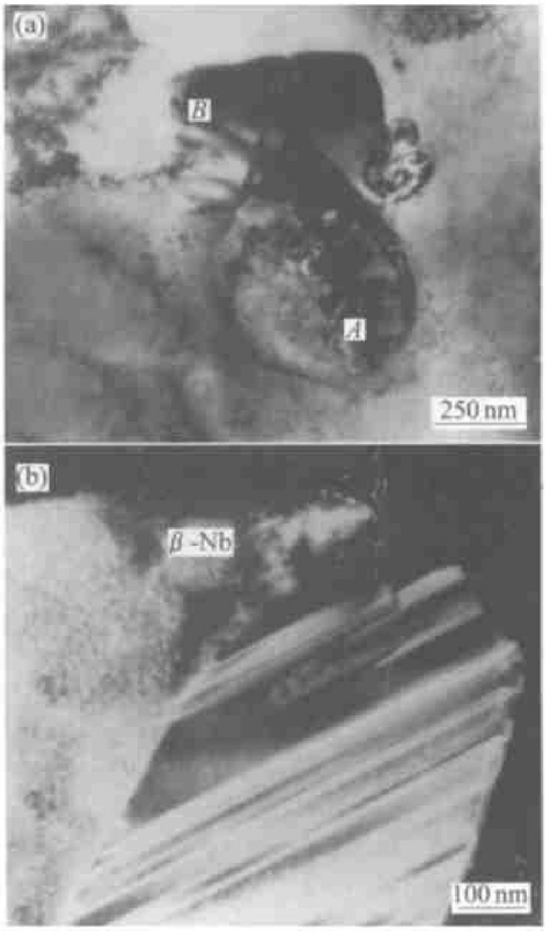

Fig. 3 TEM micrograph of $Ni_{47}Ti_{44}Nb_9$ alloy annealed at 850 ℃ for 5 h

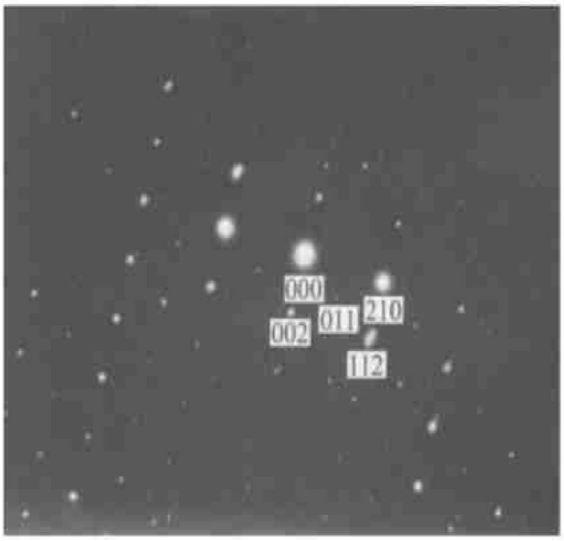

Fig. 4 Electron diffraction pattern of area *B* in Fig. 3(a)

Nishida et al[1, 2] once reported that Ni_3Ti precipitates existed during the annealing of Ti-52 % Ni alloy above 750 ℃, and have a DO_{24} type hcp cell with a= 0.506 9 nm and c= 0.830 4 nm. It is due to the presence of niobium that the lattice parameter of $(Ni, Nb)_3Ti$ is somewhat larger than that of Ni_3Ti.

The bright field image, selected area diffraction patterns and EDX spectra also support the XRD results. A diffusional phase transformation took place in $Ni_{47}Ti_{44}Nb_9$ alloy annealed at 850 ℃ for 5 h and resulted in the formation of a hcp structure with lattice parameters of a= 0.512 2 nm and c= 0.837 6 nm.

3.3 Mechanical properties

Fig. 5 shows the effects of annealing temperature on the microhardness of the NiTi matrix of $Ni_{47}Ti_{44}Nb_9$ alloy. It is clear that the microhardness of the alloy almost cannot be affected when the heat treatment temperature is below 850 ℃, but suddenly increases when annealed at 850 ℃ for 5 h. In Fig. 6 the stress-strain curve of the alloy annealed at 850 ℃ for 5 h also shows singular behavior. Compared with the alloy annealed at 750 ℃, the elongation of the alloy annealed at 850 ℃ greatly decreases.

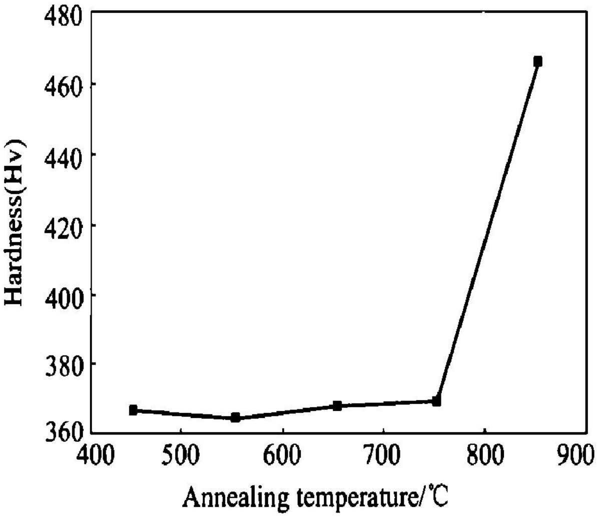

Fig. 5 Annealing temperature vs microhardness of NiTi matrix of $Ni_{47}Ti_{44}Nb_9$ alloy

All the results about mechanical properties can be attributed to the precipitation of $(Ni, Nb)_3Ti$ phase. Firstly, the matrix become Ti-rich phase (atomic ratio of Ni to Ti as 0.93) instead of Ni-rich one because of the precipitation of the alloy, which will lead to the strengthening of the matrix, also lead to an improvement in microhardness of the matrix. However, the $(Ni, Nb)_3Ti$ phase with hcp structure is very brittle and indicates a reduction in elongation.

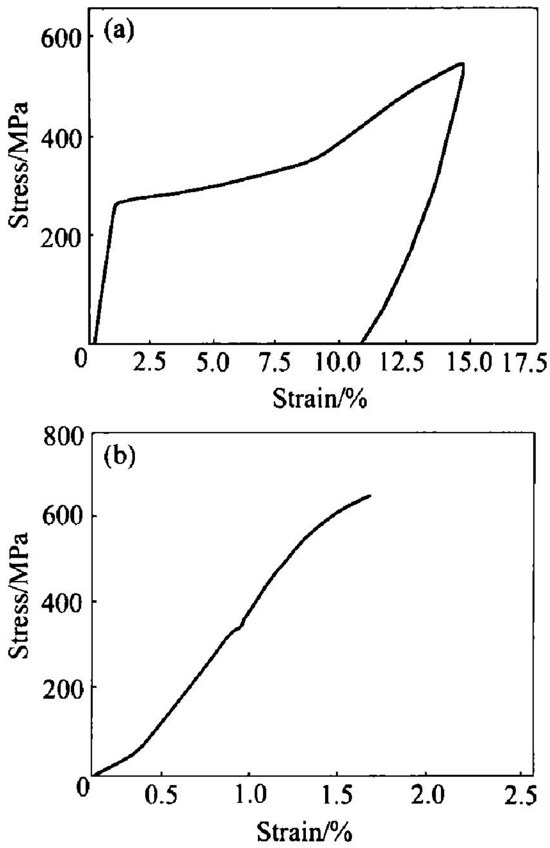

Fig. 6 Stress vs strain of $Ni_{47}Ti_{44}Nb_9$ alloy under different annealled conditions
(a) —750 ℃, 5 h; (b) —850 ℃, 5 h

4 CONCLUSIONS

1) The precipitate of $(Ni, Nb)_3Ti$ with an hcp structure occurred in $Ni_{47}Ti_{44}Nb_9$ alloy annealed at 850 ℃ for 5 h.

2) The occurrence of $(Ni, Nb)_3Ti$ leads to an improvement in microhardness of the matrix in $Ni_{47}Ti_{44}Nb_9$ alloy annealed at 850 for 5 h.

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