Precipitates and phase transformation in Ti-Ni-Cu shape memory alloy thin film

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Phase transformation in Ti-Ni-Cu shape memory alloys has been extensively studied by many researchers [1–7]. It has been shown that substitution of Ni even by up to 30 at% Cu leads to Ti-Ni-Cu alloys, which not only still exhibit an excellent shape memory effect, but also have some better properties than Ti-Ni alloys [1–3]. However, to our knowledge, most of these studies have focused on bulk alloys, seldom on thin films, especially not on the films in which Ni was largely substituted by Cu. Consequently, the present study was undertaken to investigate the structure, the size and the distribution of precipitates and their influence on the phase transformation of Ti-25at%Ni-25at%Cu thin film by combination of X-ray diffraction (XRD), transmission electron microscopy (TEM) and electric resistance measurement.

The Ti-Ni-Cu thin films were deposited onto glass substrates by magnetron sputtering in an argon atmosphere using a ternary alloy target. The source target contained 52.08at%Ti, 22.05at%Ni and 25.87at%Cu. The sputtering conditions were as follows: base pressure, 2×10^{-3} Pa; argon pressure, 5×10^{-2} Pa; sputtering power, 110 W; deposition rate 3.5 nm/min; substrate-to-target distance, 30 mm. At last, Ti-Ni-Cu films with a thickness of about 10 μm were developed. To study the influence of the precipitates' physical properties on phase transformation, two types of heat-treatment were given to the specimens: (1) Annealing at 823 K for 0.5 h, (2) annealing at 923 K for 5 h.

XRD patterns were taken on a Rigaku 12 kW rotary anode X-ray diffractometer with Cu K_α radiation. TEM observations were performed on the Jeol-2000EX. The electrical resistance was measured as a function of temperature by a four-terminal d.c.-current method.

The film composition determined by the electron energy spectrum was 50.37at%Ti, 24.49at%Ni and 25.14at%Cu. This is similar to the work of Chang *et al.* [4, 5], which showed a tendency for Ti depletion in the sputtered film relative to the effective composition of the target material.

The XRD analysis results of the two annealed samples are shown in Fig. 1. It is seen that there existed simultaneously two kinds of percipitates, $Ti_2(Ni + Cu)$ and $Ti(Ni + Cu)_3$, in the annealed samples. Though it has been reported [4] that there existed Ti_2Ni second phase in annealed Ti-Ni-Cu alloy, there are still no reports of the simultaneous existence of more than one kind of precipitate in Ti-Ni-Cu alloys.

From TEM analysis, it is shown that there exist two different kinds of precipitate in each specimen. One kind of precipitate appeared as particles. When annealing at 823 K for 0.5 h, a large number of second-phase particles appeared in a fine dispersion throughout the grain interiors, and the longer the annealing time and the higher the annealing temperature (annealing at 923 K for 5 h), the larger the size of the second-phase particles. The electron diffraction patterns revealed that

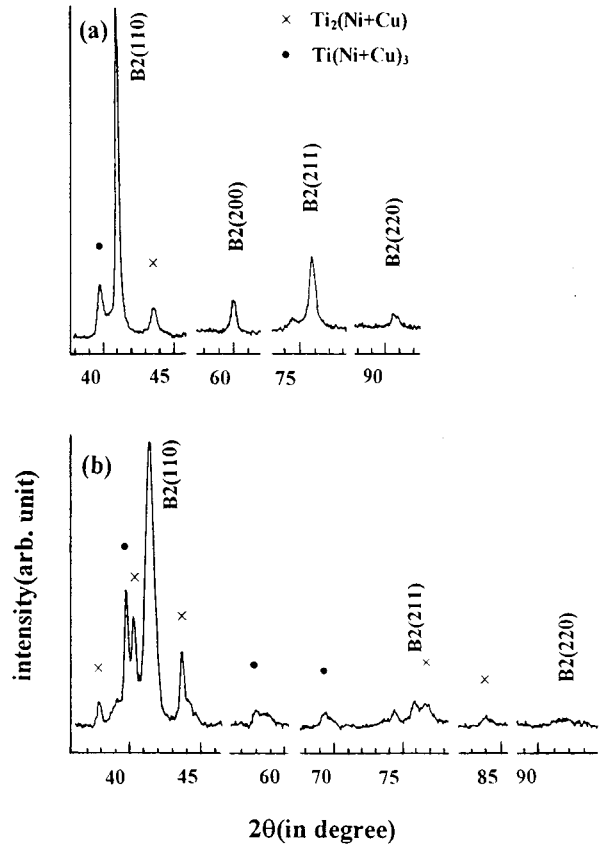

Figure 1 X-ray diffraction analysis result of annealed Ti-Ni-Cu films. (a) 823 K/0.5 h, (b) 923 K/5 h.

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TABLE I Changes in size and distribution of precipitates of annealed Ti-Ni-Cu alloy thin films with the annealing conditions

Condition of heat-treatment	Size of precipitates (nm)		Distance between precipitates (nm)	
	Particles	$\text{Bands}_{\text{length}\times\text{width}}$	Particles	Bands
823 K/30 min	5.0	11.5×1.1	14.4	1.5
923 K/5 h	10.6	25.9×3.3	27.4	3.6

these particles were f.c.c. $Ti_2(Ni + Cu)$. The other kind of precipitates appeared as bands. When annealing at 823 K for 0.5 h, the bands distributed in the grain interiors. With the prolongation of the annealing time and the enhancement of the annealing temperature (annealing at 923 K for 5 h), we found that the bands became longer and thicker. The electron diffraction patterns revealed that these precipitates were h.c.p. $Ti(Ni + Cu)_3$. The size of the precipitates and the distance between them are listed in Table I. From it, we found that with the different annealing times and temperatures, the size and distribution of the two kinds of precipitates changed remarkably. The longer the annealing time and the higher the annealing temperature, the larger the size of the precipitates. At the same time, the number of precipitates decreased and the distance between them increased. The size of the $Ti_2(Ni + Cu)$ phase, 10.6 nm, is smaller than the size in literature [4], 15 nm. The difference is probably because of the difference of the alloy's composition and heat-treatment.

Fig. 2 shows the electrical resistance-temperature curves to determine thin film's phase transformation properties. A tangential extrapolation method [8, 9] was used to determine transformation temperatures. On cooling, the forward martensitic transition starts at M_s, indicated by the rapid increase in resistance, and finishes at M_f, where the change in resistance becomes rather gradual. On heating, the reverse martensitic transformation starts at A_s, where the resistance decreases abruptly and completes at A_f. From the *R-T* curves of different specimens, we found that because of substitution of Ni by up to 25at%Cu, there is only one kind of transformation [6, 7]. The transformation temperatures determined from the *R-T* curves are listed in Table II. We can see that the transformation temperatures, M_s, M_f, A_s and A_f, increase obviously with the prolongation of the annealing time and the enhancement of the annealing temperature.

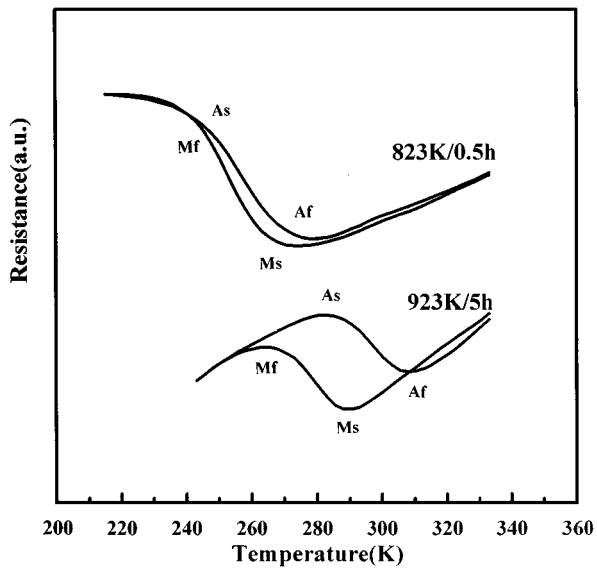

Figure 2 Electrical resistance-temperature curve of annealed Ti-Ni-Cu films. (a) 823 K/0.5 h, (b) 923 K/5 h.

TABLE II Phase transformation temperatures of Ti-Ni-Cu films under different heat-treatment conditions

Temperature/time	A_s (K)	A_f (K)	M_s (K)	M_f (K)
823 K/30 min	232.2	277	265.8	231
923 K/5 h	285.8	307.4	287	266.2

The notable increase in transformation temperature can be explained as follows. When annealing at 823 K for 0.5 h, a large number of precipitates are distributed in a fine dispersion throughout the grain interiors, which can cause the interface deformation between precipitates and parent phase. This certainly increases the average dislocation density of the thin films, and leads to the parent phase to be strengthened. In one word, it impedes the preferential nucleation and growth of martensite plates. Thus, in the alloy thin films investigated, it seems that the precipitates act as strong barriers for the *A-M* phase transformation. So, the transformation temperatures were low. With the prolongation of the annealing time and the enhancement of the annealing temperature, the size of the precipitates increased and the number of the precipitates decreased, which caused an increase in the distance between the precipitates and the release of the coordination strain around the precipitates. All of these would certainly decrease the average dislocation density of the films. In addition, coarse precipitates could enhance the compression stress fields. In particular, it has been suggested that the preferential nucleation of martensite and modification in *A* to *M* transformation sequence is favored by the development of compressive stress regions within the matrix [10, 11]. Apparently, in the alloy thin film matrix investigated, a compressive stress field developed in the neighborhood of second phase particles and promoted the preferential nucleation of martensite plates. So, the transformation temperatures were high.

Compared with other transformation temperatures [2–5], our transformation temperatures are slightly lower. This is probably because of (1) the difference of the alloy thin film's composition; (2) the difference of the condition of annealing; (3) the difference of the size and kind of precipitates.

In conclusion, the second phases actually have a large influence on the transformation of Ti-Ni-Cu alloy thin film.

References

1. O. MERCIER and K. N. MELTON, *Metall. Trans.* **10A** (1979) 387.
2. R. H. BRICKNELL, K. N. MELTON and O. MERCIER, *ibid.* **10A** (1979) 693.

3. T. H. NAM, T. SABURI and K. SHIMIZU, *Mater. Trans. JIM* **31** (1990) 959.
4. L. CHANG and D. S. GRUMMON, *Mat. Res. Soc. Symp. Proc.* **246** (1992) 141.
5. *Idem., Scripta Metall. Mater.* **25** (1991) 2079.
6. T. H. NAM, T. SABURI, Y. KAWAMURA and K. SHIMIZU, *Mater. Trans. JIM* **31** (1990) 262.
7. T. TADAKI and C. M. WAYMAN, *Metallography* **15** (1982) 247.
8. T. TODOROKI and H. TAMURA, *Mater. Trans. JIM* **28** (1987) 83.
9. J. KWARCIAK and H. MORAWIEC, *J. Mater. Sci.* **23** (1988) 551.
10. D. STROZ, J. KWARCIAK and H. MORAWIEC, *ibid.* **23** (1988) 4127.
11. L. DELUEY, The Science and Technology of Shape Memory Alloys Conf. Proceedings, Section IV, Martensitic Transformation/Shape Memory Effect (University of Barcelona 1989).

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