JMEPEG (2011) 20:618–622
DOI: 10.1007/s11665-011-9885-4

1059-9495/$19.00

Effect of Aging on the Microstructure and Shape Memory Effect of a Hot-Rolled NiTiHf Alloy

Mahdi Moshref Javadi, Majid Belbasi, Mohammad T. Salehi, and M. Reza Afshar

(Submitted August 14, 2010; in revised form February 14, 2011)

In this article, the effect of aging on the microstructure and shape memory effect (SME) of a hot-rolled $Ni_{49}Ti_{36}Hf_{15}$ alloy is studied. The alloy was prepared by vacuum induction melting (VIM) and homogenized at 1000 °C for 2 h. The homogenized alloy was then undergone 45% hot rolling at 850 °C and aging at temperatures of 500 and 600 °C for 2 h. Optical microscopy (OM) and scanning electron microscopy (SEM) conducted on the hot-rolled samples revealed that hot rolling improves microstructure, deformation, and recoverable strains such that the alloy recovers 3.10 of 3.23 and 5.61 of 6.25 strain in the homogenized and hot-rolled state, respectively. Aging, however, adversely affects the formability and SME of the alloy, which stems from the embrittling effect of the newly formed precipitates during the aging process.

Keywords high-temperature shape memory alloy, hot rolling, microstructure, Ni-Ti-Hf, shape memory effect

1. Introduction

In the most common group of shape memory alloys, binary NiTi alloys, the transformation temperatures hardly exceed 100 °C (Ref 1, 2). Recently, shape memory alloys, called NiTi-based high-temperature shape memory alloys, have been developed, in which the transformation temperatures are above 100 °C. These alloys include NiTiX (X = Pt, Pd, Au, Zr, Hf), and have the potential to meet the requirements for high-temperature applications. Among these alloys, NiTiHf alloys seem to be more practical for engineering applications, primarily due to high transformation temperatures, good thermal stability, and lower price relative to NiTiX (X = Pt, Pd, Au) (Ref 1, 3-6). Nevertheless, NiTiHf alloys suffer from poor ductility and low strength of the matrix. The former, along with a high critical stress required for reorientation of the martensite variants (Ref 7) have caused these alloys to show only about 3% fully recoverable strain, which is lower than those of NiTi alloys (Ref 8). These limitations hinder their applications; thus their properties should be improved.

This article is an invited paper selected from presentations at Shape Memory and Superelastic Technologies 2010, held May 16-20, 2010, in Pacific Grove, California, and has been expanded from the original presentation.

Mahdi Moshref Javadi, Majid Belbasi, and **Mohammad T. Salehi**, School of Metallurgy and Materials Engineering, Iran University of Science and Technology, P.O. Box 16844, Tehran, Iran; and **M. Reza Afshar**, Department of Materials Engineering, Science and Research Branch, Islamic Azad University, Tehran 14778-93855, Iran. Contact e-mails: moshrefj@gmail.com, belbasi@iust.ac.ir, salehi@ iust.ac.ir, and mafshar@srbiau.ac.ir.

To date, several features such as phase composition, shape memory properties, martensitic transformations, mechanical properties, and aging of NiTiHf have been investigated (Ref 3-15). However, no study is published on the combined effects of aging and hot rolling on NiTiHf alloys. Therefore, this study is undertaken to perform aging on a hot-rolled NiTiHf alloy and to investigate their combined influences on the microstructure and shape memory effect (SME).

2. Experimental Procedure

A $Ni_{49}Ti_{36}Hf_{15}$ alloy was prepared by vacuum induction melting (VIM) using 99.9% Ni, 99.2% Hf, and 99.7% Ti in a graphite crucible under the vacuum of 10^{-4} mbar. The cast sample was homogenized at 1000 °C for 2 h under Ar atmosphere followed by quenching in water. Then, the homogenized specimen was polished and prepared for the subsequent hot rolling. The process of hot rolling was performed at 850 °C in four passes; each applying about 10% deformation in such a way to deform the specimen 45% in total. The specimens were solution treated at 950 °C for 2 h; afterward, they were aged at 500 and 600 °C for 2 h, under the protection of Ar atmosphere. Microstructure and phase examinations were performed by optical microscopy (OM), scanning electron microscopy (SEM), x-ray diffraction (XRD) technique, and energy-dispersive x-ray spectroscopy (EDS). The etchant of $HF:HNO_3:H_2O$ = 1:4:5 was used for preparing the samples for microstructural examinations. Bending test was used for evaluation of SME, which is also described by Meng et al. (Ref 7). Schematic illustration of this method is shown in Fig. 1. At first, the specimen was deformed to deformation position at room temperature, and then unloaded to the spring back position. When heated to 300 °C, the specimen recovered its shape to heating position, and then cooled to room temperature, corresponding to the cooling position. The applied strain, ε_d, recovered strain, ε_{re}, and recovery ratio, R, can be calculated by $\varepsilon_d = d/(d + D)$, $\varepsilon_{re} = (180° - \theta_h) \times \varepsilon_d/180°$, and

$R = (\theta_d - \theta_h)/\theta_d \times 100\%$, respectively, where d is the thickness of the plate specimen and D is the diameter of the rod.

3. Results and Discussion

3.1 Microstructural Examinations

XRD pattern of the homogenized specimen is shown in Fig. 2 which demonstrates that the alloy is consisted of B19′ martensite and $(Ti,Hf)_2Ni$ second phase. This microstructure is consistent with the results published in the literature (Ref 15).

Figure 3 illustrates the microstructure of as-cast, homogenized, hot-rolled and 500 °C-aged specimens. According to Fig. 3(a), in the cast specimen, some voids are noticed throughout the rose-like structure. Through homogenizing at 1000 °C for 2 h, the microstructure changes to a less dendritic structure, and the quantity of the voids decreases. The combination of heat and deformation during the hot rolling process improves the microstructure through annihilation of the voids. In the specimen aged at 500 °C for 2 h, the second phase roughly covered the grain boundaries, and the grains grew in comparison with the microstructure of the hot-rolled specimen.

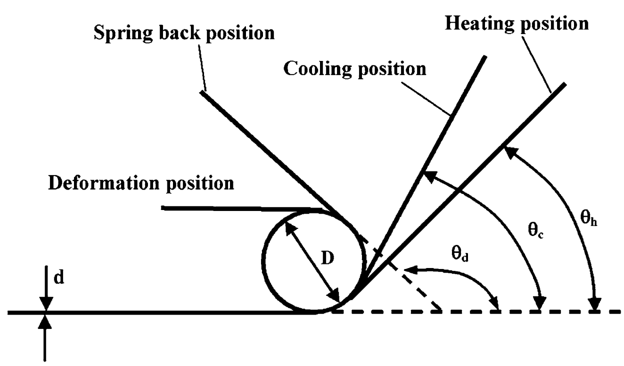

Fig. 1 Schematic illustration of shape memory effect measurement using bending test (Ref 7)

The SEM micrographs of the as-cast, hot-rolled, solution-treated and 500 °C-aged samples are illustrated in Fig. 4. Comparing as-cast and hot-rolled microstructures shows that hot rolling decreases the size of the second phases and increases their uniformity distribution. As can be seen in Fig. 4(c), the microstructure of the solution-treated specimen consists of two phases: a matrix phase and a rod-like second phase. When the specimens are aged at 500 and 600 °C, in addition to the rod-like phase (phase A), a new second phase appears which is almost spherical in shape (phase B).

The results of the EDS analysis of the second phases along with the matrix of the aged samples are shown in Table 1. These results demonstrate that phases A and B are both Hf-rich, which are close to the chemical composition of $(Ti,Hf)_2Ni$ and $(Ti,Hf)_4Ni$, respectively. The formation of the later phase is not reported in the literature (Ref 10). According to Meng et al. (Ref 10), microstructural examination confirms that the aging of non-Ni-rich NiTiHf alloys does not lead to the formation of Ni-rich $(Ti,Hf)_3Ni_4$ precipitates.

The fracture surface of the 600 °C-aged specimen, after bending at room temperature, is shown in Fig. 5 in two magnifications. The aged samples were too brittle to undergo any plastic deformation. No dimple could be observed on the

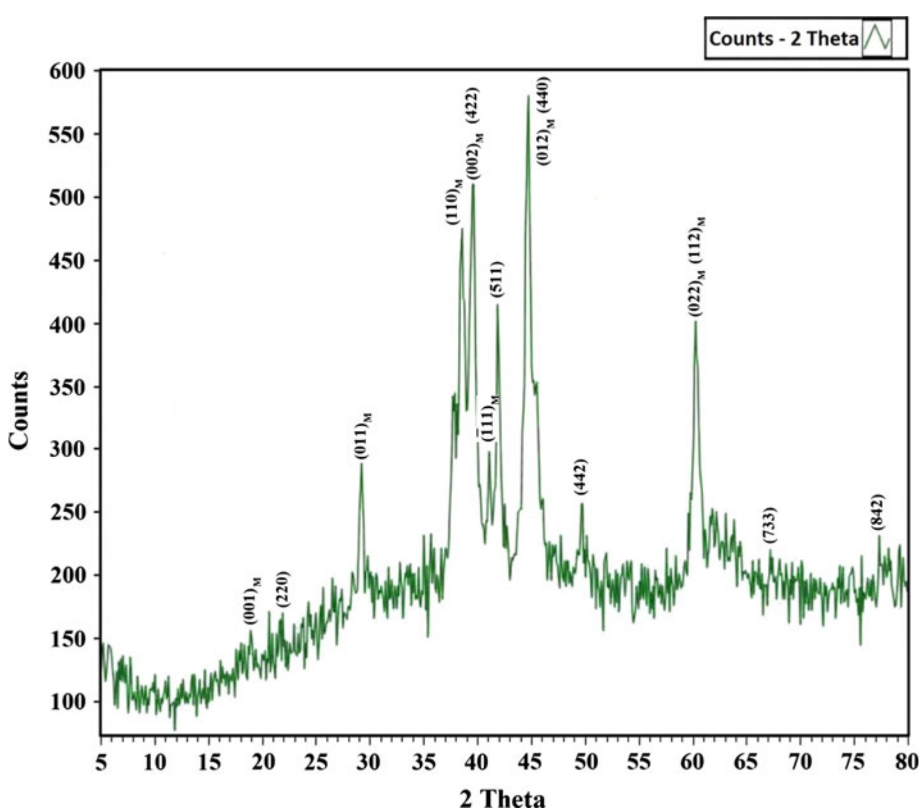

Fig. 2 X-ray diffraction pattern of the homogenized $Ni_{49}Ti_{36}Hf_{15}$ alloy

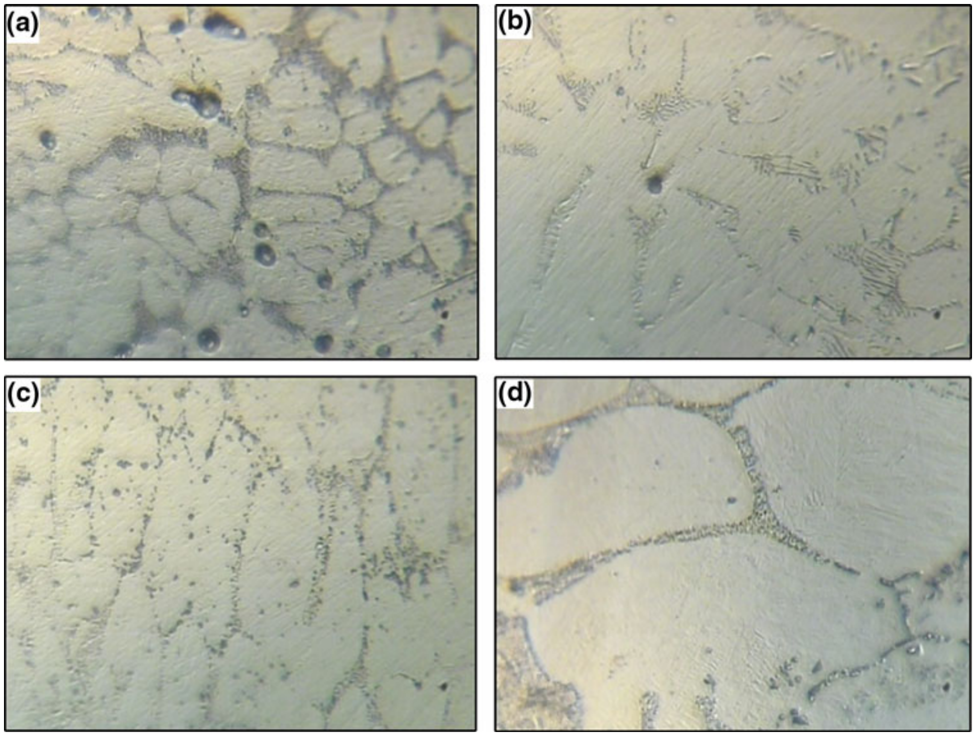

Fig. 3 Microstructure of the (a) as-cast, (b) homogenized, (c) hot-rolled, and (d) 500 °C-aged samples 400×

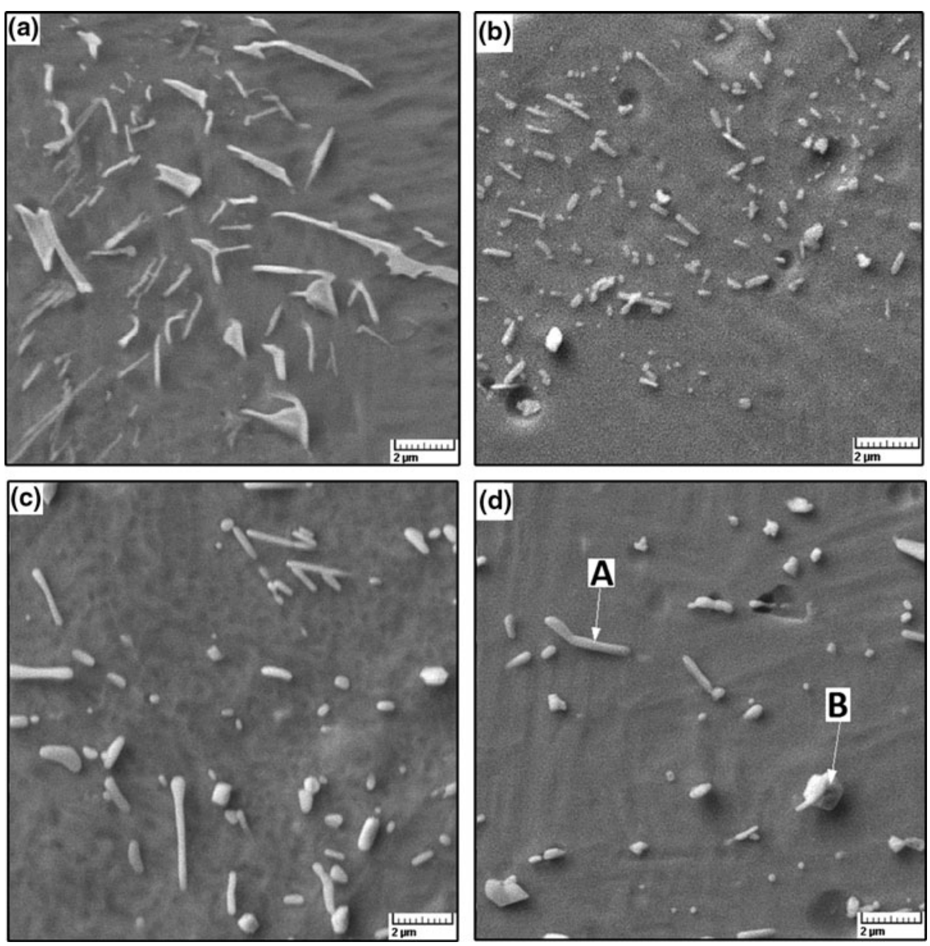

Fig. 4 SEM micrographs of the (a) as-cast, (b) hot-rolled, (c) solution-treated, and (d) 500 °C-aged specimens

Table 1 Composition of the constituents of the 500 and 600 °C-aged specimens (second phases are both Hf-rich)

Composition (at.%)	Ni	Ti	Hf
Matrix	45.68	26.17	28.15
Phase A	17.25	16.65	66.10
Phase B	30.31	23.01	46.68

Table 2 Results of SME measurements

Sample	ε_d	ε_{re}	Recovery ratio (%)
As-cast	Too brittle to deform		
As-homogenized	3.23	3.10	91.77
As-rolled	6.25	5.61	84.12
As-aged	Too brittle to deform		

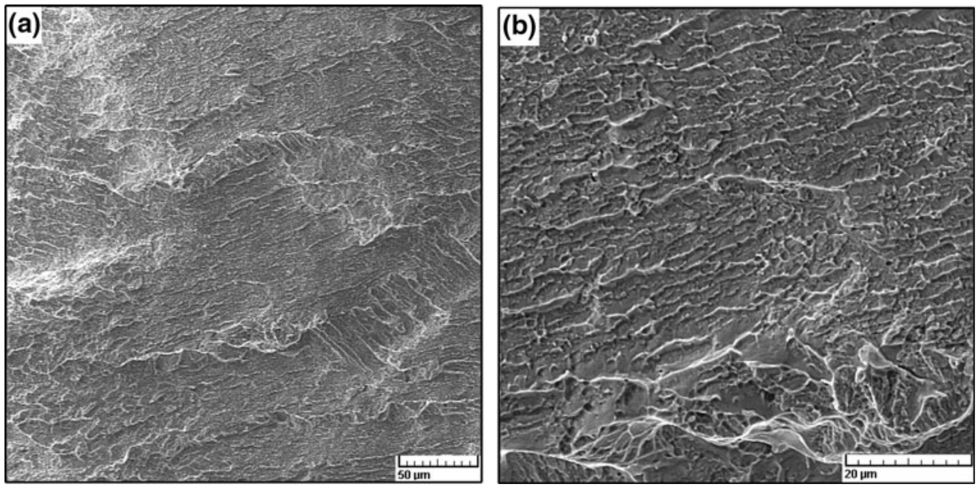

Fig. 5 Fracture surfaces of the 600 °C-aged specimen after bending at room temperature (a) 500× and (b) 2000×

fracture surface, which confirms the brittle and cleavage fracture of the aged alloy.

3.2 Shape Memory Effect

The results of SME measurements are shown in Table 2. It is should be noted that homogenized specimen with the thickness of 1 mm could not experience deformation and fractured during the process of deformation. Therefore, a 0.5-mm thickness specimen from the homogenized sample was chosen for the tests. According to the results of the SME test, the recoverable strains for the homogenized and hot-rolled specimens were 3.10 of 3.23 and 5.61 of 6.25, respectively. Hence, it is clear that hot rolling enhances the capability of the alloy to undergo and recover deformation strain. With increasing the strain applied on shape memory alloys, the recovery ratio decreases as a result of the occurrence of partial unrecoverable plastic deformation (Ref 7). Based on this fact, the recovery ratio in hot-rolled specimen is declined to 84.12% since the deformation strain is increased to 6.25 (Table 2). The amount of recovery ratio in the rolled specimen is comparable to another study (Ref 10), in which the same amount of recovery ratio is obtained by aging of the alloy at 550 °C for 2 h. There are some probable reasons for this enhancement: first, as mentioned before, hot rolling improves microstructure through annihilation of voids together with breaking the remnant dendrites. The second and more influential reason, however, concerns the low strength of the matrix in NiTiHf alloys. Since the strength of the matrix is low, plastic deformation can easily occur through the slip of dislocations which is not recoverable. Hot rolling can strengthen the matrix and prevent this kind of inappropriate deformation (Ref 7). In addition, better distribution of the fine $(Ti,Hf)_2Ni$ phase, which occurs as the result of hot rolling, can have a strengthening effect on the matrix. The role of second phase in hardening the material was also shown in NiTiPd alloys (Ref 16).

The 500 and 600 °C-aged specimens were too brittle to experience any deformation and fractured during the bending test. The poor SME of the aged specimens also emanates from their microstructures; new Hf-rich precipitates embrittle the alloy such that it cannot undergo deformation. This shows that aging cannot improve the SME of the non-Ni-rich NiTiHf, even when the alloy is hot rolled. Results confirm that only Ni_4Ti_3 precipitates, formed in the aging of Ni-rich NiTiHf alloys, can enhance SME (Ref 10) while the formation of $(Ti,Hf)_2Ni$ and $(Ti,Hf)_4Ni$ phases in this research are proved to have opposite effects.

4. Conclusions

In this article, the effect of aging on the microstructure and SME of a hot-rolled $Ni_{49}Ti_{36}Hf_{15}$ alloy was studied. The results show that, contrary to the cast alloy, hot-rolled $Ni_{49}Ti_{36}Hf_{15}$ can be used as a high-temperature shape memory alloy. Hot rolling significantly improves the microstructure via annihilation of the microstructural voids and uniform distribution of the $(Ti,Hf)_2Ni$ second phase, resulting in a recovery of 5.61 of 6.25 deformation strain for the 45% hot-rolled alloy. These amounts of deformation and recovery strain are better than those of cast and homogenized specimens. However, aging of the $Ni_{49}Ti_{36}Hf_{15}$ alloy at 500 or 600 °C for 2 h is not fruitful since in this treatment, a new kind of Hf-rich precipitate is formed, which embrittles the alloy and, consequently, the alloy cannot experience the deformation and strain recovery.

References

1. K. Otsuka and X. Ren, Physical Metallurgy of Ti-Ni-Based Shape Memory Alloys, *Prog. Mater. Sci.*, 2005, **50**, p 511–678
2. X.D. Han, R. Wang, Z. Zhang, and D.Z. Yang, A New Precipitate Phase in a TiNiHf High Temperature Shape Memory Alloy, *Acta Mater.*, 1998, **46**, p 273–281
3. G.S. Firstov, J.V. Humbeeck, and Y.N. Koval, High-Temperature Shape Memory Alloys: Some Recent Developments, *Mater. Sci. Eng. A*, 2004, **378**, p 2–10
4. P.L. Potapov, A.V. Shelyakov, A.A. Gulyaev, E.L. Svistunova, N.M. Matveeva, and D. Hodgson, Effect of Hf on the Structure of Ni-Ti Martensitic Alloys, *Mater. Lett.*, 1997, **32**, p 247–250
5. X.L. Meng, W. Cai, L.M. Wang, Y.F. Zheng, L.C. Zhao, and L.M. Zhou, Microstructure of Stress-Induced Martensite in a Ti-Ni-Hf High Temperature Shape Memory Alloy, *Scr. Mater.*, 2001, **45**, p 1177–1182
6. W. Cai, X.L. Meng, and L.C. Zhao, Recent Development of TiNi-Based Shape Memory Alloys, *Curr. Opin. Solid State Mater. Sci.*, 2005, **9**, p 296–302
7. X.L. Meng, W. Cai, L.M. Wang, Y.F. Zheng, and L.C. Zhao, Shape Memory Properties of the $Ti_{36}Ni_{49}Hf_{15}$ High Temperature Shape Memory Alloy, *Mater. Lett.*, 2000, **45**, p 128–132
8. Y.Q. Wang, Y.F. Zheng, and L.C. Zhao, The Tensile Behavior of $Ti_{36}Ni_{49}Hf_{15}$ High Temperature Shape Memory Alloy, *Scr. Mater.*, 1999, **40**, p 1327–1331
9. C. Craig Wojcik, Properties and Heat Treatment of High Transition Temperature Ni-Ti-Hf Alloys, *Mater. Eng. Perform.*, 2009, **18**, p 511–516
10. X.L. Meng, W. Cai, Y.D. Fu, Q.F. Li, J.X. Zhang, and L.C. Zhao, Shape-Memory Behaviors in an Aged Ni-Rich TiNiHf High Temperature Shape-Memory Alloy, *Intermetallics*, 2008, **16**, p 698–705
11. P.E. Thoma and J.J. Boehm, Effect of Composition on the Amount of Second Phase and Transformation Temperatures of NixTi90-xHf10 Shape Memory Alloys, *Mater. Sci. Eng. A*, 1999, **273**, p 385–389
12. Y. Tong, F. Chen, B. Tian, and Y. Zheng, Microstructure and Martensitic Transformation of Ti49Ni51-xHfx High Temperature Shape Memory Alloys, *Mater. Lett.*, 2009, **63**, p 1869–1871
13. S. Besseghini, E. Villa, and A. Tuissi, Ni-Ti-Hf Shape Memory Alloy: Effect of Aging and Thermal Cycling, *Mater. Sci. Eng. A*, 1999, **273**, p 390–394
14. S. Han, W. Zou, S. Jin, Z. Zhang, and D. Yang, The Studies of the Martensite Transformations in a Ti36.5Ni48.5Hf15 Alloy, *Scr. Mater.*, 1995, **32**, p 1441–1446
15. X.L. Meng, Y.F. Zheng, Z. Wang, and L.C. Zhao, Effect of Aging on the Phase Transformation and Mechanical Behavior of $Ti_{36}Ni_{49}Hf_{15}$ High Temperature Shape Memory Alloy, *Scr. Mater.*, 2000, **42**, p 341–348
16. S. Shirnizu, Y. Xu, S. Tanaka, K. Otsuka, and K. Mitose, Improvement of Shape Memory Characteristics by Precipitation-Hardening of Ti-Pd-Ni Alloys, *Mater. Lett.*, 1998, **34**, p 23–29