**Role of nano-precipitation on the microstructure and shape memory characteristics of a new
Ni_{50.3}Ti_{34.7}Zr₁₅ shape memory alloy**

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ABSTRACT

The microstructure and shape memory characteristics of the Ni_{50.3}Ti_{34.7}Zr₁₅ shape memory alloy were investigated as a function of aging heat treatments that result in nanometer to submicron size precipitates. Microstructure-property relationships were developed by characterizing samples using transmission electron microscopy, differential scanning calorimetry, and load-biased thermal cycling experiments. The precipitate size was found to strongly influence the martensitic transformation-precipitate interactions and ultimately the shape memory characteristics of the alloy. Aging treatments resulting in relatively fine precipitates, which are not an obstacle to twin boundaries and easily bypassed by martensite variants, exhibited higher transformation strain, lower transformation thermal hysteresis, and better thermal and dimensional stability compared to samples with relatively large precipitates. When precipitate dimensions approached several hundred nanometers in size they acted as obstacles to martensite growth, limiting martensite variant and twin size resulting in reduced functional and structural properties. Aging heat treatments were also shown to result in a wide range of transformation temperatures, increasing them above 100 °C in some cases, and affected the stress dependence of the transformation hysteresis and the stress versus transformation temperature relationships for the Ni_{50.3}Ti_{34.7}Zr₁₅ alloy.

Keywords: NiTiZr; Martensitic transformation; Precipitation; Microstructure; Shape memory alloys

1. Introduction

Shape memory alloys (SMAs) are a unique group of functional materials that can recover their original shape after relatively large deformations by changes in temperature (shape memory effect) or stress (superelasticity) as a consequence of a reversible martensitic transformation (MT). NiTi is the most popular and commonly studied SMA system due to its many favorable functional and mechanical properties (e.g., ductility, workability, large transformation strains, corrosion resistance, high level of biocompatibility, etc.) Thus, it has been used in many medical and other applications such as actuators, couplings, valves, and switches [1-4].

However, commercially available NiTi SMAs have a few drawbacks hindering their use in applications that require high transformation temperatures and high strength because they generally undergo MT below 100°C and possess low strength against dislocation plasticity, which causes dimensional instability upon thermo-mechanical cycling [3,5]. Ternary alloying has long been used as a common method to overcome these limitations, improve the shape memory properties, and increase the transformation temperatures of binary NiTi alloys. Among the high-temperature NiTiX (X=Pt, Pd, Au, Hf, Zr) ternary SMA systems, NiTiHf and NiTiZr alloys have recently drawn increased attention due to their lower material cost as compared to NiTiPt/Pd/Au systems [6,7]. Furthermore, NiTiZr alloys provide an approximately 20% weight reduction compared to NiTiHf counterparts (i.e., NiTi-20Zr versus NiTi-20Hf), have lower raw material costs, and are actually easier to process [8,9].

Eckelmeyer [10] and Mulder [11] showed that the transformation temperatures of equatomic or Ti-rich binary NiTi SMAs can be increased by replacing Ti with Zr. It was reported that Zr additions above 10 at.% result in an increase in the martensite start temperature (M_s) at a rate of 18 °C/at.% Zr [6]. Hsieh et al. [12-14] studied the martensitic transformation behavior, lattice parameters of martensite, and the room temperature phases of (Ti+Zr)-rich NiTiZr alloys. Firstov et al. [15] investigated the high temperature shape memory behavior of (Ti+Zr)-rich NiTiZr alloys under compression. Although, these (Ti+Zr)-rich NiTiZr alloys exhibit high transformation temperatures, they suffer from large thermal hysteresis and poor dimensional and thermal stability due to concurrent plasticity along with the transformation response, hampering their commercial use.

The transformation characteristics of NiTi-based SMAs can be modified through various matrix strengthening procedures such as cold working (i.e., cold rolling), precipitation hardening, or solid-solution alloying. However, cold rolling did not improve the shape memory response in the case of

thermally cycled (Ti+Zr)-rich NiTiZr SMAs [16-18]. Microhardness values increased with thermal cycling and cold rolling, but martensite start (M_s) temperatures decreased significantly [16, 18]. Furthermore, microstructural control and stability is a big concern in the (Ti+Zr)-rich NiTiZr alloys since large (Ti,Zr)Ni, (Ti,Zr)₂Ni and λ_1 (a NiTiZr ternary solid solution) second-phase particles were observed after conventional wrought alloy processing. These phases do not notably strengthen the matrix or improve the shape memory properties [14]. Solid-solution strengthening was also attempted, but again with little success. While (Ti + Zr/Hf)-rich NiTiZrHf quaternary alloys were reported to have higher annealed hardness values than their ternary NiTiZr counterparts, they exhibit higher transformation thermal hysteresis and similar shape recovery as compared to the ternary NiTiZr alloys [16].

On the contrary, Ni-rich compositions of binary NiTi SMAs can form metastable, nanosize Ni₄Ti₃ precipitates that significantly influence transformation temperatures, matrix strength, shape memory characteristics, and mechanical properties [19-27]. These fine precipitates increase the matrix strength and suppress extensive dislocation plasticity leading to improved dimensional stability upon thermo-mechanical loading and shape recovery. Additionally, transformation temperatures are altered as a result of the change in global matrix composition and local composition around the precipitates, as well as the coherency stress fields around the precipitates. All these effects are controlled by the size, volume fraction, and the interparticle spacing of the precipitates, which are a function of aging time and temperature.

Sandu and co-workers [28, 29] reported on the effects of aging on the microstructure, martensitic transformation temperatures, and mechanical behavior of Ni-rich NiTiZr SMAs, in particular Ni₅₂Ti₄₂Zr₆ (at.%). They determined that fine nanosize Ni-rich precipitates were present in the microstructure after certain heat treatments, which increased the hardness of the alloy. Although an increase in aging time was shown to increase the transformation temperatures, they were still significantly below 100°C since the Zr addition was just 6 at.% with a very high initial Ni content. More recently, we have shown in a slightly Ni-rich NiTiZr SMA, i.e., Ni_{50.3}Ti_{29.7}Zr₂₀, that precipitation hardening through the formation of nanosize precipitates results in excellent dimensional stability upon reversible MT without any need of thermo-mechanical training while also providing relatively high transformation temperatures [8]. The alloy also exhibits high strength, good superelasticity and excellent shape recovery at temperatures up to 250°C when nanosize precipitates (<40 nm) are present in the microstructure [9]. Except for these studies on Ni-rich NiTiZr SMAs with 6 at.% and 20 at.% Zr content, there has been no additional work carried out on Ni-rich NiTiZr SMAs, especially with Zr contents between these two concentrations.

Considering the promising shape memory properties and excellent dimensional stability observed in Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$, the present study was initiated to determine whether similar benefits could be developed in alloys with lower Zr content. Consequently, a $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ SMA was systematically heat treated and characterized to understand the effects of aging on the microstructure and shape memory characteristics in the present study. Differential scanning calorimetry (DSC) was used to monitor the transformation temperatures of the alloy after systematic aging heat treatments and aging time-temperature-martensitic transformation temperature diagrams were generated. The shape memory and actuation response of the alloy was determined via load-biased thermo-mechanical cycling tests under constant stress in tension. These were combined with transmission electron microscopy (TEM) observations to reveal the effect of microstructure, in particular the precipitate size and martensite morphology, on the shape memory characteristics.

2. Materials and Experimental Procedures

A Ni-rich SMA with nominal composition of $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ (at. %) was vacuum induction melted under a partial argon atmosphere using a graphite crucible and high purity elemental constituents of Ni, Ti and Hf (99.98%, 99.95% and 99.9%, respectively) and subsequently cast into a 25.4 mm diameter by 102 mm long copper mold with appropriate hot-top. The resulting ingot was homogenized at 1050 °C for 72 hours (hrs), sealed in a mild steel can, and then hot extruded at 900°C with an area reduction of 7:1.

Samples for DSC experiments, circular in shape with dimensions of 5 mm in diameter and 1 mm in thickness, and dog-bone shaped tensile samples for load-biased thermo-mechanical cycling, with 1.5 mm x 3 mm x 8 mm gage sections and tensile axis parallel to the extrusion direction, were cut from the extruded rod using wire electro-discharge machining (EDM). All the samples were first solution heat treated (SHT) at 900°C for 1 hour (h) in argon and subsequently water quenched (WQ) to assure a single phase structure before the precipitation heat treatments. Subsequently, the solution-treated samples were subjected to systematic isothermal aging treatments at temperatures from 450°C to 600°C for durations of 1 h to 200 h followed by water quenching in order to modify the precipitate structure and resulting transformation characteristics.

A TA Instruments, Q20TM differential scanning calorimeter was used to measure the stress free transformation temperatures of the heat treated samples with a heating and cooling rate of 10°C min⁻¹. Three thermal cycles were conducted on each specimen between -80°C and 200°C and the difference in M_s temperatures between the first and third cycle ($M_{s1}-M_{s3}$) was determined as a measure of the cyclic

thermal stability of the transformation temperatures. Transformation thermal hysteresis values were measured as the difference between the first austenite finish (A_f) and M_s temperatures ($A_f - M_s$).

On the basis of the DSC observations, samples showing relatively high transformation temperatures, low thermal hysteresis (ΔT), or good thermal stability were selected for load-biased thermal cycling experiments to investigate the effect of aging treatment on the shape memory response of the alloy. During these experiments, the samples were first loaded to a constant tensile stress in the fully austenitic state and thermally cycled between -40°C and 200°C . Upon completion of the thermal cycle, the stress was increased in 50 MPa increments to the next level and the process was repeated until the specimens failed. A servo-hydraulic MTS test frame was used to conduct the thermo-mechanical cycling experiments. Specimens were heated and cooled through thermal conduction from the grips, which in turn were heated using resistive heating bands and cooled by flowing liquid nitrogen through copper tubing wrapped around the grips. The sample temperature during the experiment was measured using a K-type thermocouple attached directly to the gage section of the sample. The heating and cooling rate was $10^\circ\text{C min}^{-1}$. The evolution of axial strain throughout the thermo-mechanical cycles was monitored using an MTS high-temperature extensometer mounted directly on the gage section of the specimen. The load-biased shape memory characteristics such as transformation temperatures, recovered transformation strain, unrecovered strain levels (an indication of dimensional instability), and thermal hysteresis were investigated as a function of applied stress through these experiments.

To analyze the initial microstructure and chemical composition of the solution heat treated $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples, specimens were prepared by mechanical polishing down to a final step of 0.05 μm colloidal silica and investigated using a Cameca SX-100 electron microprobe (EM) equipped with X-ray energy dispersive spectrometry (EDS) and wavelength dispersive spectrometry (WDS) capabilities. Specimens for TEM analysis were prepared via mechanical grinding down to 100 μm thickness followed by twin jet electropolishing using a 30% HNO_3 and 70% methanol solution at approximately -20°C . The resulting thin foils were investigated using a JEOL 2010 high resolution microscope with a LaB_6 filament operated at 200 kV and equipped with an EDS detector.

3. Results and Discussion

3.1. Microstructure of $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$

Compositional analysis based on WDS measurements of the SHT sample, shown in Table 1, indicates ~ 0.1 at.% Zr loss and a slight gain in Ni compared to the nominal alloy composition. The matrix was fully austenitic at room temperature with a grain size ranging from 25 μm to 100 μm as seen in the back-scattered electron (BSE) image shown in Fig. 1. The composition is quite uniform in the matrix as shown by the very small variation in the measured compositions in Table 1. No secondary phases were visible except heterogeneously distributed white particles ($< 3\mu\text{m}$ in size), which were found to be zirconium carbide via EDS. The zirconium carbide particles were formed during vacuum induction melting of the alloy due to reaction with the graphite crucible, in turn, decreasing the Zr content of the SHT matrix as demonstrated by the WDS investigation.

The transformation temperatures, thermal hysteresis, and thermal stability of all aged samples were investigated via DSC and these results will be discussed in detail below. The microstructures of those samples that showed relatively low thermal hysteresis (sample aged at 500 $^{\circ}\text{C}$ for 200 h, referred to as NTZ500/200h), relatively good thermal stability (samples aged at 550 $^{\circ}\text{C}$ for 24 h and 100 h, referred to as NTZ550/24h and NTZ550/100h, respectively) and relatively high transformation temperatures (sample aged at 600 $^{\circ}\text{C}$ for 100 h, referred to as NTZ600/100h) were further investigated using TEM. Bright field TEM and high resolution bright field TEM (HRTEM) images of these $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples are shown in Fig. 2.

A dense distribution of spindle like precipitates, 20-70 nm in length and 10-16 nm in width, embedded in a fully austenitic matrix at room temperature, were present after aging at 500 $^{\circ}\text{C}$ for 200 h (Fig. 2a). At higher resolution (Fig. 2b), the precipitates show a perfect continuity of atomic planes at the austenite (B2) – precipitate boundary (inset image of Fig. 2b), which is consistent with previous TEM observations on the same alloy that indicate a coherent precipitate phase [31]. When the samples were aged at higher temperatures, such as 550 $^{\circ}\text{C}$ or 600 $^{\circ}\text{C}$, the specimens exhibited higher transformation temperatures and consequently the matrix was mostly a monoclinic (B19') martensite phase at room temperature (Figs. 2c to f).

After aging for 24 h at 550 $^{\circ}\text{C}$, the precipitates remained spindle shaped with sizes around 30-90 nm in length and 10-20 nm in width (Fig. 2c). In this condition, the precipitate size was sufficiently small so

that the strain fields around the precipitates upon the forward transformation were accommodated by the growing martensite variants, and hence, the precipitates were easily absorbed by the propagating martensite plates, as seen in Fig. 2c. In other words, the precipitates do not stop the martensite interface motion and thus, a single martensite variant consists of large number of precipitates in them.

Precipitates coarsen upon further aging at 550°C for 100 h, and reach a size of 75-160 nm in length and 15-30 nm in width (Fig. 2d). However, martensite plates can still absorb the precipitates upon transformation. Even at this size, the precipitate was not large enough to sufficiently interfere with the forward transformation or change the martensite morphology. Moreover, a good continuity of the atomic planes with a small amount of tilt was still visible across the interface (a white line parallel to these atomic planes was drawn to indicate the continuity) as shown in the HRTEM image (Fig. 2e) taken from the precipitate (P) – martensite (M) boundary in NTZ550/100h sample. The fast fourier transform (FFT) images belonging to the B19' martensite matrix and the precipitate phase were also included as insets and labeled with letter “M” and “P”, respectively. For the specific martensite variant shown in Fig. 2e, the change in the interplanar distance with MT is small and the atomic planes across the matrix/precipitate interface can maintain good continuity and hence coherency. However, although it was not observed in the NTZ550/24h and NTZ550/100h samples, larger changes in interplanar distances may happen leading to a remarkable loss of the coherency between the non-deforming precipitates and the martensite matrix for some other martensite variants. Such observations were reported for other Ni-rich NiTiHf and NiTiZr alloys in which large distortions of atomic planes were seen at the interface between martensite and precipitates leading to misfit dislocations [30].

The exact mechanism of how the martensite plates absorb the precipitates is not yet known, however there are several parameters, such as crystallography of both phases, their lattice mismatch, relative stiffnesses, and the amount of martensitic transformation strain, that influence the process. As a consequence, the effect of precipitates on martensitic transformation seen in different SMA systems can be quite different. Therefore, further research including detailed TEM investigations and molecular dynamics simulations should be performed to clarify the mechanisms governing the interaction process between martensite growth and precipitates.

Significant coarsening of the precipitates was observed after aging at 600 °C for 100 h (Fig. 2f), reaching several hundred nanometers in size (150-450 nm in length and 25-90 nm in width). At this size the precipitates act as impenetrable obstacles for the martensite variants. These large precipitates, which are indicated with white arrows in Fig. 2f, clearly interfere with the martensite propagation and

have a strong influence on the martensite morphology and microstructure. Fig. 2f shows that the martensite formation was constrained between precipitates and consisted of fine internal twins in order to accommodate the transformation shear and incompatibility between austenite and martensite phases while being constrained between the large precipitates. Similar effects of precipitate size on the martensite morphology were also reported for Ni-rich binary NiTi [24, 25, 31] and ternary NiTiHf [32] and NiTiZr [8, 9] alloys as well as several other SMA systems such as CuZnAl [33, 34] and CoNiGa [35] alloys.

The precipitate phase in the present $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ SMA had the same crystal structure as the precipitates identified recently in other Ni-rich NiTiHf and NiTiZr alloys. The selected area diffraction pattern (SADP), in Fig. 2g, (taken along the $[001]_{\text{B2}}$ zone axis), shows two variants of precipitates simultaneously with $1/3\langle 110 \rangle$ satellite spots (red arrows) and another two variants with $1/4\langle 210 \rangle$ satellites (blue arrows), which are typical for the so-called H-phase. Details on the crystallographic properties and the structure of the H-phase precipitates were previously reported by Yang et al. [36] and Santamarta et al. [30].

It is worth nothing that the ZrC particles, initially formed in the microstructure (Fig. 1) due to the use of graphite crucibles during alloy melting, exhibit a much larger particle size and interparticle distance which is orders of magnitude larger than the interparticle distance between even the largest H-phase precipitates formed after aging at 600 °C for 100 h thermal treatment (Fig. 2f). Therefore, the effect of ZrC particles on the martensite microstructure is expected to be insignificant as compared to the H-phase precipitation.

3.2. Transformation temperatures and characteristics

No martensitic transformation (MT) was detected in the DSC thermograms recorded down to -80°C for the SHT sample and for the samples aged at 450°C, even for aging times as long as 200h. Furthermore, the transformation temperatures were still below -80°C during the initial stages of aging at 500°C (i.e., 1h and 3h aging), and the MT peaks were visible only after 10 h or longer aging at 500°C. All the aged samples showed single step transformation behavior during forward and reverse MT from B2 austenite to B19' martensite or vice-versa. As seen from the representative DSC curves for the samples aged at 550 °C (Fig. 3), no multiple step or R-phase peaks were observed contrary to the observations of Javadi et al. [37] and Meng et al. [38-40] on several Ni-rich NiTiHf alloys, which have the same type of precipitates [30, 36]. The multi-step transformations in these studies were generally attributed to

heterogeneous distribution of the nanosize precipitates. However, the single step transformations seen in the present samples are in accordance with the microstructures shown in Fig. 2, which consist of homogeneously distributed H-phase precipitates in the matrix. The present observations of a single stage martensitic transformation are also consistent with other studies on Ni-rich NiTiHf alloys of similar composition [32, 41] and other Ni-rich NiTiZr alloys [8, 9].

A summary of the A_f and M_s temperatures obtained in the $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples aged at 500 °C, 550 °C and 600 °C for various durations is presented in Figs. 4a and 4b, respectively. As seen in these figures, the transformation temperatures for $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ occur over a large range: from 40 °C to 140 °C for A_f and from -20°C to 80°C for M_s . This 100°C temperature window is as a consequence of the different precipitate volume fractions formed during aging. Transformation temperatures of the samples aged at 550 °C and 600 °C increased rapidly during the initial stages of aging, i.e., up to 24 h of aging, and then more gradually with further aging up to 200 h. In contrast, the transformation temperatures for samples aged at 500 °C only increased after 48 h aging and were essentially constant from 10 h to 48 h aging (the changes of ± 3 °C lie within the error of the DSC method).

Previous studies on binary Ni-rich NiTi [21] and Ni-rich NiTiHf alloys [32, 41] showed that the MT temperatures decrease during the initial stages of low temperature aging. This was attributed to difficulties in nucleation of martensite caused by a high density of very fine nanometric precipitates, resulting in an interparticle spacing that is similar or smaller than the critical size for martensite nucleation, thus requiring additional undercooling to form. This initial decrease in M_s at low aging temperatures is generally followed by an increase when aging temperatures or times are increased. At higher aging temperatures or times, the precipitates coarsen resulting in larger interparticle distances. Thus, martensite nucleation is less inhibited by the precipitates and the MT temperatures increase because of the resulting compositional change of the matrix. An increasing volume fraction of Ni-rich precipitates (as in this case [30]) results in a matrix composition that is less Ni-rich and closer to stoichiometry, resulting in an increase in transformation temperatures.

The transformation temperatures of the present $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ SMA in the SHT condition and aged samples at 400 °C and 450 °C up to 200 h are below the DSC detection limit. Higher aging temperatures are needed to create sufficient precipitate volume fraction and matrix composition change to raise the transformation temperatures to the level accessible by the existing DSC. At 550 °C and 600 °C, the matrix composition changes quite rapidly during the first few hours of aging (up to 24 h) and, therefore, transformation temperatures increase more dramatically with initial aging time. The transformation

temperatures continue to increase gradually with further aging at these temperatures until the increase becomes nearly insignificant after 100 h (~4 °C increase at 550 °C and 7 °C increase at 600 °C between the 100 h and 200 h heat treatments) as the equilibrium volume fraction of precipitate phase is reached. The volume fraction of precipitate phase is barely high enough to raise the transformation temperatures over -80 °C after aging at 500 °C for 10 h, though the MT temperatures show a considerable increase after more than 48 h of aging.

As seen in Fig. 3, three stress free DSC cycles were carried out on each sample in order to assess the thermal stability of the transformation temperatures. Fig. 5a shows the shift in M_s temperatures as indicated by the difference between the first and the third DSC cycles ($M_{s1} - M_{s3}$). The change in M_s during thermal cycling is a measure of thermal stability, thus a material showing negligible or no change in M_s is assumed to be “thermally stable”. The change in transformation temperatures with stress free thermal cycling has been generally attributed to defect generation during the repetitive motion of the transformation interface and the accommodation of the transformation shape change through the formation of dislocations and other defects at the austenite-martensite interface [3]. Although there is no clear trend in the amount of shift in the M_s temperatures as a consequence of thermal cycling in samples aged for a few tens of hours, the difference tends to reach a plateau after 48 h of aging and does not change significantly thereafter. The smallest temperature changes are obtained after aging at 500°C (around 4-5 °C shift in transformation temperature), while the largest differences are observed in the samples aged at 600°C (>10°C). This is due to differences in precipitate size and interparticle distances for samples aged at different temperatures. The matrix hardening is more efficient due to the presence of smaller precipitates and their denser distribution after low temperature aging. But in general, the thermal stability of the present $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ SMA is worse than the Ni-rich NiTiHf alloy with a similar composition ($\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Hf}_{15}$) [32, 41]. The reason for this difference is not clear, but it could be due to better lattice compatibility between the austenite and martensite phases in NiTiHf alloys than that in NiTiZr alloys with similar stoichiometries.

Fig. 5b represents the thermal hysteresis values of the aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples determined as the difference between the A_f and M_s temperatures ($A_f - M_s$) of the first DSC cycle. The thermal hysteresis values vary between 53°C and 66°C and are comparable to the thermal hysteresis measured in the aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Hf}_{15}$ alloy [32, 41]. Although there is no clear relationship between the aging time and thermal hysteresis, it is obvious that the thermal hysteresis values generally decrease up to 24 h of aging, then follow almost a stable behavior up to 200 h (slight fluctuations are in the range of error in

the DSC experiments) (Fig. 5b). In SMAs, the increase in matrix strength due to precipitation hardening generally decreases the energy dissipation during the transformation, and hence, the thermal hysteresis also decreases. Therefore, at fixed aging temperatures, the initial increase in precipitate volume fraction with aging time increases matrix strength, and thus, decreases thermal hysteresis. However, once the precipitate volume fraction saturates as in aging times longer than 48 h, there is no further increase in the matrix strength and the transformation hysteresis stabilizes and may even begin to increase as the precipitates coarsen and spacing between the precipitates increases. With an increase in aging temperature, the thermal hysteresis values also increase. This is again due to the larger precipitate sizes obtained at higher aging temperatures as well as a smaller volume fraction of precipitate phase as the aging temperatures approach the solvus temperature of the alloy, and hence, result in a lower matrix strength. Moreover, when the precipitates are several hundreds of nanometers in size and cannot be absorbed by the martensite variants during transformation, the number of intervariant boundaries and their interaction increases (Fig. 2d). This could also contribute to the increase in thermal hysteresis observed for longer aging times at 550 and 600°C.

The data derived from the DSC measurements (A_f and M_s in Figs. 4a and 4b, respectively), were re-plotted to generate the aging time-temperature-martensitic transformation temperature diagrams for the A_f and M_s temperatures of the $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy shown in Figs. 6a and 6b, respectively. These diagrams are useful for the selection of processing parameters for a particular alloy such as $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$, which generate desired transformation temperatures for a given application. The aging times are converted to minutes and the horizontal axis of the diagrams is presented in logarithmic scale to clearly identify trends in the transformation temperatures as a function of aging time and temperature. Each curve in the diagrams represents the loci of a constant A_f or M_s . As seen in Figs. 6a and 6b, the transformation temperatures always increase with an increase in aging time for a fixed aging temperature (i.e., negative slope of the constant transformation temperature curves with time) in accordance with the trends seen in Fig. 4. Similarly, the transformation temperatures consistently increase with an increase in aging temperature at fixed aging times. No transformation peak was recorded for short aging durations at aging temperatures below 550°C (i.e., 1 h or 3 h at 500°C) as indicated in the bottom left part of the diagrams (grey shaded area).

3.3. Load-biased Shape Memory Response

The shape memory response of the $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy was studied via load-biased thermal cycling tests in tension. The experiments were carried out on those samples that exhibited good thermal

stability (NTZ550/24h and NTZ550/100h), relatively low thermal hysteresis (NTZ500/200h), and relatively high transformation temperatures (NTZ600/100h). The strain vs. temperature responses of all four sample conditions under various applied stress levels are presented in Figs. 7a-7d. Critical shape memory characteristics such as transformation temperatures, thermal hysteresis, recovered transformation and unrecovered strain levels were determined as a function of applied stress by analyzing each thermal cycle as demonstrated in Fig. 7e.

Samples NTZ550/24h and NTZ600/100h were also selected in order to compare the effect of significantly different microstructures (Fig. 2) on the thermo-mechanical response of the alloy. In the NTZ550/24h sample, the precipitates were smaller than 90 nm and were absorbed by the martensite plates. In this case (Fig. 7b), perfect shape recovery, (i.e., no unrecovered strains upon heating to austenite), was observed even at 300 MPa applied stress, due to the increased matrix strength. Similar load-biased thermo-mechanical responses were obtained for the NTZ500/200h and NTZ550/100h samples (Figs. 7a and 7c). On the other hand, the NTZ600/100h sample contained large precipitates (>100 nm, Fig. 2f) that limited the growth of martensite variants. This sample exhibited small unrecovered strains under 200 MPa and 250 MPa stress levels and failed at stresses above 250 MPa. This notably different behavior of the NTZ600/100h sample is due to the presence of large precipitates that significantly alter the martensite morphology. These large particles strongly interfere with the growth of martensite variants as well as reorientation or detwinning of martensite.

All the samples mentioned above showed failure when they were tested at stress levels of 250 MPa and above. Independent of the precipitate size or martensite microstructure, the cracks leading to somewhat premature failure should initiate at surface asperities or the largest defects in the microstructure, which are the micron size ZrC particles in both cases above. The precipitates much smaller than ZrC particles would not be the major factor for the initiation of cracks in the presence of the large ZrC particles. However, all the samples with fine precipitates and large variants (NTZ500/200h, NTZ550/24h and NTZ550/100h) showed failure when they were tested at stress levels higher than 300 MPa, while the samples with large precipitates and fine martensite variants and twins showed premature failure at lower stress levels. NTZ600/100h samples always failed when they were tested at stress levels 250 MPa and higher. These observations clearly indicate that the samples with large precipitates are consistently more brittle than the samples with fine precipitates. Therefore, these precipitates most likely control the crack propagation while ZrC particles control the crack initiation. From the observed results, the microstructure with densely populated fine precipitates does not

accelerate the crack propagation due probably to the high coherency between lattice parameters of the precipitate and austenite phases [30], which leads to low stress fields developed at the interface of small, nanometer range precipitates. On the other hand, for the samples with large precipitates, any externally applied stress on this type of microstructure leads to an increase in the local strain and stress, mainly at the tip of the large precipitates, which should enhance the crack propagation. Eventually, the latter samples become more brittle and fail at lower stress levels than the samples with fine precipitates. Similar observations were also reported in furnace cooled Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples consisting of large precipitates [8,9].

The recovered transformation strains and unrecovered strain levels (which is a measure of dimensional stability) of the aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ specimens are summarized as a function of applied bias stress in Fig. 8. The recovered transformation strain showed a continuous increase with increasing applied stress reaching approximately 2.5% for the NTZ500/200h, NTZ550/24h and NTZ550/100h samples under 300 MPa applied stress. However, the NTZ600/100h sample failed while loading to 300 MPa and reached a maximum recovered transformation strain of only 1.2% under 250 MPa. The unrecovered strain levels were determined at temperatures 30°C above the A_f temperature for each applied stress level, calculated as the difference in strain between the heating and cooling curves. Except the NTZ600/100h sample, all the aged samples show perfect dimensional stability up to 300 MPa stress levels as a consequence of the increased resistance to plastic deformation due to precipitation hardening. These results suggest that no training is necessary for achieving dimensional stability in the present alloy since no bulk plastic deformation was evident during the first few cycles. However, because the precipitates are much larger after aging for 100 h at 600°C, precipitation hardening is less prominent as compared to other aged samples with relatively smaller precipitates. Therefore, the NTZ600/100h sample exhibited unrecovered strain starting at 200 MPa applied stress (0.05%), which increased to 0.15% at 250 MPa. The significant resistance to plastic deformation in the 500 and 550 °C aged samples originates from the existence of nanosize precipitates, which have coarsened beyond an optimal size for strengthening in the NTZ600/100h sample. The present Ni-rich $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy shows much better shape recovery than (Ti + Hf/Zr)-rich NiTiZr/Hf alloys [12, 42, 43], while demonstrating comparable stability to other precipitation hardened Ni-rich NiTiZr/Hf alloys [8, 9, 32].

The maximum recovered transformation strains observed for the $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy are less than values previously reported for several ternary Ni-rich NiTiHf alloys and binary NiTi. However, as seen in Fig. 8, the recovered transformation strain levels have not peaked or reached a plateau region with

stress, indicating that the martensite reorientation/detwinning were not complete under the current applied stress levels. Therefore, the aged samples would be expected to generate higher recovered transformation strains at higher stresses. However, along with the increase in matrix hardness with precipitation, the samples were relatively brittle and failed at stress levels above 300 MPa. Therefore, the true extent of the recovered transformation strains for the alloy was not achieved for any of the aged conditions.

The effect of precipitation strengthening is also evident in the transformation thermal hysteresis values of the aged samples summarized in Fig. 9. As mentioned above, precipitation hardening was less prominent in the NTZ600/100h condition due to the larger precipitate sizes. This is consistent with the larger thermal hysteresis that was obtained in this sample, both under stress and zero stress conditions ($\Delta T > 50\text{ }^{\circ}\text{C}$) as compared to the samples with smaller precipitates ($\Delta T < 50\text{ }^{\circ}\text{C}$). It can also be argued that the increased number of precipitate-martensite variant interfaces, small martensite variants, and fine internal twins, due to the large precipitates, which acted as obstacles to martensite propagation in the NTZ600/100h samples, can result in increased energy dissipation and thus contribute to a larger thermal hysteresis as compared to the samples with small precipitates and large martensite variants.

The thermal hysteresis decreased in all the aged samples up to 150 MPa and changed only slightly thereafter with further loading for the NTZ500/200h, NTZ550/24h and NTZ550/100h samples. However, in the case of NTZ600/100h sample, the initial decrease in the hysteresis up to 150 MPa was followed by an increase above 150 MPa that is consistent with the increase in unrecovered strain levels observed in Fig. 8. Thus, the generation of defects such as dislocations under applied stress levels of 200 MPa and above, are responsible for this increase in thermal hysteresis. Finally, the overall range of thermal hysteresis values obtained in the aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples shown in Fig. 9 is comparable to that observed in a Ni-rich $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Hf}_{15}$ alloy [32].

It should be noted that the thermal hysteresis values obtained from the stress free DSC experiments (calculated as $A_f - M_s$ and shown in Fig. 5b) are $\sim 10\text{ }^{\circ}\text{C}$ larger than the zero stress thermal hysteresis levels measured from load-biased thermal cycling experiments (shown in Fig. 9). Basically, the hysteresis is determined at the onset and completion of the transformation in DSC, while the hysteresis is computed at about 50% transformation level (calculated as the width between the midpoints of the heating and cooling curves as demonstrated in Fig. 7e). Moreover, in DSC, the transformation indicator is the latent heat, whereas it is the shape change, i.e., tensile strain, in the load-biased thermal cycling

experiments. In some cases, even though the transformation starts and the latent heat can be measured, shape change may still not occur due to the formation of self-accommodating martensite. Therefore, differences in zero stress thermal hysteresis levels measured from DSC and load-biased thermal cycling experiments can be expected.

The change in M_s temperature as a function of applied stress, i.e., Clausius-Clapeyron (CC) relationship, with the best linear fit lines for the aged samples is given in Fig. 10. As seen in Fig. 10, M_s actually follows a bilinear relationship with different fits at low and high stresses. At low stress levels, as a consequence of the relatively soft austenite phase and martensite variant-variant interactions, due to the co-existence of self-accommodated and oriented martensite variants, local defects may be generated leading to energy dissipation. Therefore, M_s temperature shows a decrease in NTZ550/24h and NTZ600/100h cases with increasing stress for the stress levels less than 100 MPa. In the case of NTZ500/200h and NTZ550/24h samples, there is almost no change in M_s with stress below 100 MPa. There seems to be a direct correlation between the precipitate size / austenite strength and the deviation from the critical stress for martensitic transformation vs. temperature slope in Fig. 10, i.e. the stronger the matrix is, the less deviation from the CC slope occurs at low stress levels. Similar observations were also reported for ternary NiTiHf [32] and binary NiTi [44] alloys, where the aforementioned deviation was reduced and eventually conventional linear CC relationship was obtained at all stress levels when the austenite strength was increased by either precipitation hardening (peak aging) or grain size refinement.

For stresses greater than 100 MPa, the M_s of all four cases exhibit a linear stress dependence with CC slopes of 13.7 MPa/°C, 8.4 MPa/°C, 14.8 MPa/°C and 23.7 MPa/°C, respectively. Furthermore, as seen in Fig. 10, higher stresses are needed to increase M_s in the sample with large precipitates (NTZ600/100h with the CC slope of 23.7 MPa/°C) as compared to the samples with smaller precipitates. The exact reason for such high CC slope in the sample with large precipitates and different martensite morphology is not completely known. However, three factors should play a role: (1) changes in martensitic transformation – precipitate interactions as a result of the coherency loss with increasing precipitate size and associated changes in strain energy around the precipitates; (2) the change in the matrix strength and composition with the increase in precipitate size and volume fraction; and (3) the change in martensite morphology and variant / twin size with increasing precipitate size. Clearly, more systematic work is needed to understand the role of martensite morphology and precipitate size on the stress vs. temperature phase diagrams of these SMAs.

4. Summary and Conclusions

The present work reports on the effect of precipitation on the microstructure and shape memory properties of the Ni-rich $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy for the first time. Based on the reported experimental results, the following conclusions can be made:

1. Spindle-shaped precipitates form after aging at 500 °C, 550 °C and 600 °C. Martensite variants may easily grow and absorb the relatively smaller precipitates (< 160 nm) during transformation while several hundred nanometer long precipitates, which form after aging at 600 °C, strongly interfere with martensite variant growth and results in a refined twin structure. The precipitate crystal structure was found to be the same as the H-type precipitates previously identified in Ni-rich NiTiHf and NiTiZr alloys.
2. The transformation temperatures of the $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy can be modified over a wide range as a consequence of the change in matrix composition due to the precipitation. The stress free thermal hysteresis of the aged samples varies between 53-66 °C and is comparable to Ni-rich NiTiHf alloys with similar compositions and stoichiometry.
3. Aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples with relatively smaller precipitates (< 160 nm) show excellent dimensional stability and a maximum of 2.5 % transformation strain under applied stress levels as high as 300 MPa. The precipitation hardening was less prominent in aged samples with precipitates several hundred nanometers in size, resulting in unrecovered strain during thermomechanical cycling at stresses equal to or greater than 200 MPa. Samples with large precipitates also exhibit higher thermal hysteresis due to the increased number of precipitate-martensite interfaces and finer variants and internal twins with a contribution at higher stresses due to the onset of plasticity during thermomechanical cycling. Finally, the CC slope for the sample with the largest precipitates (NTZ600/100h with a CC slope of 23.7 MPa/°C) was 2-3 times larger than that for samples with relatively finer precipitates, which ranged from 8.4 to 14.8 MPa/°C for all other aged samples.
4. Although the DSC results indicated that the thermal stability of the present $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ SMA is inferior to the comparable Ni-rich $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Hf}_{15}$ alloy [32], overall the microstructure and the shape memory response of the aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy was similar to its NiTiHf counterpart. Considering the fact that Zr also provides weight and cost savings compared to Hf, NiTiZr alloys

could be viable alternatives to NiTiHf alloys for high temperature shape memory alloy applications and warrant further study.

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FIGURES

Figure 1: Back-scattered electron micrograph of the solution heat treated (SHT) Ni_{50.3}Ti_{34.7}Zr₁₅ SMA. White particles are carbide inclusions (mainly ZrC). No other second phases were observed in the microstructure at this scale. The austenite grain size ranges from 25 μm to 100 μm.

Figure 2: Bright field transmission electron microscopy images of $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ (at.%): (a) sample aged at 500°C for 200 h, (b) HRTEM image of the precipitate – B2 interface in the sample aged at 500°C for 200 h, (c) sample aged at 550°C for 24 h, (d) sample aged at 550°C for 100 h, (e) HRTEM image of the precipitate – B19' interface and the corresponding FFT images of the sample aged at 550°C for 100 h and (f) sample aged at 600°C for 100 h. A white line is drawn to show continuity of atomic planes at the interface in image (e) and the precipitates are marked with arrows in image (f). (g) The SADP image taken from the sample aged at 550°C for 100 h, consisting of two variants of H-phase precipitates with $1/3\langle 110 \rangle$ satellites (red arrows) and another two variants with $1/4\langle 210 \rangle$ satellites (blue arrows).

Figure 3: Representative DSC curves for $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples aged at 550°C for various times. Each case consists of three heating-cooling cycles. The A_f and M_s temperatures were measured using the intercept method as demonstrated on the DSC curve of the sample aged at 550°C for 10 h.

Figure 4: Summary of the transformation temperatures for $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples aged at 500°C, 550°C and 600°C for different times: (a) Austenite finish (A_f) temperatures and (b) Martensite start (M_s) temperatures.

Figure 5: Summary of (a) the shift in M_s ($M_{s1} - M_{s3}$) temperatures during stress free DSC cycling, and (b) the thermal hysteresis ($A_f - M_s$) of the $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ alloy aged at 500°C, 550°C and 600°C for various durations.

(a)

(b)

Figure 6: Aging time-temperature-martensitic transformation temperature diagrams revealing the effect of aging temperature and time on the A_f (a) and M_s (b) temperatures of the $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ SMA. The data is derived from the DSC measurements and plotted as lines of constant transformation temperatures.

(a)

(b)

(c)

(d)

(e)

Figure 7: The strain vs. temperature responses of aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples under various tensile stress levels: a) aged at 500°C for 200 h, b) aged at 550°C for 24 h, c) aged at 550°C for 100 h and d) aged at 600°C for 100 h. (e) Schematic representation of how the shape memory characteristics are determined from the load-biased thermo-mechanical cycling experiments in tension. The figure shows one thermal cycle at a constant stress level. M_s and M_f indicate the martensite start and martensite finish temperatures, respectively, and A_s and A_f refer to austenite start and austenite finish temperatures, respectively. The thermal hysteresis is calculated as the width between the midpoints of the heating and cooling curves.

Figure 8: Summary of the recovered transformation strains and unrecovered strain levels for aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples as a function of applied tensile stress.

Figure 9: Summary of the thermal hysteresis of aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples during thermal cycling in tension as a function of applied stress.

Figure 10: The stress vs. temperature relationships for the start of the martensitic transformation, M_s , for aged $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ samples during thermal cycling in tension.

TABLES

Table 1

Composition of the present $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ SMA after solution heat treatment at 900 °C for 1h, measured using WDS. $\pm$ indicates the standard deviation from a total of 10 measurements over the specimens.

	Ni (at.%)	Ti (at.%)	Zr (at.%)
Measured	50.37 ± 0.10	34.75 ± 0.07	14.88 ± 0.14
Nominal	50.3	34.7	15.0