Transactions of the Materials Research Society of Japan 32[3] 639-642 (2007)

Application of Ni-free Ti-Mo-Sn shape memory alloys to medical tools

Y. Sutou, A. Furukawa*, M. Suzuki*, K. Yamauchi* and M. Nishida**
Department of Materials Science, Graduate School of Engineering, Tohoku University, 6-6-11 Aoba-yama, Sendai 980-8579, Japan
Fax: 81-795-7338, e-mail: ysutou@material.tohoku.ac.jp
*Tohoku University Biomedical Research Organization, Aoba-yama 6-6-02, Sendai 980-8579, Japan
** Kumamoto University, Kumamoto 860-8555, Japan

Superelastic properties of Ni-free Ti-Mo-Sn shape memory alloys (SMAs) were investigated using tensile testing. The solution-treated Ti-Mo-Sn alloys showed a recoverable strain of over 3%, while the alloy heat treated at around 923 K exhibited a high tensile strength of over 1000 MPa. Based of those results, a new type of guidewire with functionally graded properties from the tip to the end was developed using Ti-Mo-Sn SMA core wire. This guidewire is expected to show excellent pushability and torquability superior to those of stainless steel and Ti-Ni guidewires. In addition, Ti-Mo-Sn tubes, which are expected to be used for metallic catheters, were fabricated. The superelastic properties of those tubes are also reported.
Key words: Ti-Mo-Sn, superelasticity, guidewire, catheter, superelastic tubes

1. INTRODUCTION

Recently, shape memory alloys (SMAs) with superelasticity (SE) are attracting considerable attention as core materials for minimally invasive surgical devices such as guidewires, catheters, stents, and so on [1-4]. Although Ti-Ni SMAs possessing excellent SE are currently widely used in such medical devices, the toxicity and hypersensitivity of Ni have been problematic [5]. Thus, the development of biocompatible Ni-free SMAs is strongly required. Recently, biocompatible Ti-based SMAs such as Ti-Mo-based alloys [6-8] and Ti-Nb-based alloys [9-13] have been studied by many researchers. Maeshima and Nishida, the latter being one of the present authors, have also developed Ti-Mo-Sn SMAs, which show a good SE based on β (disordered bcc) to α" (orthorhombic martensite) stress-induced martensitic transformation [7].

A guidewire, which generally consists of a metal core wire, is indispensable for introducing the catheter into a blood vessel. The tip portion of the guidewire must be sufficiently flexible to pass through the meandering blood vessels, while in the body portion of the guidewire, a high elastic modulus and strength against bending are required so that the tip portion of guidewire can be pushed into the narrow blood vessel with smooth transmission of the torque from the end to the tip portion of the guidewire. Currently, Ti-Ni SMAs and stainless steel (AISI304) wires are widely used for the core materials of guidewires. Although Ti-Ni SE wire shows excellent flexibility and shape retention, its pushability and torquability are insufficient because of low rigidity. On the other hand, stainless steel wire possesses a high strength, but its response to rotation in the meandering blood vessels is poor because plastic deformation easily occurs. In this paper, a new type of SE guidewire using a Ti-Mo-Sn SMA core wire in which mechanical properties such as SE and strength from the tip to the body portion can be gradually changed by heat-treatment control are presented. Moreover, SE properties of Ti-Mo-Sn tubes which hold promise as a new class of metallic catheters are also investigated.

2. EXPERIMENTAL PROCEDURES

Ti-5at.%Mo-5at.%Sn (designated as 5Mo-5Sn) and Ti-6at.%Mo-4at.%Sn (designated as 6Mo-4Sn) alloys were prepared by cold crucible induction melting (CCIM). The cast alloy was hot-forged and hot-rolled at 1173 K and then cold-drawn down from a diameter of 8 mm to a diameter of 1.0 - 0.34 mm with interpass annealing at 1023 K for 600 seconds, the total reduction rate after interpass annealing being about 60% (10% reduction at every step). The as-cold-drawn wires encapsuled in an evacuated quartz tube were heat treated in the temperature range of 923-1073 K for 300 – 900 seconds and then either quenched in water by breaking the quartz tube or air cooled. Tensile testing was carried out at a strain rate of 0.83×10^{-2} mm/s at room temperature, the gauge length of the wires being 50 mm. The functionally graded core wire for guidewire was fabricated using Ti-Mo-Sn wire with a diameter of 0.34 mm. Details of the heat-treatment methods are described below.

Ti-Mo-Sn tubes with various diameters were fabricated by 3-roll rolling and cold-drawing hot-forged 15-mm-diameter Ti-Mo-Sn bars with a 12-mm-diameter hole created by electro-discharge machining.

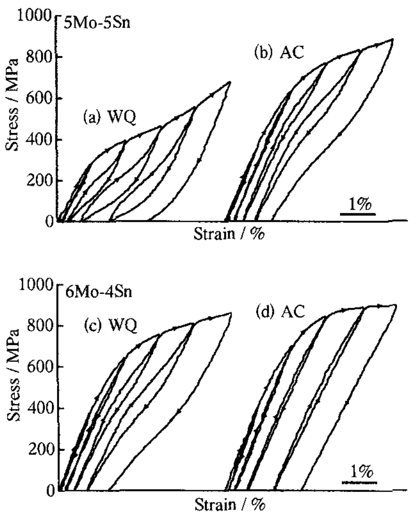

Fig. 1 Cyclic stress-strain curves in Ti-Mo-Sn wires with a diameter of 1.0 mm.

3. RESULTS AND DISCUSSION

3.1 Superelasticity of Ti-Mo-Sn wires

Figures 1 (a) and (c) show the cyclic stress-strain curves of the wire solution treated at 1073 K followed by quenching in ice water (WQ) in the 5Mo-5Sn and 6Mo-4Sn wires, respectively, the diameter of the wires being 1.0 mm. The wires were first loaded with tension up to a strain of 1% and then unloaded. Next, they were reloaded up to a strain of 2% in the second cycle and then unloaded and so forth. The 6Mo-4Sn wire shows much better SE than the 5Mo-5Sn wire at room temperature. Although it is supposed that the martensitic transformation temperatures of the 5Mo-5Sn is higher than those of the 6Mo-4Sn because the yield stress of the 5Mo-5Sn wire is much lower than that of the 6Mo-4Sn wire, both wires show excellent SE at even 123 K, which means that the martensitic transformation temperatures should be below 123 K. The cyclic stress-strain curves of the 5Mo-5Sn and 6Mo-4Sn wires solution treated at 1073 K followed by air cooling (AC) are shown in Fig. 1(b) and (d), respectively. It can be seen that the mechanical properties and SE strain strongly depend on the cooling rate and that the yield stress of both wires increases with decreasing cooling rate. The 5Mo-5Sn AC wire shows much better SE than the 5Mo-5Sn WQ wire, while SE is hardly observed in the 6Mo-4Sn AC wire. This would be caused by athermal ω phase formation during cooling [7]. The ω phase usually suppresses the martensitic transformation, which means that the martensitic transformation temperatures decrease with the formation of the ω phase.

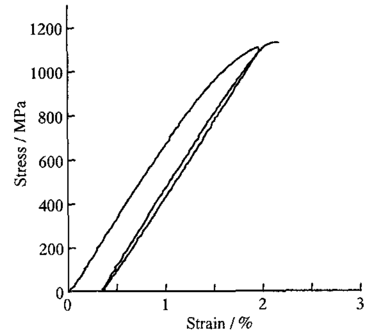

Fig. 2 Cyclic stress-strain curve in 5Mo-5Sn wire heat treated at 923 K.

3.2 High strength Ti-Mo-Sn wire

The present authors have previously reported that the mechanical properties of the 6Mo-4Sn alloy strongly depend on the heat-treatment temperature [14]. A high Young's modulus and high strength can be obtained by heat treatment at below the recrystallization temperature of about 973 K. Figure 2 shows the cyclic stress-strain curve of 5Mo-5Sn wire heat treated at 923 K for 180 seconds, the diameter of the wire being 0.34 mm. It is seen that a high Young's modulus of over 80 GPa and tensile strength of about 1200 MPa can be obtained in the 5Mo-5Sn thin wire. Moreover, it is noted that the 5Mo-5Sn rigid wire heat treated at 923 K is not fractured even by elbow-shaped bending.

3.3 Functionally graded Ti-Mo-Sn wire

Based on the above results, a core wire with a diameter of 0.34 mm and a length of 1500 mm for a guidewire with functionally graded properties was actually manufactured. In this study, a 5Mo-5Sn wire was used for the proto-type guidewire because the 5Mo-5Sn shows good SE even if the quenching rate is slow, as shown in Fig. 1. In order to obtain a rigid 5Mo-5Sn wire, the entire length of wire was heat treated at 923 K. Only the tip portion of wire with a length of 1500 mm was then solution treated at 1023 K followed by air-cooling, as indicated in Fig. 3. Figure 3 shows the temperature distribution of the furnace

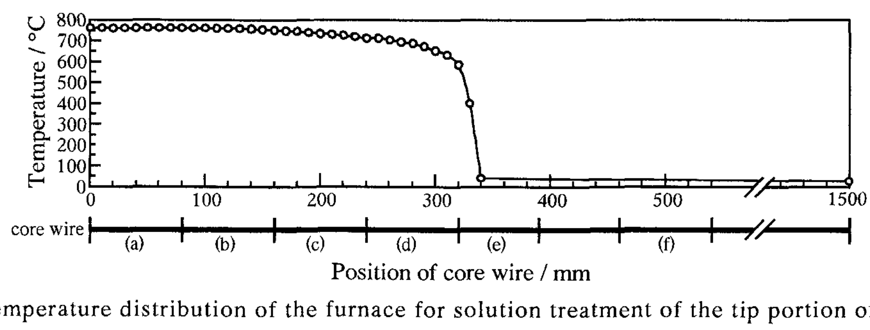

Fig. 3 Temperature distribution of the furnace for solution treatment of the tip portion of core wire.

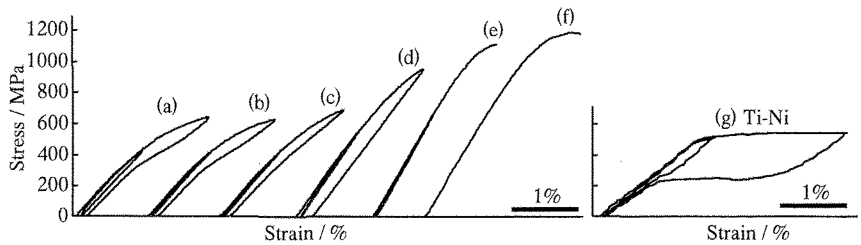

Fig. 4 (a)-(f) Cyclic stress-strain curves of each position of the core wire and (g) Ti-Ni SE core wire.

used in the present study. The furnace temperature is drastically changed around a position of 300-340 mm from the tip. Figures 4(a)-(f) show the stress-strain curves of each part of the core wire as indicated in Fig. 3, where the wires were tensile loaded to a strain of about 2%. Figures 5(a) and (b) show the plots of the Young's modulus E and the tensile stress σ_m defined from the stress-strain curves in Fig. 4 vs. the position of the core wire, respectively, where σ_m is the stress level when a strain of 2% is applied. It can be seen that while the tip portion of the core wire shows a low Young's modulus of 47 GPa, a low σ_m of 645 MPa and good SE, the strength of the wire increases gradually and the body portion possesses a high Young's modulus of 76 GPa and high strength of about 1200 MPa. Figure 5(g) shows the stress-strain curves of a Ti-Ni SE core wire with a diameter of 0.34 mm for use as a practical guidewire. The tip portion of 5Mo-5Sn core wire has almost the same Young's modulus as the Ti-Ni SE wire, while the Young's modulus and the σ_m of the body portion of the 5Mo-5Sn core wire are much higher than those of Ti-Ni SE core wire. The inset in Fig. 5(a) shows a proto-type Ti-Mo-Sn guidewire having functionally graded properties. A hydrophilic coating is usually applied to facilitate smooth movement of the guidewire in the blood vessel. Since the present guidewire with functionally graded properties has a SE tip portion and a highly rigid body portion, it is expected to show excellent pushability and torquability and better handling ability than conventional guidewires[16]. Usually, doctors themselves reshape the tip portion of the guidewire as they desire. The Ti-Mo-Sn SE wire with imperfect shape recovery, as shown in Fig. 4(a), is considered to show good reshapability and stable SE properties after reshaping.

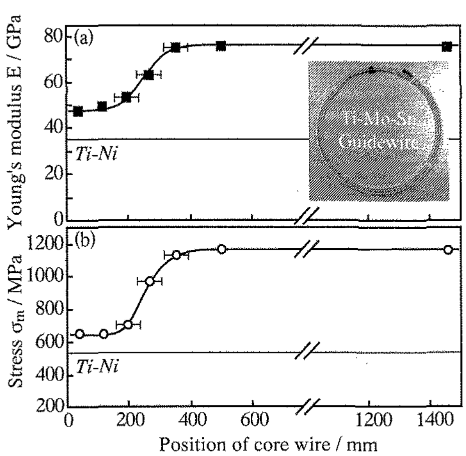

Fig. 5 Plots of (a) Young's modulus E and (b) tensile stress σ_m vs. position of the core wire.

3.4 Ti-Mo-Sn superelastic tubes

Figure 6 shows 6Mo-4Sn tubes with various dimensions. Since the Ti-Mo-Sn alloys possess good ductility, tubes as small as ϕ1.0mm × t0.1mm can be obtained. Figures 7(a), (b) and (c) show the cyclic tensile stress-strain curves of a ϕ3.6 mm × t0.3 mm 5Mo-5Sn tube, a ϕ2.36 mm × t0.19 mm 6Mo-4Sn tube and a ϕ1.0 mm × t0.1 mm 6Mo-4Sn tube, respectively, the tubes being heat treated at 1073 K for 300 seconds in a vacuum followed by quenching into water. These Ti-Mo-Sn tubes show SE similar to that of the wires. It can be seen that the SE of the ϕ1.0 mm 6Mo-4Sn tubes is worse than that of the ϕ2.36 mm tubes. Figure 8 shows the outer and inner diameter dependence of the recoverable strain ε_r in the 6Mo-4Sn tubes, where the ε_r is the recoverable strain after application of a strain of 3%. The ε_r depends on the diameter of tubes and decreases with decreasing diameter. This dependence is considered to be related to the grain size and the development of texture. In the Cu-based SMAs, it is known that the SE depends on the grain size and the formation of texture and, especially, that the SE drastically deceases with decreasing grain size [15, 16]. The grain size and texture dependence of SE in

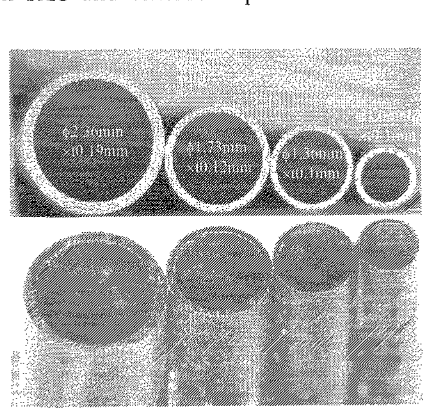

Fig. 6 6Mo-4Sn tubes with various dimensions.

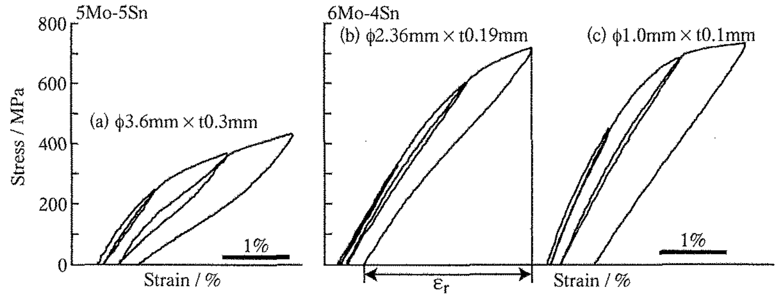

Fig. 7 Cyclic stress-strain curves of Ti-Mo-Sn SE tubes.

Ti-Mo-Sn based SMAs will be reported in near future. These Ni-free Ti-Mo-Sn SE tubes are expected to be used in catheters and stents. In the case of the Ti-Ni SE tubes for catheters, not only the outer surface but also the inner surface of the tube is coated by resin because Ti-Ni contains a large amount of Ni element and the inner surface becomes rough due to its low cold-workability. On the other hand, since Ni-free Ti-based alloys possess high corrosion resistance and excellent biocompatibility [17], a new class of metallic flexible catheters with a fine diameter and thin walls and capable of contact with the blood can be expected.

4. CONCLUSIONS

The Ti-Mo-Sn SMAs exhibit good cold-workability and their mechanical properties such as SE and rigidity can be varied through heat treatment. Based on these results, a new type of guidewire with functionally graded characteristics was developed using Ni-free SE wire. This guidewire with functionally graded characteristics is expected to show better steerability than guidewires employing Ti-Ni SE or stainless steel core wires. Moreover, since Ni-free Ti-Mo-Sn SMAs are expected to show excellent biocompatibility, they can be used as catheters without an inner resin coating and as stents.

ACKNOWLEDGEMENTS

This study was supported by the Special Coordination Funds for Promoting Science and Technology of Encouraging Development of Strategic Research Centers Program. One of the authors (Y. S.) also acknowledges the "SUZUKEN MEMORIAL FOUNDATION" for financial support.

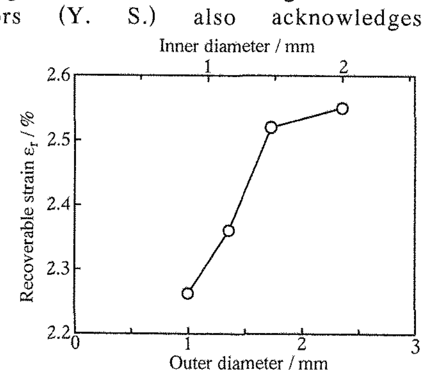

Fig. 8 Size dependence of recoverable strain in the 6Mo-4Sn tubes.

REFERENCES

[1] J. Stice, "Engineering aspects of shape memory alloys," Ed. by T. W. Duerig, K. N. Melton, D. Stockel and C. M. Wayman, Butterworth-Heinemann Ltd, London (1990) pp.483-87.
[2] S. Miyazaki, "Shape Memory Materials," Ed. by K. Otsuka and C. M. Wayman, Cambridge University Press, Cambridge (1998) pp. 267-81.
[3] K. Otsuka and X. Ren, *Intermetallics*, **7**, 511-28 (1999).
[4] T. Duerig, A. Pelton and D. Stöckel, *Mater. Sci. Eng.* A, **A273-275**, 149-60 (1999).
[5] G. Schmalz, U. Schuster and H. Schweikl, *Biomaterials*, **19**, 1689-94 (1998).
[6] HY. Kim, Y. Ohmatsu, JI. Kim, H. Hosoda and S. Miyazaki, *Mater. Trans.*, **45**, 1090-95 (2004).
[7] T. Maeshima and M. Nishida, *Mater. Trans.*, **45**, 1101-05 (2004).
[8] T. Maeshima, S. Ushimaru, K. Yamauchi and M. Nishida, *Mater. Trans.*, **47**, 513-17 (2006).
[9] K. Nitta, S. Watanabe, N. Masahashi, H. Hosoda and S. Hanada, "Structural Biomaterials for 21th Century," Ed. by M. Niinomi, TMS, Warrendale, Pennsylvania (2001) pp. 25-34.
[10] H. Hosoda, Y. Fukui, T. Inamura, K. Wakashima, S. Miyazaki and K. Inoue, *Mater. Sci. Forum*, **426-432**, 3121-25 (2003).
[11] Y. Fukui, T. Inamura, H. Hosoda, K. Wakashima and S. Miyazaki, *Mater. Trans.*, **45**, 1077-82 (2004).
[12] HY. Kim, H. Satoru, JI. Kim, H. Hosoda and S. Miyazaki, *Mater. Trans.*, **45**, 2443-48 (2004).
[13] H. Hosoda, Y. Fukui, T. Inamura, K. Wakashima and S. Miyazaki, *Mater. Sci. Forum*, **475-479**, 2329-32 (2005).
[14] Y, Sutou, K. Yamauchi, T. Takagi, T. Maeshima and M. Nishida, *Mater. Sci. Eng. A*, in press (2006).
[15] Y. Sutou, T. Omori, R. Kainuma, N. Ono and K. Ishida, *Metall. Mater. Trans. A*, **33A**, 2817-24 (2002).
[16] Y. Sutou, T. Omori, K. Yamauchi, N. Ono, R. Kainuma and K. Ishida, *Acta Mater.*, **53**, 4121-33 (2005).
[17] A. Kawashima, S. Watanabe, K. Asami, and S. Hanada, *Mater. Trans.*, **44**, 1405-11 (2003).

(Received January 20, 2007;Accepted May 10, 2007)