Phase Transformation Behavior and Shape Memory Characteristics of Ti-Ni-Cu-Mo Alloys

Tae-Hyun Nam¹, Jung-Phil Noh¹, Shin-Goo Hur², Ji-Soon Kim³ and Seung-Baik Kang⁴

¹Division of Materials Engineering, Gyeongsang National University & ERI, Gyeongnam 660-701, Korea

²Biosmart Ltd, Ulsan 689-890, Korea

³Department of Materials Science and Engineering, Ulsan University, Ulsan 680-749, Korea

⁴Seoul Municipal Boramae Hospital, Seoul 156-102, Korea

Phase transformation behavior, the shape memory characteristics and the superelasticity of Ti-Ni-Cu-Mo alloys have been investigated by means of electrical resistivity measurements, X-ray diffraction, thermal cycling tests under constant load and tensile tests. A fully annealed Ti-44.7Ni-5Cu-0.3Mo alloy transformed in two-stage, *i.e.*, the B2-B19-B19' on cooling and the B19'-B19-B2 on heating. Fully annealed Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys transformed in one-stage on, *i.e.*, from the B2 to the B19 on cooling and from the B19 to B2 on heating. The maximum recoverable elongation decreased from 6.0 to 2.4% with increasing Cu-content from 5 to 20 at%. Transformation hysteresis associated with the B2-B19 transformation decreased from 11 to 5 K with increasing Cu-content from 5 to 20 at%. Substitution of Mo for Ni in Ti-Ni-Cu alloys improved the superelasticity.

(Received November 19, 2001; Accepted April 15, 2002)

Keywords: titanium-nickel-copper-molybdenum alloys, transformation behavior, shape memory characteristics, superelasticity

1. Introduction

The B2-B19 transformation in the Ti-Ni-Cu alloys has been known to be very attractive in applications for an actuator, since it showed relatively large transformation elongation (2.5–3.2%) and small hysteresis (4–12 K).¹⁾ The B2-B19 transformation was observed in Ti-Ni-Cu alloys whose Cu-content is more than 7.5 at%.^{2,3)} In a practical point of view, however, the B2-B19 transformation in Ti-Ni-Cu alloys whose Cu-content is lower than 10 at% seems to be not available for applications, because the B19 and the B19' martensites coexist at any temperatures in the alloys.^{1,3)} In order to apply shape memory alloys to an actuator, they should be deformed to wire form. On the other hand, Ti-Ni-Cu alloys whose Cu-content is more than 12.5 at% are so brittle that a plastic deformation is almost impossible.¹⁾ Therefore, it is desirable to induce only the B2-B19 transformation in Ti-Ni-Cu alloys with low Cu content which show good plastic deformability.

Substitution of Mo for Ni in a Ti-Ni binary alloy was known to decrease the B2-B19' transformation start temperature largely and induce the R phase transformation.^{4,5)} Therefore, it was expected that substitution of Mo for Ni in Ti-Ni-Cu alloys suppressed the B2-B19' transformation also and that induced the B2-B 19 transformation. Recently, the present authors found that substitution of Mo for Ni in a Ti-45Ni-5Cu alloy induced the B19 martensite.⁶⁾ In addition, they found also that shape memory characteristics and superelasticity of a Ti-45Ni-5Cu alloy were improved largely by substitution of Mo.⁷⁾ However, details of phase transformation behavior, the shape memory characteristics and the superplasticity of Ti-Ni-Cu-Mo alloys are not known well. The purpose of the present study is to investigate phase transformation behavior, the shape memory characteristics and the superelasticity of Ti-Ni-Cu-Mo alloys.

2. Experimental Procedure

50Ti-(49.7-X)Ni-XCu-0.3Mo(at%) ($X = 5, 10, 15, 20$) alloy ingots were prepared by vacuum induction melting in a graphite crucible. After hot rolled into $\Phi 3$ mm rods at 1123 K, they were deformed to $\Phi 1.5$ mm wires or 1.2 mm sheets by cold working. Specimens for electrical resistivity measurements, thermal cycling tests under constant load and tensile tests were prepared from the wires. Specimens for X-ray diffraction were prepared from the sheets. Since a Ti-29.7Ni-20Cu-0.3Mo alloy was unable to be hot rolled, specimens were cut from the ingot directly. All specimens were fully annealed at 1123 K for 3.6 ks in vacuum, and then electropolished with an electrolyte which consists of 95%CH₃COOH and 5%HClO₄ in volume.

In order to investigate the transformation behavior, electrical resistivity measurements, X-ray diffraction were carried out. Electrical resistivity measurements were made by means of typical four terminal technique at the cooling/heating rate of 0.017 K/s. X-ray diffractions were made in a temperature range between 383 and 83 K using CuK α . Thermal cycling tests under constant load⁸⁾ were made to investigate the shape memory characteristics. Tensile tests were carried out to investigate the superelasticity with a strain rate of $6.6 \times 10^{-5} \text{ s}^{-1}$.

3. Results and Discussion

3.1 Phase transformation behavior of Ti-Ni-Cu-Mo alloys

Figures 1(a)–(d) show electrical resistivity vs. temperature curves of Ti-44.7Ni-5Cu-0.3Mo, Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys, respectively. In the curve of (a), on cooling the specimen from 380 K, electrical resistivity starts to decrease abruptly at 277 K. On further cooling the specimen, it starts to increase

Fig. 1 Electrical resistivity vs. temperature curves of Ti-Ni-Cu-Mo alloys.

at 265 K and then has the maximum at 225 K. On heating the specimen, electrical resistivity increases up to 229 K and then decreases. On further heating, it starts to increase at 266 K, and then its increasing rate decreases at 280 K. From the previous study,⁶⁾ the abrupt decrease in resistivity at 277 K on cooling was known to be due to the B2-B19 transformation and the increase in resistivity at 265 K on cooling was done to be due to the B19-B19' transformation. The decrease in resistivity at 229 K on heating was ascribed to the B19'-B19 transformation and the increase in resistivity at 266 K on heating was done to the B19-B2 transformation.

In the curve of (b), on cooling the specimen from 347 K, electrical resistivity decreases, and then starts to increase slightly at 285 K. On further cooling, it starts to decrease at 268 K. On heating the specimen, it increases up to 263 K, and then it decreases. On further heating, it starts to increase at 300 K. In the curve of (c), on cooling the specimen, electrical resistivity decreases gradually, and then starts to increase at 294 K. On further cooling, it starts to decrease at 290 K. On heating the specimen, it increases up to 295 K, and then decreases. On further heating, it starts to increase at 299 K. In the curve of (d), on cooling the specimen, electrical resistivity decreases gradually, and then starts to increase at 302 K. On further cooling, it starts to decrease at 296 K. On heating the specimen, it increases up to 300 K, and then decreases. On further heating, it starts to increase at 306 K.

In order to explain the electrical resistivity curves of Figs. 1(b)–(d), X-ray diffraction experiments were made with successively cooling and heating specimens. Figure 2 shows X-ray diffraction patterns of a Ti-39.7Ni-10Cu-0.3Mo alloy. At 298 K, a diffraction peak corresponding to the B2 parent phase appears. The diffraction peak designated by Cu is originated from the specimen holder. On cooling the specimen, intensity of the diffraction peak of the B2 phase decreases, while the diffraction peaks of the B19 martensite appear as seen in the diffraction pattern obtained at 253 K. On further cooling, the diffraction peak of the B2 phase disappears, and only those of the B19 martensite are found as seen in the pattern obtained at 213 K. Even cooling the specimen down to 83 K, only diffraction peaks of the B19 martensite

Fig. 2 X-ray diffraction patterns of a Ti-39.7Ni-10Cu-0.3Mo alloy.

Fig. 3 X-ray diffraction patterns of a Ti-34.7Ni-15Cu-0.3Mo alloy.

are observed, and any diffraction peaks corresponding to the B19' martensite are not found. On heating the specimen, the diffraction peak of the B2 phase appears at 263 K. On further heating, diffraction peaks of the B19 martensite disappear, and only that of the B2 phase is observed as shown in the pattern obtained at 323 K. Peak shifts in X-ray diffraction patterns during heating and cooling are attributed to temperature dependence of lattice parameters. Therefore, in Fig. 1(b), the slight increase in resistivity at 281 K on cooling is attributed to the B2-B19 transformation and the decrease in resistivity at 263 K on heating is done to the B19-B2 transformation.

Figure 3 shows X-ray diffraction patterns of a Ti-34.7Ni-15Cu-0.3Mo alloy. At 298 K, diffraction peaks corresponding to the B2 parent phase and the B19 martensite appear. In addition, the diffraction peak corresponding to Cu_2Ti phase is found in the pattern. On cooling the specimen, the diffraction peak of the B2 phase disappears, while intensity of them of the B19 martensite increases as seen in the diffraction pattern obtained at 273 K. Even cooling the specimen down to 123 K, only diffraction peaks of the B19 martensite and Cu_2Ti are observed. On heating the specimen, the diffraction peak of the B2 phase appears at 283 K. On further heating, intensity of

diffraction peaks of the B19 martensite decreases, while that of the B2 phase increases as seen in the pattern obtained at 303 K. Therefore, the increase in resistivity at 294 K on cooling in Fig. 1(c) is attributed to the B2-B19 transformation and the decrease in resistivity at 295 K on heating in Fig. 1(c) is done to the B19-B2 transformation.

X-ray diffraction patterns of a Ti-29.7Ni-20Cu-0.3Mo alloy are shown in Fig. 4. At 308 K, diffraction peaks corresponding to the B2 parent phase, the B19 martensite appear and Cu₂Ti appear. On cooling the specimen, the intensity of the diffraction peak of the B2 phase decreases, while those of the B19 martensite increase as can be seen in the pattern obtained at 298 K. On further cooling, at 88 K, the diffraction peak of the B2 phase disappears. On heating the specimen, at 313 K, diffraction peak of the B2 phase appears. Therefore, the increase in resistivity at 302 K on cooling in Fig. 1(d) is attributed to the B2-B19 transformation and the decrease in resistivity at 300 K on heating in Fig. 1(d) is done to the B19-B2 transformation.

From Figs. 1–4, it is concluded that a Ti-44.7Ni-5Cu-0.3Mo alloy transforms in two-stages on cooling and heating, *i.e.*, the B2-B19-B19' on cooling and the B19'-B19-B2 on heating. In addition, it is concluded that Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys transform in one-stage on cooling and heating, *i.e.*, from the B2 to the B19 on cooling and from the B19 to B2 on heating. The B2-B19 transformation start temperature (M_s'), its finish temperature (M_f'), the B19-B2 transformation start temperature (A_s') and its finish temperature (A_f') were measured from Fig. 1. In addition, the B19-B19' transformation start temperature (M_s), its finish temperature (M_f) and the B19'-B19 transformation start temperature (A_s) were determined from the curve of Fig. 1(a). Results obtained are shown in Table 1. With increasing Cu-content, transformation temperatures associated with the B2-B19 transformation are found to rise.

It was known that a Ti-45Ni-5Cu transformed in one-stage, *i.e.*, from the B2 to the B19' on cooling and from the B19' to the B2 on heating.^{1,2)} In addition, it was known that Ti-40Ni-10Cu and Ti-35Ni-15Cu alloys transformed in two-

stages, *i.e.*, the B2-B19-B19' on cooling and the B19'-B19-B2 on heating.^{1,2)} Comparing with Figs. 1–4, it is found that substitution of Mo for Ni in Ti-Ni-Cu alloys suppresses a formation of the B19' martensite and stabilizes the B19 martensite.

3.2 Deformation behavior of Ti-Ni-Cu-Mo alloys

In order to investigate deformation behaviors of Ti-Ni-Cu-Mo alloys, tensile tests were made at 283 K where only the B2 parent phase exists in a Ti-44.7Ni-5Cu-0.3Mo, the B2 and the B19 martensite coexist in a Ti-39.7Ni-10Cu-0.3Mo alloy and only the B19 martensite exists in a Ti-34.7Ni-15Cu-0.3Mo alloy. A Ti-29.7Ni-20Cu-0.3Mo alloy was so brittle that it was fractured prior to plastic deformation. Figures 5(a)–(c) show stress-strain curves of Ti-44.7Ni-5Cu-0.3Mo, Ti-39.7Ni-10Cu-0.3Mo and Ti-34.7Ni-15Cu-0.3Mo alloys, respectively. Two plateaus are seen in the curve of (a). The plateau corresponding to about 50 MPa is ascribed to the stress-induced B2-B19 transformation and that corresponding to 150 MPa is done to the stress-induced B19-B19' transformation. Two plateaus are also found in the curve of (b). The plateau corresponding to 120 MPa is ascribed to a rearrangement of the B19 martensite variants and that corresponding to about 250 MPa is done to the stress induced B2-B19 transformation. One plateau is found in the curve of (c), which is ascribed to a rearrangement of the B19 martensite.

3.3 Shape memory characteristics of Ti-Ni-Cu-Mo alloys

Figure 6 shows elongation-temperature curves of a Ti-44.7Ni-5Cu-0.3Mo alloy. All the curves are characterized by two-stage elongation. Details of the curves will be ex-

Fig. 4 X-ray diffraction patterns of a Ti-29.7Ni-20Cu-0.3Mo alloy.

Table 1 Transformation temperatures of Ti-Ni-Cu-Mo alloys.

Cu-content	Transformation temperatures (K)							
	M_s'	M_f'	A_s'	A_f'	M_s	M_f	A_s	A_f
5	277	—	266	280	265	225	229	—
10	285	268	263	300				
15	294	290	295	299				
20	302	296	300	306

Fig. 5 Stress-strain curves of Ti-Ni-Cu-Mo alloys deformed at 283 K.

Fig. 6 Elongation vs. temperature curves of a Ti-44.7Ni-5Cu-0.3Mo alloy.

plained referring to the curve obtained at 40.6 MPa. On cooling the specimen from 303 K, the specimen starts to elongate suddenly at 273 K. This abrupt elongation is attributed to the B2-B19 transformation, and therefore the temperature is defined as $Ms'(l)$. A tangential extrapolation method is used to determine the $Ms'(l)$, as indicated in the figure. On further cooling, a small elongation gradually continues, and then the rate of elongation starts to increase again at a temperature. This increase is due to the B19-B19' transformation, and therefore the temperature is defined as $Ms(l)$. On further cooling, the elongation gradually increases, and then it is almost saturated. On heating, the elongation starts to be recovered at a temperature of $As(l)$. The recovery is attributed to the B19'-B19 transformation. On further heating, the elongation is recovered gradually, and then recovered abruptly at a temperature of $As'(l)$. This abrupt recovery is attributed to the B19-B2 transformation. Since the elongation at temperature below about 230 K is very small, the elongation between $Ms'(l)$ and 230 K is adopted as a transformation elongation (ϵ_0) associated with the B2-B19-B19' transformation.

As seen in Fig. 6, the B2-B19 and the B19-B19' transformation are not well separated in curves obtained at the stress more than 60.0 MPa. This is attributed to the fact that the stress dependence of the transformation temperature of the B19-B19' transformation is larger than that of the B2-B19 transformation.⁸⁾ Very small residual elongation (ϵ_R) less than 0.3% is seen in the curve obtained at 80.6 MPa, and it becomes 0.6% at 100.3 MPa. In a Ti-45Ni-5Cu(at%) alloy, it has been reported that a large ϵ_R more than 0.5% appeared at

about 60 MPa and that increased up to 1.1% with increasing the applied stress up to 99.0 MPa. ϵ_R is originated from plastic deformation.¹⁾ Therefore, it is considered that substitution of Mo for Ni of a Ti-45Ni-5Cu(at%) alloy increases the critical stress for slip deformation. The transformation hysteresis designated in the curves is found to be increase from 11 to 19 K with increasing applied stress from 40.6 to 100.3 MPa. The increase in hysteresis is ascribed to the facts that the B2-B19 and B19-B19' transformation overlaps and ϵ_R increases with increasing applied stress.

Figures 7-9 show elongation-temperature curves of Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys. Irrespective of alloy compositions, all the curves are characterized by one-stage elongation due to the B2-B19 transformation. ϵ_0 associated with the B2-B19 transformation is defined as an elongation occurred between $Ms'(l)$ and $Mf'(l)$. It is to be noted here that ϵ_R of Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys is less than 0.3% under the applied stress of about 120 MPa. In Ti-Ni-Cu alloys, ϵ_R was reported to be more than 0.5% under the similar stress level.¹⁾ Transformation hysteresis associated with the B2-B19 transformation is found to decrease from 9 to 5 K with increasing Cu-content from 10 to 20 at%.

From Figs. 7-9, $Ms'(l)$ was measured, and then plotted against the applied stress in Fig. 10. As can be seen, $Ms'(l)$ increases linearly with increasing the applied stress. The temperature dependence of the stress required to induce the B2-B19 transformation in Ti-Ni-Cu-Mo alloys is al-

Fig. 7 Elongation vs. temperature curves of a Ti-39.7Ni-10Cu-0.3Mo alloy.

Fig. 8 Elongation vs. temperature curves of a Ti-34.7Ni-15Cu-0.3Mo alloy.

most constant without regard to the Cu-content, *i.e.*, about 8 MPa/K, which is very similar to that of Ti-Ni-Cu alloys.¹⁾ ε_0 obtained from thermal cycling tests under various stresses is plotted against the applied stress, as shown in

Fig. 11. ε_0 plotted for a Ti-44.7Ni-5Cu-0.3Mo alloy is associated with the B2-B19-B19' transformation, while those for Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys are associated with the B2-B19

Fig. 9 Elongation vs. temperature curves of a Ti-29.7Ni-20Cu-0.3Mo alloy.

Fig. 10 Stress dependence of $M_s'(I)$ in Ti-Ni-Cu-Mo alloys.

Fig. 11 Stress dependence of transformation elongations in Ti-Ni-Cu-Mo alloys.

transformation. Since residual elongation is nearly zero for stresses less than 60 MPa in a Ti-44.7Ni-5Cu-0.3Mo alloy, the transformation elongation at 60 MPa is the maximum recoverable one, 6.0%. In a Ti-45Ni-5Cu alloy, the maximum recoverable elongation was known to be 3.3%.¹⁾ This is ascribed to the fact that the maximum recoverable elongation of a Ti-45Ni-5Cu alloy was associated with the B2-B19' transformation, while that of a Ti-44.7Ni-5Cu-0.3Mo alloy was done with the B2-B19-B19' transformation.

Since residual elongations are nearly zero for stresses less than 100 MPa in Ti-39.7Ni-10Cu-0.3Mo and Ti-34.7Ni-15Cu-0.3Mo alloys, the transformation elongations

at 100 MPa are the maximum recoverable ones which are 2.9% and 2.5%, respectively. In the case of a Ti-29.7Ni-20Cu-0.3Mo alloy, the residual elongation is not observed even at 120.4 MPa. Therefore, the transformation elongation at 120.4 MPa is adopted as the maximum recoverable one, 2.4%. The maximum recoverable elongations of Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys associated with the B2-B19 transformation are similar to those of Ti-40Ni-10Cu, Ti-35Ni-15Cu and Ti-30Ni-20Cu alloys.¹⁾

Fig. 12 Stress-strain curves of Ti-Ni-Cu and Ti-Ni-Cu-Mo alloys deformed at Af' of each alloy.

3.4 Superelasticity of Ti-Ni-Cu-Mo alloys

In order to investigate the superelasticity of Ti-Ni-Cu-Mo alloys, tensile tests were made at Af' temperature, and the stress-strain curves obtained are shown in Fig. 12. For comparison, the stress-strain curves of Ti-Ni-Cu alloys fully annealed at 1123 K are also shown. All the alloys exhibit the superelasticity, except for a Ti-45Ni-5Cu alloy. The unrecovered strains after unloading were recovered completely in Ti-Ni-Cu-Mo alloys on heating up to 373 K, while those were not recovered completely in Ti-Ni-Cu alloys. The strain unrecovered after heating up to 373 K is due to plastic deformation. This suggests that substitution of Mo for Ni in Ti-Ni-Cu alloys increases the critical stress for slip deformation. The pseudoelastic recovery defined by e_R/e_T in Ti-Ni-Cu-Mo alloys is found to be 87%–94%, while that in Ti-Ni-Cu alloys is found to be 33–90%. This means that the superelasticity is improved by substitution of Mo for Ni in Ti-Ni-Cu alloys. Complete superelasticity was observed in thermomechanically treated Ti-Ni-Cu alloys.^{9–11)}

4. Conclusions

Phase transformation behavior, the shape memory characteristics and the superelasticity of Ti-Ni-Cu-Mo alloys were

investigated, and then the following conclusions were obtained.

(1) A Ti-44.7Ni-5Cu-0.3Mo alloy transformed in two-stages on cooling and heating, *i.e.*, the B2-B19-B19' on cooling and the B19'-B19-B2 on heating.

(2) Ti-39.7Ni-10Cu-0.3Mo, Ti-34.7Ni-15Cu-0.3Mo and Ti-29.7Ni-20Cu-0.3Mo alloys transformed in one-stage on cooling and heating, *i.e.*, from the B2 to the B19 on cooling and from the B19 to B2 on heating.

(3) The maximum recoverable elongation decreased from 6.0 to 2.4% with increasing Cu-content from 5 to 20 at%.

(4) Transformation hysteresis associated with the B2-B19 transformation decreased from 11 to 5 K with increasing Cu-content from 5 to 20 at% in constant loading test with no residual strain condition.

(5) Substitution of Mo for Ni in Ti-Ni-Cu alloys improved the superelasticity.

Acknowledgements

This work was supported by Korea Energy Management Corporation.

REFERENCES

- 1) T. H. Nam, T. Saburi and K. Shimizu: *Mater. Trans., JIM* **31** (1990) 959–967.
- 2) Y. Shugo, H. Hasegawa and T. Honma: *Bull. Res. Inst. Mineral Dress. Metall., Tohoku Univ.* **37** (1981) 79–86.
- 3) T. Fukuda, T. Chihara, Y. Tsuzuki and T. Saburi: *Trans. Mat. Res. Soc. Jpn.* **18B** (1994) 1065–1068.
- 4) V. E. Gunter: *Medical materials and implants with shape memory effect*, (Tomck, 1998) pp. 180–182.
- 5) T. H. Nam, D. W. Jung, J. P. Noh and H. W. Lee: *J. Mater. Sci.* **36** (2001) 4181–4188.
- 6) T. H. Nam, J. P. Noh and D. W. Jung: *J. Mater. Sci. Lett.* **20** (2001) 713–715.
- 7) J. P. Noh, D. W. Jung, H. W. Lee and T. H. Nam: *Mater. Sci. and Technol.* **17** (2001) 1544–1550.
- 8) T. H. Nam, T. Saburi, Y. Kawamura and K. Shimizu: *Mater. Trans., JIM* **31** (1990) 262–269.
- 9) S. Miyazaki, I. Shiota, K. Otsuka and H. Tamura: *MRS Int'l. Mtg. on Adv. Mats.* **9** (1989) 153–158.
- 10) S. M. Tan and S. Miyazaki: *Mater. Sci. Eng.* **A237** (1997) 79–86.
- 11) T. Ranucci, S. Besseghini and G. Airoidi: *Mater. Sci. Forum* **327–328** (2000) 143–146.