Constant-Strain Thermal Cycling of a $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ High-Temperature Shape Memory Alloy

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Abstract The effect of various pre-straining routines on the recovery stresses of a Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ high-temperature shape memory alloy was investigated in tension and compression. The recovery stresses, obtained by means of constant-strain thermal cycling, were evaluated after isothermal (up to ± 2 % applied strain at room temperature) or after isobaric thermal cycling at stress levels between ± 100 and 400 MPa. The material exhibited high force generation capability with recovery stresses of nearly 1.5 GPa on the first cycle under particular pre-strain conditions. The recovery stresses are shown to decay during subsequent cycles using an upper cycle temperature of 300 °C with a saturated stress level nearing 1.1 GPa in compression.

Keywords High-temperature shape memory alloy · Recovery stress · Constant-strain · Training · NiTiHf

Introduction

Recovery stress in shape memory alloys (SMAs) is an important, but often overlooked property normally obtained by dimensionally constraining the martensitic phase transformation. These stresses are generated on

heating of oriented martensite phase to the higher temperature austenite phase while a sample is dimensionally constrained [1]. On cooling, the stresses gradually relax to a minimum stress state depending on the material and any prior deformation history [2, 3], although there exist cases where the cooling stage also results in a slight stress generation as shown in [4]. The mechanisms behind this stress generation have been described previously by a number of researchers. Benafan et al. [5] have attributed the stress generation on heating to transformation of reoriented/detwinned martensite to the parent austenite above the start of the reverse transformation temperature, offset by thermal stresses. In such a case, the span of the hysteresis loops was widened due to the constraints. Similarly, Jiang et al. [6] have reported that the oriented martensite transforms to the parent phase in addition to the retained martensite that is oriented due to the gradually increased recovery stress. Li et al. [2] reported on the influence of stress on the formation of the parent phase and the plastic deformation of both phases during constrained heating. Malard et al. [1] have also concluded that the stress evolution is due to a sequence of dynamic processes involving activation of reverse martensitic transformation and residual stress relaxation followed by other mechanisms on prolonged heating.

This stress recovery phenomenon has been used in numerous applications such as fastening and joining [7, 8], rock splitting [9, 10], safety/release mechanisms [11, 12], shape memory-reinforced hybrid composites [6, 13], concrete confinement [14], medical devices [15, 16], and many other applications. The stress generation is also relevant to actuator applications where jamming loads (e.g., in case the actuator is impeded from moving) need to be determined for proper hardware sizing.

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Recovery stresses in many SMA systems have been shown to reach levels on the order of 800 MPa. The magnitude of the recovery stress is dependent on the amount of oriented martensite present in the material; thus maximizing the amount of oriented martensite such as pre-straining [17–19] will magnify these stresses. Plastic deformation, as with other shape memory properties, can supersede this process. Therefore, methods that increase the strength of the alloy will also tend to increase the recovery stress, such as precipitate strengthening (aging effects), grain refinement, alloying, thermomechanical processing, and other factors [20–23]. With the recent advent of high strength, high-temperature SMAs, stress recovery is one area that to date has not been assessed.

Thus, the purpose of this work is to investigate the stress recovery capability of a precipitation-strengthened, $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ (at.%), high-temperature SMA in uniaxial tension and compression. This material has been shown to exhibit outstanding strength and stability during constant-stress, thermal cycling experiments (i.e., actuation) [24–27], at least for a limited number of cycles. On the other hand, constant-strain thermal cycling experiments to determine the recovery stress of this specific alloy have not been previously reported. Part of this current study is also aimed towards evaluating several pre-strain routines for optimization of the recovery stress.

Experimental Methods

Material

A polycrystalline, Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ (at.%) alloy was used in this work. After induction melting, the ingot was vacuum-homogenized for 72 h at 1050 °C and furnace cooled, followed by hot extrusion (Ext. 189) at 900 °C through an area reduction ratio of $\sim 7:1$. Test specimens were machined from the extruded rods and subjected to an aging treatment of 3 h at 550 °C under argon gas atmosphere followed by air cooling. This aging treatment was previously shown to provide an optimum balance of thermomechanical properties [28, 29]. Two specimen geometries were used in this study; the first consisted of a dog-bone tensile specimen with final gage dimensions of 5.08 mm in diameter and 15.24 mm in length. This geometry was used for all tensile testing and for compression testing where critical loads for buckling were not reached. For tests with high compressive loads, the second geometry consisted of a cylinder with final dimensions of 5 mm diameter and 10 mm length. Various physical and thermomechanical properties of heat-treated alloys of similar NiTiHf composition are available in the literature [24–27, 30, 31].

Thermomechanical Testing

Thermomechanical tests were conducted using two 810 MTS servohydraulic load frames with FlexTestTM digital controllers equipped with Ameritherm[®] induction heating systems. One system was set up with extension rods with threaded inserts and backing rods for tensile/compression testing of the dog-bone-shaped samples, and the other was equipped with flat carbide platens for testing the cylindrical compression samples. Prior to any testing, each specimen was mounted on the frame and subjected to two essentially no-load (<1 MPa) thermal cycles between a lower and an upper cycle temperature of 30 and 300 °C at a rate of 20 °C/min, respectively. This step was done to relieve any residual stresses resulting from the sample machining and handling and to promote a starting structure consisting of self-accommodated martensite.

For the dog-bone specimen geometry, the strains were measured using a high-temperature extensometer with a 12.7-mm gage length and $-10/+20$ % strain range. For the cylindrical compression samples, strains were measured using a Micro-EpsilonTM, non-contacting LED-based micrometer (model #: ODC 2600-40). For both sample geometries, temperature was controlled and measured using a EurothermTM temperature controller and type K thermocouples spot-welded to each specimen. The transformation temperatures martensite start (M_s), martensite finish (M_f), austenite start (A_s), and austenite finish (A_f) were determined from the stress-free strain–temperature response using the intercept method [32] and were 141, 126, 156, and 170 ± 2 °C, respectively.

Pre-strain Methodologies

The stress generation capability (i.e., recovery stress) of the alloy under investigation was examined using several pre-straining procedures. The first method, referred to as “isothermal pre-straining,” consisted of straining the material in the martensite phase at room temperature to a particular strain and holding the strain constant at the target value. At this point, the samples were thermally cycled between the limit temperatures in a strain-controlled condition for 20 heat/cool cycles. The second pre-straining method is referred to as “isobaric thermal cycling.” This technique consisted of applying two constant-stress, thermal cycles followed by unloading to zero stress at room temperature. The remnant strain (after the unload step) was then held fixed followed by 20 constant-strain thermal cycles.

Throughout the constant-strain thermal cycling experiments (after all pre-straining methods), a lower and upper cycle temperature of 40 and 300 °C, respectively, and a heating/cooling rate of 20 °C/min were used. All

mechanical loading was performed at room temperature in strain-controlled mode at a rate of $1 \times 10^{-4} \text{ s}^{-1}$.

Results and Discussion

Isothermal Pre-straining

The stress–strain curves for the aged $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy in uniaxial tension and compression are shown in Fig. 1. The reference curves presented in solid lines (i.e., the loading and unloading curves) were used to guide the pre-straining limits and are not part of the training procedures. These initial curves were also limited to $\pm 1 \text{ GPa}$ where the deformation is fully reversible (no plastic strain) as was shown previously [27]. The actual training pre-strains used, indicated by the labeled circles, were chosen within the $\pm 1 \text{ GPa}$ curves in order to avoid any plasticity contribution from the initial loading. Also note that each pre-strain was performed on a new sample and only the end-points are plotted as shown by the open circles. The multiple pre-strain levels served to examine different magnitudes of martensite variant reorientation/detwinning and its concomitant effect on the subsequent stress generation and stability.

The resultant recovery stresses corresponding to selected pre-strains are shown in Fig. 2 and in Fig. 3 for tension and compression pre-strains, respectively. These curves were generated by straining to the desired strain level at room temperature, holding the imposed strain constant, followed by thermal cycling between the upper and lower cycle temperatures. On the first heating cycle, the stresses are shown to relax (in both tension and compression) up to where the apparent A_s ($\sim 160^\circ\text{C}$) is reached. This is mainly attributed to the material's change in compliance as was observed in other alloy systems [33, 34]. The initial

heating from a reoriented/detwinned martensite (due to pre-straining) results in a stiffness decrease which appears as a stress relaxation. Once the material goes through the phase transformation, the martensite is thermally textured [35] and self-accommodated [36] on the first cooling cycle. The succeeding constant-strain thermal cycles showed a characteristic stress–temperature hysteresis loop. The stresses built up on heating and relaxed to zero or to a slightly compressive (Fig. 2) or tensile (Fig. 3) stress upon cooling. With increasing pre-strain, the characteristic transformation temperatures are shown to shift, particularly the A_f and M_s shifted to higher temperatures, while the A_s and M_f exhibited a minor change. This is rather expected since the start of the transformation on heating (i.e., apparent A_s) senses minimum external stresses, while the apparent A_f is resisted by the buildup of high external stress. On cooling, the apparent M_s temperature was shifted higher as a function of increasing pre-strains, but the M_f was relatively insensitive to the applied strains due to the stress at M_f being nearly zero for all applied strain conditions. Also, keeping in mind that this transition is a function of stress, the transformation temperatures are known to shift according to the Clausius–Clapeyron relationship. It is also noted that transformation temperature behavior exhibited a “Class II”-type thermoelastic transformation where the A_s is less than the M_s ($A_s < M_s$) [37, 38]. Initially the difference between these two temperatures was small, but increased significantly with increasing pre-strains. Although this behavior has been attributed to the accumulation of strain energy due to the martensitic transformation, causing early reverse transformation on heating [39], it is the M_s in this case that shifts higher in temperature due to the mechanical stress buildup. Furthermore, it has been shown previously that even after the apparent A_f , there is still retained martensite present [5], which can initiate transformation early on cooling.

Fig. 1 Stress–strain responses of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy deformed at room temperature in **a** tension and **b** compression. The open symbols indicate the pre-strain level imposed for each specimen as part of the isothermal training

Fig. 2 Stress–temperature responses (recovery stress) of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy corresponding to the tensile isothermal loading

The heating portion of the stress–temperature responses, mostly for the tension case (Fig. 2), exhibited a two-step transformation where the inflection point occurred at around 165 °C (between 300 and 400 MPa). It is at this temperature and stress where the very first heating cycles changed directions. This two-step heating behavior is attributed to the relatively easy martensite transformation initially as the less constrained variants transform to the austenite correspondence, followed by a more difficult martensite to austenite transition for the preferentially aligned variants (textured martensite) as the volume fraction decreases on heating. As a result, with the increase in external stress, the constrained variants require additional thermal energy to complete the lattice conversion.

While transformation temperature behavior is critical, of similar significance are the stresses generated as a function of pre-strains. The maximum stresses generated, measured at the upper cycle temperature, are plotted as a function of cycle number in Fig. 4a, c, and as a function of pre-strain level in Fig. 4b, d. Noting the stress magnitudes, it is shown that this NiTiHf alloy exhibited much higher recovery stresses when compared to conventional NiTi or other ternary alloys such as NiTiCu [40]. Stresses in excess of 1 GPa in tension and 1.3 GPa in compression were obtained using the current training methodologies. The

differences in stress recovery arise from the tension–compression asymmetry observed in this material [27], in addition to the materials' thermal expansion contribution. In tension, the thermal expansion on heating works against the stress generation indicated by the negative linear slopes (i.e., stress decreases) before and after the occurrence of the phase transformation, while in compression the thermal expansion is in the direction of stress, contributing to the total stress generation.

Recalling that the imparted pre-strains were chosen to be within the elastic and martensite reorientation/de-twinning limits (i.e., no plastic deformation) [27], it is evident from Figs. 2 and 3 that stresses generated at pre-strains of $\pm 1\%$ or higher resulted in stress evolution with cycling (both in tension and compression). Some of this evolution is attributed to the incomplete phase transformation at the selected upper cycle temperature, but it is also postulated that the occurrence of some plastic deformation in the austenite phase takes place at these higher stresses and temperatures [26]. The stress evolution can also be visualized in Fig. 4a, c for tension and compression, respectively. Although the stresses degenerate with cycling (for pre-strains above $\pm 1\%$), it appears that a stable behavior was approached after the twentieth constant-strain cycles.

Fig. 3 Stress–temperature responses (recovery stress) of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy corresponding to the compressive isothermal loading

Fig. 4 Recovery stresses measured in the austenite phase at 300 °C as a function of cycle number in **a** tension and **c** compression, and as a function of pre-strain level in **b** tension and **d** compression

To further shed some light onto the evolution behavior, each specimen was thermally cycled under ~ 0 MPa (in load-controlled condition) after the twentieth constant-

strain cycle. That is, after completing the twentieth cycle in strain control, the testing mode was switched to load control followed by thermal cycling under nominally zero

stress. The resulting strain–temperature responses are shown in Fig. 5 for both tension and compression data. Even though the transformation to the martensite phase under constant-strain (Figs. 2, 3) results in little to no external stress, the microstructure retains texture mainly through martensite variant reorientation/detwinning, along with possible plastic deformation particularly for the high applied strain cases. This is evident by the strain recovery after load removal and during subsequent stress-free thermal cycles for both tension (Fig. 5a) and compression

(Fig. 5b). It is shown that most of the remnant strain after the load removal (performed after the 20th constant-strain cycle) can be recovered upon heating under no-load cycling conditions.

The successive transformation strains corresponding to the 0 MPa cycles are an example of the two-way shape memory effect (TWSME) and increased with increasing pre-strain for the tensile case (Fig. 5a). This is indicative of internal stress fields that induce the same martensite variants during transformation. The microstructural

Fig. 5 Strain–temperature responses of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ at 0 MPa stress. Each two cycles were performed subsequent to the twentieth constant-strain, thermal cycle for **a** post-tension and **b** post-compression training

features responsible for this behavior have been attributed to a number of mechanisms such as dislocation arrays [41], retained martensite [42], and aligned precipitates [43], among others. As an example, it is believed that the double step transition shown on the first heating curve of Fig. 5a-4 is due to retained martensite. For the compression case (Fig. 5b), the no-load thermal cycles under low pre-strains exhibited a transformation characteristic of tensile variants. This, however, changes to compressive variants with further pre-strains such as the case of -1% pre-strain.

Isobaric Training

The strain–temperature curves for the aged $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy in uniaxial tension and compression are shown in Fig. 6. The transformation strain capability for this material was previously shown to exceed 3.74% [25] in tension and 2.65% [27] in compression using applied stresses of $+500$ and -700 MPa, respectively. However, stresses in excess of 500 MPa resulted in some dimensional instabilities associated with yielding of the austenite phase [27]. As a result, the stresses selected for this training were limited to within ± 400 MPa where the material exhibited stable behavior. Although a single cycle was sufficient to reorient the martensite phase, two thermomechanical cycles were used which are shown to overlap except for the initial heating stage.

At the end of the second cycle, the material was unloaded to zero stress where the remnant strain was held constant, followed by thermal cycling. The recovery stresses corresponding to this isobaric training are shown in Fig. 7 for tension and compression stresses. Unlike the isothermal training, there was no stress relaxation on the very first heating cycle since the martensite was already textured through the thermomechanical cycling under the constant-stress. The first heating cycle resulted in buildup of recovery stresses that proved to be higher than the previous training methodology. For instance, pre-straining to -2% with a conjugate stress of ~ 1 GPa (Fig. 1) resulted in a recovery stress of -1.3 GPa, while isobarically training at -400 MPa (Fig. 7b-3) led to over -1.45 GPa of recovery stress on the first cycle. It is noted that the irregularity shown in Fig. 7b-3 (i.e., sharp increase on heating around 220°C) during the first heating cycle is an experimental error associated with the extensometer and does not represent the actual material behavior. The succeeding cycles provide a more representative behavior.

A summary of the maximum stresses generated, measured at the upper cycle temperature, are plotted as a function of cycle number in Fig. 8a, c, and as a function of the applied training stress in Fig. 8b, d. Although this method yielded higher initial stresses, there was a significant decay in stresses during subsequent cycles. This is largely due to plastic deformation of the austenite phase due to the high stresses reached. Nonetheless, the stresses

Fig. 6 Constant-stress strain–temperature responses of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ in **a** tension and **b** compression

Fig. 7 Stress–temperature responses (recovery stress) of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy corresponding to the isobaric training in **a** tension and **b** compression

Fig. 8 Recovery stresses measured in the austenite phase at 300 °C as a function of cycle number in **a** tension and **c** compression, and as a function of applied training stress in **b** tension and **d** compression

trended toward a stable value and began to saturate around the twentieth cycle. Whether this material is used one time or in a cyclic fashion, the stresses obtained are much higher than can be achieved in conventional NiTi alloys.

Conclusions

The recovery stresses of a precipitation-strengthened, Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ (at.%) high-temperature shape memory alloy were assessed in tension and compression modes. Based on the macroscopic results the following conclusions can be made:

1. Isothermal training, consisting of room temperature deformation of the martensite phase, resulted in recovery stresses nearing 1 GPa in tension and -1.3 GPa in compression with pre-strains of 1.5 and -2% , respectively, as observed on the very first thermal cycle.
2. Isobaric training, consisting of constant-stress thermal cycling, resulted in recovery stresses nearing 1.1 GPa in tension and -1.45 GPa in compression with training stresses of 200 and -400 MPa, respectively, as observed on the very first thermal cycle.
3. In general, this Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy exhibited inherently good force generation capability with activation temperatures above 100°C . Two training methods were investigated to maximize force generation from which isobaric training was found to be the most efficient method and yielded the highest blocking stresses.

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References

1. Malard B, Pilch J, Sittner P, Delville R, Curfs C (2011) In situ investigation of the fast microstructure evolution during electropulse treatment of cold drawn NiTi wires. *Acta Mater* 59:1542–1556
2. Li Y, Cui LS, Xu HB, Yang DZ (2003) Constrained phase-transformation of a TiNi shape-memory alloy. *Metall Mater Trans A* 34:219–223
3. Fu Y, Du H (2002) Relaxation and recovery of stress during martensite transformation for sputtered shape memory TiNi film. *Surf Coat Technol* 153:100–105
4. Stalmans R, Van Humbeeck J, Delaey L (1992) Effects of training on the shape memory behavior of Cu–Zn–Al alloys. *Mater Trans JIM* 33:289–293
5. Benafan O, Padula SA II, Noebe RD, Brown DW, Clausen B, Vaidyanathan R (2013) An in situ neutron diffraction study of shape setting shape memory NiTi. *Acta Mater* 61:3585–3599
6. Jiang D, Cui L, Zheng Y, Zhao X, Li Y (2009) Constrained martensitic transformation in an in situ lamella TiNi/NbTi shape memory composite. *Mater Sci Eng A* 515:131–133
7. Borden T (1991) Shape memory alloys: forming a tight fit. *Mech Eng* 113(10):67–72
8. Stoeckel D, Borden T (1992) Actuation and fastening with shape memory alloys in the automotive industry. *Metall Wissenschaft Und Technik* 46:668–672
9. Benafan O, Noebe RD, Halsmer TJ (2015) Shape memory alloy rock splitters (SMARS)—a non-explosive method for fracturing planetary rocklike materials and minerals, NASA/TM-2015-218832
10. Nishida M, Kaneko K, Inaba T, Hirata A, Yamauchi K (1991) Static rock breaker using TiNi shape memory alloy. *Mater Sci Forum* 56:711–716
11. Massad JE, Buchheit TE, McLaughlin JT (2008) Characterization of shape memory alloys for safety mechanisms. Sandia report, SAND2007-8000
12. Crane WM (2010) Development of a nano-satellite micro-coupling mechanism with characterization of a shape memory alloy interference joint. In: M.S. Thesis, Naval Postgraduate School, Monterey, California
13. Turner TL (2001) Thermomechanical response of shape memory alloy hybrid composites, NASA/TM-2001-210656
14. Choi E, Hu JW, Lee J-H, Cho B-S (2015) Recovery stress of shape memory alloy wires induced by hydration heat of concrete in reinforced concrete beams. *J Intell Mater Syst Struct* 26:29–37
15. Petrini L, Migliauacca F (2011) Biomedical applications of shape memory alloys. *J Metall* 2011:501483. doi:10.1155/2011/501483
16. Hartl DJ, Chatzigeorgiou G, Lagoudas DC (2010) Three-dimensional modeling and numerical analysis of rate-dependent irrecoverable deformation in shape memory alloys. *Int J Plast* 26:1485–1507
17. Cai W, Zhang CS, Zhao LC (1994) Recovery stress of Ni–Ti–Nb wide-hysteresis shape memory alloy under constant strain and thermomechanical cycling. *J Mater Sci Lett* 13:8–9
18. Yan X, Van Humbeeck J (2011) Influence of pre-strain on recovery stress of annealed NiTi thin wire during isothermal holding. *J Alloys Compd* 509:1001–1006
19. Sittner P, Vokoun D, Dayananda GN, Stalmans R (2000) Recovery stress generation in shape memory $\text{Ti}_{50}\text{Ni}_{45}\text{Cu}_5$ thin wires. *Mater Sci Eng A* 286:298–311
20. Uchida K, Shigenaka N, Sakuma T, Sutou Y, Yamauchi K (2008) Effects of pre-strain and heat treatment temperature on phase transformation temperature and shape recovery stress of Ti–Ni–Nb shape memory alloys for pipe joint applications. *Mater Trans* 49:1650–1655
21. Sadiq H, Wong MB, Al-Mahaidi R, Zhao XL (2010) The effects of heat treatment on the recovery stresses of shape memory alloys. *Smart Mater Struct* 19:035021
22. Wang CP, Wen YH, Peng HB, Xu DQ, Li N (2011) Factors affecting recovery stress in Fe–Mn–Si–Cr–Ni–C shape memory alloys. *Mater Sci Eng A* 528:1125–1130
23. Yu Zhang Y, Liu F (2014) Effects of mechanical treatment and pre-deformation on shape recovery stress of $\text{Ti}_{50}\text{Ni}_{47}\text{Fe}_3$ shape memory alloy. *Mater Sci Forum* 787:267
24. Benafan O, Noebe RD, Padula SA II, Vaidyanathan R (2012) Microstructural response during isothermal and isobaric loading of a precipitation-strengthened Ni–29.7Ti–20Hf high-temperature shape memory alloy. *Metall Mater Trans A* 43A:4539–4552
25. Bigelow GS, Garg A, Padula SA II, Gaydos DJ, Noebe RD (2011) Load-biased shape-memory and superelastic properties of a precipitation strengthened high-temperature $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy. *Scr Mater* 64:725–728
26. Coughlin DR, Phillips PJ, Bigelow GS, Garg A, Noebe RD, Mills MJ (2012) Characterization of the microstructure and mechanical

- properties of a 50.3Ni–29.7Ti–20Hf shape memory alloy. *Scr Mater* 67:112–115
27. Benafan O, Garg A, Noebe RD, Bigelow GS, Padula SA II, Gaydosh DJ, Schell N, Mabe JH, Vaidyanathan R (2014) Mechanical and functional behavior of a Ni-rich Ni_{50.3}Ti_{29.7}Hf₂₀ high temperature shape memory alloy. *Intermetallics* 50:94–107
 28. Karaca HE, Saghaian SM, Ded G, Tobe H, Basaran B, Maier HJ, Noebe RD, Chumlyakov YI (2013) Effect of nanoprecipitation on the shape memory and material properties of an Ni-rich NiTiHf high temperature shape memory alloy. *Acta Mater* 61:7422–7431
 29. Hornbuckle BC, Sasaki TT, Bigelow GS, Noebe RD, Weaver ML, Thompson GB (2015) Structure–property relationships with H-phase precipitation in a Ni–29.7Ti–20Hf (at.%) shape memory alloy. *Mater Sci Eng A* 637:63–69
 30. Karaca HE, Saghaian SM, Basaran B, Bigelow GS, Noebe RD, Chumlyakov YI (2011) Compressive response of nickel-rich NiTiHf high-temperature shape memory single crystals along the [1 1 1] orientation. *Scr Mater* 65:577–580
 31. Yang F, Coughlin DR, Phillips PJ, Yang L, Devaraj A, Kovarik L, Noebe RD, Mills MJ (2013) Structure analysis of a precipitate phase in an Ni-rich high-temperature NiTiHf shape memory alloy. *Acta Mater* 61:3335–3346
 32. ASTM-F2082-06, standard test method for determination of transformation temperature of nickel–titanium shape memory alloys by bend and free recovery, F2082-06 (2010)
 33. Benafan O, Noebe RD, Padula SA II, Gaydosh DJ, Lerch BA, Garg A, Bigelow GS, An K, Vaidyanathan R (2013) Temperature-dependent behavior of a polycrystalline NiTi shape memory alloy around the transformation regime. *Scr Mater* 68:571–574
 34. Stebner A, Padula S, Noebe R, Lerch B, Quinn D (2009) Development, characterization, and design considerations of Ni_{19.5}Ti_{50.5}Pd₂₅Pt₅ high-temperature shape memory alloy helical actuators. *J Intell Mater Syst Struct* 20:2107–2126
 35. Ye B, Majumdar BS, Dutta I (2007) Texture memory and strain-texture mapping in a NiTi shape memory alloy. *Appl Phys Lett* 91:061918
 36. Benafan O, Noebe RD, Halsmer TJ (2016) Static rock splitters based on high temperature shape memory alloys for planetary explorations. *Acta Astronaut* 118:137–157
 37. Tong HC, Wayman CM (1974) Characteristic temperatures and other properties of thermoelastic martensites. *Acta Metall* 22:887–896
 38. Tong HC, Wayman CM (1974) Some stress–temperature–energy relationships for thermoelastic martensitic transformations. *Scr Metall* 8:93–100
 39. Kaufman L, Cohen M (1958) Thermodynamics and kinetics of martensitic transformations. *Prog Metal Phys* 7:165–246
 40. Carosio S, Pozzolini P, Van Humbeeck J, Firstov G, Sutherland I, Tinnion E, Jowitt F (2003) Application of shape memory alloys to develop a massive actuator for rock splitting. In: Pelton AR, Duerig T (eds) SMST 2003: proceedings of the international conference on shape memory and superelastic technologies. Pacific Grove, pp 629–637
 41. Perkins J, Sponholz R (1984) Stress-induced martensitic transformation cycling and two-way shape memory training in Cu–Zn–Al alloys. *Metall Mater Trans A* 15:313–321
 42. Wada K, Liu Y (2008) On the mechanisms of two-way memory effect and stress-assisted two-way memory effect in NiTi shape memory alloy. *J Alloys Compd* 449:125–128
 43. Nishida M, Honma T (1984) All-round shape memory effect in Ni-rich TiNi alloys generated by constrained aging. *Scr Metall* 18:1293–1298