JMEPEG (2005) 14:761-764
DOI: 10.1361/105994905X75574

1059-9495/$19.00

Superelasticity in β Titanium Alloys with Nitrogen Addition

T. Furuhara, S. Annaka, and T. Maki

(Submitted August 24, 2005)

Deformation behavior at room temperature was examined in near-β titanium alloys, Ti-10V-2Fe-3Al, containing small amounts of N up to 0.2 mass%. After a β solution treatment, thermally induced α″ martensite is formed in the N-free alloy but no martensite is formed in the 0.1 and 0.2% N alloys. In the N-free alloy, stress-induced α″ martensite transformation occurs during deformation at room temperature, and a shape memory effect by heating after deformation is exhibited, as was previously reported. In the N-containing alloys, shape recovery over 90%, which is much larger than that in the N-free alloy, was obtained by unloading after a bending deformation. In the 0.1% N alloy, forward and reverse martensite transformations are observed during tensile deformation by in-situ optical microscopy, confirming the occurrence of superelasticity in this alloy. On the other hand, a large elastic strain over 1% is obtained in the 0.2% alloy by strengthening of β matrix, although the α″ martensite introduced by further deformation does not disappear by unloading.

Keywords β titanium alloy, martensite, nitrogen, phase transformation, superelasticity

1. Introduction

It is well known that shape memory effect and superelasticity occur though stress-induced martensite transformation (Ref 1). TiNi-based alloys with an ordered body-centered cubic (bcc) (B2) matrix phase are the most widely used shape memory and superelastic alloys. For biomedical use, however, Ni-free shape memory and superelastic alloys are preferred, and thus, attention has been paid recently to Ni-free β titanium alloys.

One of the deformation mechanisms in β titanium alloys is stress-induced α″ (orthorhombic) martensite transformation from a disordered bcc β matrix (Ref 2). A shape memory effect due to the stress-induced α″ martensite transformation was reported in a Ti-Nb binary alloy (Ref 3), Ti-Mo-Al ternary alloys (Ref 4), and a commercial near-β titanium alloy, Ti-10V-2Fe-3Al (Ref 5, 6). Lee Park et al. (Ref 7) also developed Ti-V-Al shape memory alloys with an atomic ordering of Al. Furthermore, several shape memory and superelastic alloys have recently been developed in titanium alloys with various combinations of substitutional elements (Ref 8-13).

Interstitial elements, such as carbon, nitrogen, and oxygen, were avoided in the development of practical titanium alloys because these elements deteriorate ductility and toughness. However, attention was paid to the large solution strengthening by these elements in the recent development of low-cost titanium alloys (Ref 14-16). It was also recently pointed out that oxygen is important for TiNb-based, low-modulus, superelastic, and high-strength alloys (Ref 17, 18).

In this current study, an attempt to develop superelastic alloys was made by the addition of interstitial alloying elements to β titanium alloys. Nitrogen (N) was chosen to be used for the strengthening of β phase in Ti-10V-2Fe-3Al. It was reported that athermal ω transformation often suppresses the α″ (orthorhombic) martensite transformation in Ti-V-Al alloys (Ref 19, 20). If N suppresses athermal ω transformation as oxygen (O) does in Ti-V-O alloys (Ref 21), then stress-induced β→α″ martensite transformation would be promoted over a wider temperature-composition range, broadening the possibility of shape memory and superelastic titanium alloys. The deformation behavior and the corresponding microstructure change at room temperature of the N-added alloys were studied in comparison with those of the N-free alloy.

2. Experimental Procedure

Table 1 shows the chemical compositions of the alloys used in the current study. Ti-10V-2Fe-3Al-N alloys containing 0.1 and 0.2 mass% N (hereafter 0.1 N and 0.2 N alloys) as well as the N-free alloy were prepared by arc melting. After homogenizing and hot rolling or forging, the specimens were solution-treated in the β single-phase region and quenched into water. The solution treatment conditions performed were 1123 K-3.6 ks for the N-free alloy, 1173 K-1.8 ks for the 0.1 N alloy, and 1273 K-1.8 ks for the 0.2 N alloy, respectively, resulting in similar β grain sizes (140-155 μm) in those alloys. Microstructure was observed by optical microscopy (OM) and transmission electron microscopy (TEM). TEM specimens were prepared by ion thinning after mechanical polishing. Vickers

Table 1 Chemical compositions of the alloys used (mass%)

	V	Fe	Al	N	O	C	H	Ti
N-free	9.67	1.81	3.04	0.009	0.063	…	0.0010	Bal.
0.1 N	9.66	2.04	2.98	0.11	0.081	0.012	0.0200	Bal.
0.2 N	10.95	2.01	3.27	0.22	0.13	0.013	…	Bal.

This paper was presented at the Beta Titanium Alloys of the 00's Symposium sponsored by the Titanium Committee of TMS, held during the 2005 TMS Annual Meeting & Exhibition, February 13-16, 2005 in San Francisco, CA.

T. Furuhara, Institute for Materials Research, Tohoku University Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan; **T. Maki,** Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan; and **S. Annaka,** Graduate Student, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan. Contact e-mail: furuhara@imr.tohoku.ac.jp.

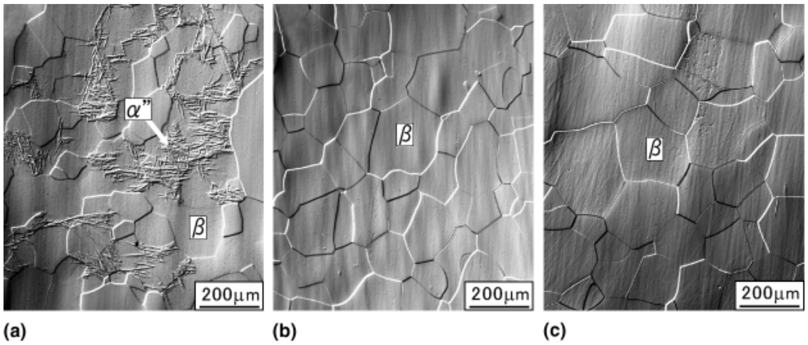

Fig. 1 Optical micrographs of the solution-treated and quenched specimens: (a) N-free, (b) 0.1 N, and (c) 0.2 N alloys

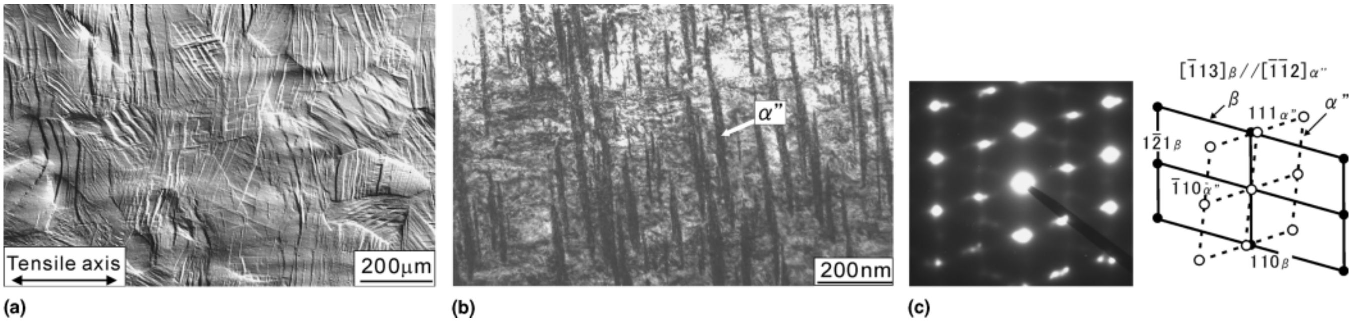

Fig. 2 Microstructure of the N-free alloy 2% deformed in tension: (a) OM micrograph, (b) TEM micrograph, and (c) corresponding SADP with a key diagram

hardness was measured with a load of 9.8 N. Sheet specimens 0.25 mm thick were deformed by bending at room temperature. The bend angle and radius are 110° and 5 mm, respectively. The maximum strain reaches 2.5% at the surface. Each spring-back after unloading and the shape recovery after holding at 573 K for 5 s was determined as the ratio of the recovered angle to 110°.

3. Results and Discussion

Figure 1 shows the OM microstructures of the N-free and N-added alloys quenched to room temperature after the β solution treatments. The β matrix is mostly retained, and some martensite plates are formed by quenching in the N-free alloy (Fig. 1a). As reported previously, this martensite phase is orthorhombic α″ (Ref 5, 6). On the other hand, martensite is not formed in the 0.1 N (Fig. 1b) or 0.2 N (Fig. 1c) alloy by quenching. In the in-situ OM observations, no further martensite transformation took place in cooling to 130 K.

Figure 2 shows the OM and TEM micrographs of the N-free alloy deformed in tension by 2% at room temperature. Some banded structures are formed by deformation (Fig. 2a). In the TEM micrograph (Fig. 2b), fine, plate-shaped products are formed by deformation. The corresponding selected area diffraction pattern (SADP) and its key diagram in Fig. 2(c) reveal that those plates are orthorhombic α″ martensite.

The OM micrographs in Fig. 3 show the variation of surface relieves in the 0.1 N alloy during the in-situ OM observation when the specimen was deformed up to 1.5% under tension at room temperature. By deformation, surface reliefs by the stress-induced martensite transformation appear on the polished surface in Fig. 3(c). As deformation proceeds, new reliefs are formed (Fig. 3e). These relieves mostly disappear by unloading (Fig. 3d and f). This clearly indicates that superelasticity due to the stress-induced α″ martensite transformation is obtained in this alloy.

The OM micrographs in Fig. 4 show the variation of surface reliefs in the 0.2 N alloy during the in-situ OM observation during tensile deformation at room temperature up to 1.3%. Until the strain exceeds 1%, no surface relief is formed and the specimen is deformed only elastically (Fig. 4b). After 1.3% deformation, surface relieves by the stress-induced α″ martensite transformation appear on the polished surface in Fig. 4(c). Those relieves do not disappear by unloading, implying that superelasticity is not appeared in this alloy.

Fig. 5(a) shows the Vickers hardness of the solution-treated Ti-10V-2Fe-3Al-N alloys. The hardness increases as N content increases. Figure 5(b) is the shape recovery after the unloading and subsequent heating to 573 K. The N-free alloy exhibits a recovery of 60% by unloading after bending. By heating, the remaining strain is mostly recovered by the shape memory effect reported by Duelig et al. (Ref 5, 6). In the 0.1 N alloy, the shape recovery after unloading is increased to 90%. A remaining strain is recovered by heating in this alloy as in the N-free alloy. The shape recovery that reaches 95% occurs mostly after unloading in the 0.2 N alloy, but no recovery occurs after heating. Thus, it is concluded the addition of 0.1 N results in the superelasticity, although the deformation by bending is mostly produced elastically in the 0.2 N alloy due to solid solution strengthening of the β matrix by N addition. The Young's moduli determined as averaged values in the elastically deformed region are 50-60 GPa in these alloys. The tensile properties of the alloys will be reported elsewhere in more detail (Ref 22).

Lee Park et al. (Ref 7) considered short-range ordering of Al is important for the shape memory effect in the Ti-V-Al shape memory alloys containing more than 4 mass% Al. Because Ti-10V-2Fe-3Al-N contains 3 mass% Al, it is important to

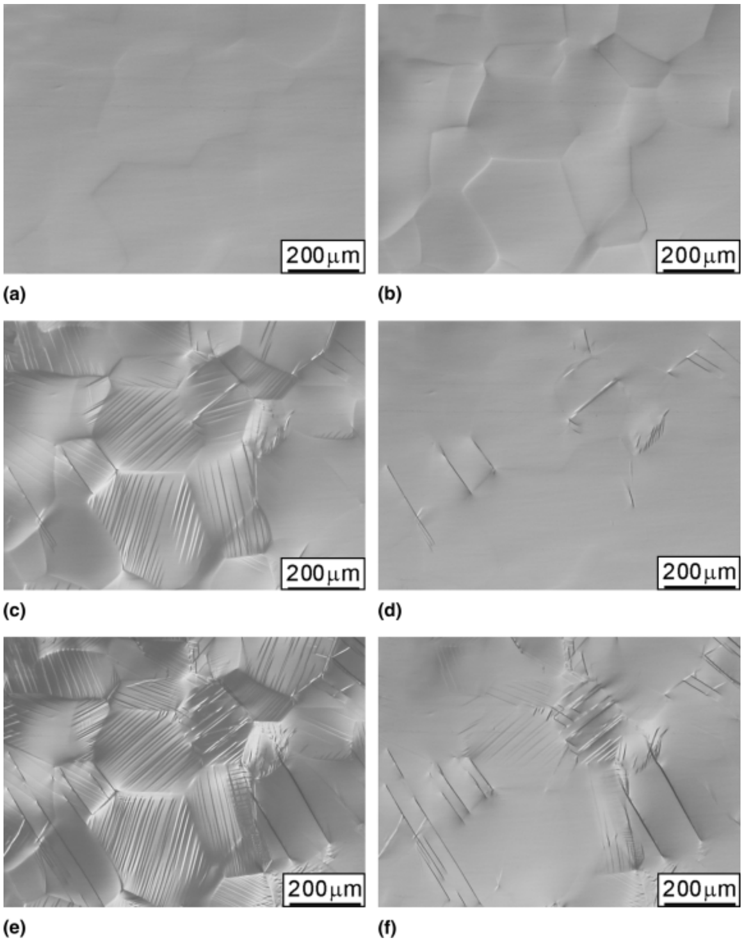

Fig. 3 Optical micrographs showing the formation and reversion of surface relieves during the in-situ tensile deformation at room temperature (Ti-10V-2Fe-3Al-0.1N): (a) before deformation, (b) 0.5% deformed, (c) 1.0% deformed and (d) unloaded, and (e) 1.5% deformed and (f) unloaded

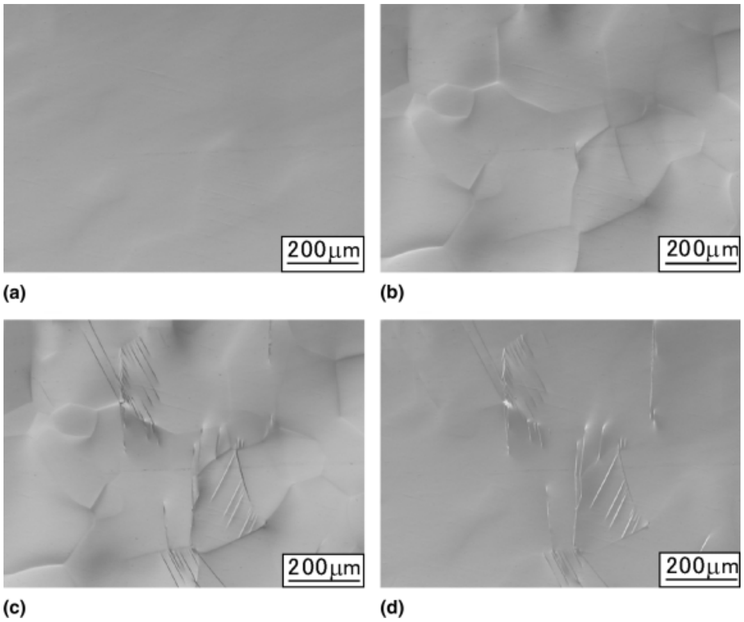

Fig. 4 Optical micrographs showing the microstructure change in the in-situ tensile deformation at room temperature (Ti-10V-2Fe-3Al-0.2N): (a) before deformation, (b) 1.0% deformed, (c) 1.3% deformed, and (d) unloaded

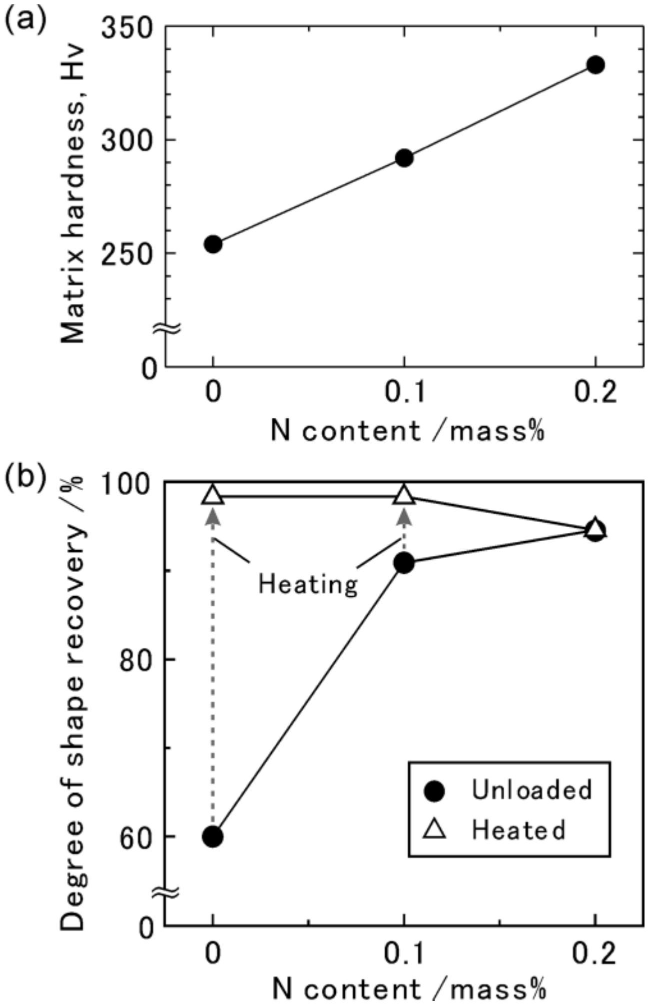

Fig. 5 Variation of (a) hardness and (b) shape recovery with addition of N

examine the deformation behavior of Al-free alloys. However, superelastic behaviors are observed in several Al-free alloys (Ref 9, 11-13, 23) and even in Ti-Nb binary alloys (Ref 24). Although the mechanism of superelasticity needs to be examined further, it is clear that Al is not always necessary for the superelasticity of β titanium alloys.

4. Conclusions

The addition of N > 0.1 mass% suppresses the formation of thermally induced α″ martensite in Ti-10V-2Fe-3Al. Those alloys are deformed by stress-induced martensite transformation at room temperature. Forward and reverse stress-induced martensite transformations are observed in the 0.1 mass% N alloy during tensile tests by in-situ optical microscopy, confirming the occurrence of superelasticity in this alloy. The addition of N also increases the amount of elastic deformation of β matrix by solid solution strengthening.

Acknowledgment

The authors are grateful to Kobe Steel, Ltd. for providing the materials used.

References

1. K. Otsuka and K. Shimizu, Pseudoelasticity and Shape Memory Effects in Alloys, *Int. Met. Rev.,* Vol 31 (No. 3), 1986, p 93-114
2. J.C. Williams, Critical Review, Kinetics and Phase Transformations, *Titanium Science and Technology,* by R.I. Jaffee and H.M. Burte, Ed., Plenum Press, 1973, p 1433-1493
3. C. Baker, The Shape-Memory Effect in a Titanium-35 wt.% Niobium Alloy, *Met. Sci. J.,* Vol 5, 1971, p 92-100
4. H. Sasano and T. Suzuki, Shape Memory Effect in Ti-Mo-Al Alloys, *Proceedings of the 5th International Conference on Titanium,* G. Lutjering, U. Zwicker, and W. Bunk, Ed., DGM, 1985, p 1667–1676
5. T.W. Duelig, J. Albrecht, and D. Ritcher, Shape Memory in Ti-10V-2Fe-3Al, *Scr. Metall.,* Vol 16 (No. 3), 1982, p 957-961
6. T.W. Duelig, J. Albrecht, D. Ritcher, and P. Fischer, Formation and Reversion of Stress Induced Martensite in Ti-10V-2Fe-3Al, *Acta Metall.,* Vol 30 (No. 12), 1982, p 2161-2172
7. J.S. Lee Park, C.Y. Lei, and C.M. Wayman, Atomic Ordering in Ti-V-Al Shape Memory Alloys, *Mater. Sci. Eng. A*, Vol 132, 1991, p 237-244
8. T. Grosdidier and M.J. Philippe, Deformation Induced Martensite and Superelasticity in a β-Metastable Titanium Alloy, *Mater. Sci. Eng. A,* Vol 291, 2000, p 218-223
9. E. Takahashi, T. Sakurai, S. Watanabe, N. Masahashi, and S. Hanada, Effect of Heat Treatment and Sn Content on Superelasticity in Biocompatible TiNbSn Alloys, *Mater. Trans.,* Vol 43 (No. 12), 2002, p 2978-2983
10. Y. Fukui, T. Inamura, H. Hosoda, K. Wakashima, and S. Miyazaki, Mechanical Properties of a Ti-Nb-Al Shape Memory Alloy, *Mater. Trans.,* Vol 45 (No. 4), 2004, p 1077-1082
11. H.Y. Kim, Y. Ohmatsu, J.I. Kim, H. Hosoda, and S. Miyazaki, Mechanical Properties and Shape Memory Behavior of Ti-Mo-Ga Alloys, *Mater. Trans.,* Vol 45 (No. 4), 2004, p 1090-1095
12. T. Maeshima and M. Nishida, Shape Memory Properties of Biomedical Ti-Mo-Ag and Ti-Mo-Sn Alloys, *Mater. Trans.,* Vol 45 (No. 4), 2004, p 1096-1100
13. T. Maeshima and M. Nishida, Shape Memory and Mechanical Properties of Biomedical Ti-Sc-Mo Alloys, *Mater. Trans.,* Vol 45 (No. 4), 2004, p 1101-1105
14. H. Fujii, S. Soeda, M. Hanaki, and H. Okano, Development of High-Performance, Low Alloy Ti-Fe-O-N Series, *Titanium '95 Science and Technology,* P.A. Blenkinsop, W.J. Evans, and H.M. Flower, Ed., TIM, 1996, p 2309-2316
15. S. Kojima and H. Oyama, New Alpha-Beta Titanium Alloy, KS Ti-4.5Al-4Cr-0.5Fe-0.2C, Possessing Both Extremely Low Flow Stress during Hot Working Similar to Grade 2 and High Strength Comparable to Grade 5, *Ti-2003 Science and Technology,* G. Lutjering and J. Albrecht, Ed., Wiley-VCH, 2004, p 3089-3095
16. S. Kojima and H. Oyama, New Coilable High-Strength Alpha-Beta Titanium Alloy, KS Ti-9, with Properties Comparable to Ti-6Al-4V, *Ti-2003 Science and Technology,* G. Lutjering and J. Albrecht, Ed., Wiley-VCH, 2004, p 3097-3102
17. T. Saito, T. Furuta, J.-H. Hwang, S. Kuramoto, K. Nishino, N. Suzuki, R. Chen, A. Yamada, K. Ito, Y. Seno, T. Nonaka, H. Ikehata, N. Nagasako, C. Iwamoto, Y. Ikuhara, and T. Sakuma, Multifunctional Alloys Obtained via a Dislocation-Free Plastic Deformation Mechanism, *Science,* Vol 300, 2003, (No. 5618), p 464-467
18. T. Saito, T. Furuta, J.-H. Hwang, S. Kuramoto, K. Nishino, N. Suzuki, R. Chen, A. Yamada, K. Ito, Y. Seno, T. Nonaka, H. Ikehata, N. Nagasako, C. Iwamoto, Y. Ikuhara, and T. Sakuma, Multi Functional Titanium Alloy "GUM METAL", *Mater. Sci. Forum,* Vol 426-432, 2003, p 681-688
19. T. Maeda and H.M. Flower, The Effect of Aluminium on the Phase Transformations in Ti-15%V, *Proceedings of the 6th World Conference on Titanium,* R. Lacomb, R. Tricot, and G. Beranger, Ed., Les Editions de Physique, 1988, p 1589-1594
20. T. Maeda and H.M. Flower, The Effect of Aluminium on the Phase Transformations in Ti-19V and 23V Alloys, *Titanium '92 Science and Technology,* F.H. Froes and I.L. Caplan, Ed., TMS, 1993, p 705-712
21. N.E. Paton and J.C. Williams, The Influence of Oxygen Content on the Athermal β-ω Transformation, *Scr. Metall.,* Vol 7 (No. 6), 1973, p 647-650
22. T. Furuhara, S. Annaka, Y. Tomio, and T. Maki, Superelasticity in Ti-10V-2Fe-3Al Alloys with Nitrogen Addition, submitted to *Materials Science and Engineering A*.
23. N. Sakaguchi, M. Niinomi, and T. Akahori, Tensile Deformation Behavior of Ti-Nb-Ta-Zr Biomedical Alloys, *Mater. Trans.,* Vol 45 (No. 4), 2004, p 1113-1119
24. H.Y. Kim, H. Satoru, J.I. Kim, H. Hosoda, and S. Miyazaki, Mechanical Properties and Shape Memory Behavior of Ti-Nb Alloys, *Mater. Trans.,* Vol 45 (No. 7), 2004, p 2443-2448