Relationship between crystallographic compatibility and thermal hysteresis in Ni-rich NiTiHf and NiTiZr high temperature shape memory alloys

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ABSTRACT

The relationship between the crystallographic compatibility of austenite and martensite phases and the transformation thermal hysteresis (ΔT) of Ni-rich Ni_{50.3}Ti_{29.7}Hf₂₀ and Ni_{50.3}Ti_{29.7}Zr₂₀ alloys undergoing B2 to B19' martensitic transformation was studied as a function of microstructure, via differential scanning calorimetry, transmission electron microscopy, and X-ray diffraction. An experimental linear relationship of ΔT vs λ_2 (the second eigenvalue of the transformation stretch matrix) was observed for these NiTi(Hf/Zr) alloys, but with a **shallower slope** as compared to the universal behavior followed by alloys showing B2 to B19 martensitic phase transformation. Several ternary NiTiCu and binary NiTi alloys undergoing the B2 to B19' transformation were also found to deviate from the universal behavior attributed to alloys that undergo a B2 to B19 transformation, and instead, follow the trend revealed for the present alloy systems. Aged NiTi(Hf/Zr) samples, which consist of very fine nano-precipitates, followed the newly established ΔT vs λ_2 linear relationship, due to only minor changes in the microstructure. In contrast, samples with large precipitates, exhibited a large deviation from this relationship due to much more drastic changes in microstructure. Finally, despite the poor crystallographic compatibility of the austenite and martensite lattices observed in the present alloys, rationalized by large deviation of λ_2 values from 1, relatively low ΔT values were measured. This behavior is actually consistent with the newly established relationship for ΔT vs λ_2 for B2-B19' transforming alloys, which is much less sensitive to compatibility (**shallower slope**). It is concluded that such a difference in the ΔT vs λ_2 slope must be a consequence of the crystallography of monoclinic martensite formation in NiTi-based alloys as long as other factors such as plasticity or major constraints to the martensitic transformation do not intervene.

Keywords: High Temperature Shape Memory Alloys; Martensitic transformation; Microstructure; Thermal Hysteresis; Crystallographic compatibility

1. Introduction

NiTi shape memory alloys (SMAs) have been implemented in many industrial and biomedical applications due to their superior corrosion resistance and distinct mechanical properties such as large shape memory effect, superelasticity, and good ductility. However, the use of binary NiTi SMAs is limited to temperatures below ~ 100 °C, because of their inherently low transformation temperatures. Although ternary alloying of NiTi-based SMAs with noble metals (Pd, Pt and Au) has been a successful approach to increase the transformation temperatures, the high cost of these ternary alloys (NiTiPd, NiTiPt and NiTiAu) has prevented their widespread commercialization. More recently, NiTiHf and NiTiZr high temperature shape memory alloys (HTSMAs) have drawn a great deal of attention as cheaper alternatives to Pd, Pt and Au alloyed NiTi-based HTSMAs [1,2].

The (Ti + Hf/Zr)-rich compositions of NiTiHf and NiTiZr alloys were widely studied in the past due to their high transformation temperatures, however these alloys suffer from a large thermal hysteresis of transformation and poor thermal and dimensional stability, preventing their commercial use [3-16]. More recently, slightly Ni-rich compositions (Ni content higher than 50 at. %) of both alloy systems were shown to demonstrate excellent shape recovery (which is a measure of dimensional stability) with reasonable transformation strain levels (2-4 %) and excellent superelastic behavior while exhibiting relatively high transformation temperatures after proper precipitation heat treatments [17-26]. These studies showed that very fine precipitates (recently identified as H phase precipitates [27, 28]) can form after aging treatments in Ni-rich compositions, which not only significantly increase the resistance to plastic deformation, but also help maintain relatively high transformation temperatures by altering the matrix Ni content.

Along with the stability of superelastic and shape memory behaviors, appropriate transformation temperatures, and adequate reversible strains, it is also important to evaluate the thermal hysteresis of an SMA for most practical applications. As for the latter, it has been reported that the crystallographic compatibility between the martensite and austenite phases correlates surprisingly well with transformation thermal hysteresis through a factor known as λ_2 , which is the middle eigenvalue of the transformation stretch tensor [29-32]. This will be further discussed in detail below. However, these previous studies [29-32] reported a correlation between λ_2 and the thermal hysteresis of single phase NiTi(Cu/Pd/Pt/Au) SMAs showing B2 (cubic austenite) to B19 (orthorhombic martensite) transformation. With the exception of Bucsek et al. [33], little effort has been spent determining whether the same type of analysis applies to the recently discovered Ni-rich NiTiZr and NiTiHf alloys showing B2 to B19'

(monoclinic martensite) transformation. Furthermore, to the best of the authors' knowledge no studies are present on any SMA system investigating the relationship between transformation thermal hysteresis and crystallographic compatibility as a function of microstructure in two-phase systems. Therefore, in this work, Ni-rich NiTiHf and NiTiZr alloys were heat treated under different conditions to provide various microstructures (precipitate size, morphology, and volume fraction) and investigated with differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and X-ray diffraction (XRD) experiments. The aim of this investigation was to explore the correlation between λ_2 and the thermal hysteresis of these B2 to B19' transforming alloys as a function of microstructure.

2. Transformation thermal hysteresis and λ_2

In the last two decades, extensive research was performed to develop SMA systems with low transformation hysteresis, but without the guidance of a theoretical approach, these studies were generally based on trial and error. Recently, a new theory has been established [29, 32] predicting that the thermal hysteresis in SMAs can be remarkably minimized through improving the crystallographic compatibility of the martensite and austenite phases. Two main conditions of crystallographic compatibility were proposed, which if satisfied, should result in low hysteresis: (1) $\det \mathbf{U} = \lambda_1 \lambda_2 \lambda_3 = 1$ and (2) $\lambda_2 = 1$ where $\mathbf{U}$ stands for the transformation stretch matrix that converts the austenite lattice to the martensite lattice and $\lambda_1 \leq \lambda_2 \leq \lambda_3$ are the ordered eigenvalues of $\mathbf{U}$. Furthermore, the determinant of the transformation stretch matrix ($\det \mathbf{U}$) corresponds to the relative volume change ($\Delta V/V$) during martensitic transformation. The transformation stretch matrix, $\mathbf{U}$, can be determined using the lattice parameters of the austenite and martensite phases and their symmetries. Details on how to derive the transformation stretch matrix and its specific components and eigenvalues can be found elsewhere [29, 34].

The first condition, $\det \mathbf{U} = \lambda_1 \lambda_2 \lambda_3 = 1$, indicates that no volume change should occur during martensitic transformation, whereas the second condition, $\lambda_2 = 1$, shows that austenite lattice is directly compatible with a single variant of martensite. Cui et al. [32] studied the lattice parameters and the thermal hysteresis of NiTiCu and NiTiPd thin films. Surprisingly, only a weak correlation between the volume change ($\det \mathbf{U}$) and the thermal hysteresis was obtained since some alloys with the largest thermal hysteresis showed $\det \mathbf{U}$ values very near 1. However, all these alloys showed a clear correlation between hysteresis and λ_2 with a significant decrease of the hysteresis when λ_2 approaches 1. Zhang et al. [29] also reported on the same correlation for NiTiAu, NiTiPt and NiTiPd alloys where a symmetrical drop in hysteresis was seen on both sides of $\lambda_2 = 1$ along with a minimum when $\lambda_2 = 1$. Therefore, both

the observations of Cui et al. [32] and Zhang et al. [29] indicate a strong correlation between thermal hysteresis and λ_2 for alloys undergoing B2 to B19 (orthorhombic martensite) transformation.

In SMA systems with λ_2 values deviating from 1, a complex arrangement of microstructures forms during the martensitic transformation. In general, none of the martensitic variants is completely compatible with the austenite by itself, but a mixture of variants forming a layered or “mosaic” microstructure can be almost compatible with austenite. In this case, a transition layer between the austenite and the twinned martensite is generally formed to store the elastic energy arising from the lattice mismatch. Additional to the elastic energy, there is also an interfacial energy stored due to the twin boundaries between these variants. Therefore, as a consequence of the incompatibility between austenite and martensite, both elastic and interfacial energy must be overcome to trigger the phase transformation. As a result, SMAs should be supercooled below or superheated above its equilibrium transformation temperature to initiate and complete the forward and reverse transformations, respectively. Such additional superheating or supercooling in SMAs with λ_2 values deviating from 1 in turn contribute to the thermal hysteresis, together with other dissipative processes like lattice friction, formation of permanent defects (dislocations), etc. However, when the $\lambda_2 = 1$ condition is satisfied, austenite is compatible with a single variant of martensite and hence no elastic transition layer is necessary and there is no interfacial energy arising from the formation of internal twins. In this case, the additional dissipative processes are generally very small in magnitude and the hysteresis may be significantly decreased. The microstructural evidence of this type of microstructure, with λ_2 values very close to 1, was shown by Delville et al. [31] through transmission electron microscopy (TEM) studies on NiTiPd SMAs. Indeed, large twin-less martensite plates were commonly revealed in Ni₃₉Ti₅₀Pd₁₁ samples, having $\lambda_2 = 1.0001$ and the lowest thermal hysteresis among the NiTiPd compositions studied. Hence, due to the good compatibility between austenite and a single variant of martensite, a twin-less transformation occurs minimizing the overall energy of interfaces and therefore decreasing the transformation hysteresis.

3. Material and methods

Ingots of Ni-rich Ni_{50.3}Ti_{29.7}Hf₂₀ and Ni_{50.3}Ti_{29.7}Zr₂₀ (at. %) high temperature SMAs were produced via vacuum induction melting in a graphite crucible under a partial argon atmosphere using high purity elemental materials (99.98% Ni, 99.95% Ti, 99.9% Hf, 99.9% Zr). The melts were cast into a 25.4 mm diameter by 102 mm long copper mold. The resulting ingots were vacuum homogenized at 1050 °C for 72 h and furnace cooled to room temperature and then sealed in a mild steel can followed by hot

extrusion at 900 °C with an area reduction of ~ 7:1. The DSC and XRD experiments were carried out on circular shaped samples with 3 mm (for DSC) and 10 mm (for XRD) diameter by 1 mm in thickness. All the samples were extracted from the extruded rods via wire electro-discharge machining and solution heat treated (SHT) at 900 °C for 1 h followed by water quenching (WQ) to dissolve any secondary phases that may have formed during material processing.

Our previous studies on Ni-rich NiTi(Hf/Zr) alloys [17-20,28] confirmed that the H-phase precipitate size has a significant effect on martensite morphology. Based on the observations of these studies, several precipitation heat treatments were chosen to apply on the SHT specimens to obtain two-phase microstructures with different precipitate sizes and resulting martensite morphologies. This allowed us to study the thermal hysteresis – microstructure – crystallographic compatibility relationships in B19' martensitic alloys. The first two groups of samples were aged at 500 °C for 48 h and at 550 °C for 3 h followed by WQ, while a third group of samples were held at 700 °C for 5 minutes and furnace cooled (FC) to 100 °C in 48 h and then subjected to WQ. Finally, a fourth group of samples were investigated in the SHT state (900 °C for 1 h followed by WQ) as a reference material without any precipitates. Hereafter, the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ (labeled as NTH) and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ (labeled as NTZ) samples are coded to indicate their composition and the heat treatment conditions. For instance NTZ/SHT, NTZ/500°C/48h and NTZ/FC/48h correspond to the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples that were only solution heat treated, SHT and aged at 500 °C for 48 h, and SHT and furnace cooled from 700 °C to 100 °C in 48 h, respectively. All the samples were sealed in quartz tubes under argon atmosphere to prevent oxidation during heat treatments and water quenched by breaking the quartz tubes.

The stress free austenite start (A_s), austenite finish (A_f), martensite start (M_s), and martensite finish (M_f) temperatures of the SHT and precipitation heat treated samples were determined using a TA Instruments, Q20™ differential scanning calorimeter operated with a heating/cooling rate of 10 °C min⁻¹. The stress free thermal hysteresis (ΔT) was calculated as $\Delta T = A_f - M_s$. The overall microstructure and the precipitate size of the precipitation heat treated samples were investigated through transmission electron microscopy (TEM) using a JEOL 2010 high resolution microscope with a LaB₆ filament operated with an accelerating voltage of 200 kV at room temperature. The thin foils for the TEM studies were prepared via mechanical grinding of 3 mm discs down to 100 µm thickness followed by double jet electropolishing using a 30% HNO₃ and 70% methanol solution at -20 °C.

A Bruker-AXS D8 X-ray diffractometer operated with CuK α radiation (1.5406 Å) was used to measure the martensite (B19') and austenite (B2) lattice parameters. X-ray samples were prepared by mechanical grinding through 1200 grit SiC abrasive paper. The XRD patterns of the martensite phase in all samples

were acquired at room temperature (RT) and the lattice parameters were calculated through a Rietveld refinement of the obtained patterns. In order to obtain the XRD patterns of the austenite phase, the samples were first heated above their A_f and then slowly cooled to a temperature above their M_s inside the XRD device, while they were still in the fully austenitic state. Since any lattice parameter calculation for the austenite phase at temperatures above RT would involve thermal expansion effects, the XRD measurements were performed at several different temperatures, i.e., $M_s + 10\text{ }^\circ\text{C}$, $M_s + 30\text{ }^\circ\text{C}$, $A_f + 20\text{ }^\circ\text{C}$, etc., in order to reveal the temperature dependency of the austenite peak positions (2Θ). Finally, the austenite peak positions (2Θ) gathered from each high temperature XRD scan were extrapolated to RT and implemented in the Bragg Law formula to calculate the austenite lattice parameter. The samples were heated on a Pt heating-strip while an external thermocouple was attached to the sample surface to monitor the actual sample temperature. Using the measured lattice parameters of the martensite and austenite phases at RT, the eigenvalues (λ_1 , λ_2 and λ_3) of the transformation stretch matrix ($\mathbf{U}$) and the relative volume change, calculated as $\Delta V/V (\%) = 100 (\det \mathbf{U} - 1)$, were obtained. The reader should refer to the literature [34] for details on the calculation of such values.

4. Results and discussion

4.1. Transformation thermal hysteresis and microstructure

Fig. 1 shows the stress free DSC curves of the SHT and precipitation heat treated $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ (NTZ) and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ (NTH) samples. After SHT, the thermal hysteresis (ΔT) was $46\text{ }^\circ\text{C}$ and $34\text{ }^\circ\text{C}$ in the NTZ/SHT and NTH/SHT samples, respectively. ΔT decreased by almost $6\text{ }^\circ\text{C}$ in NTZ and NTH samples after aging at $500\text{ }^\circ\text{C}$ for 48 h and $550\text{ }^\circ\text{C}$ for 3 h as compared to the respective SHT cases. However, as seen from Fig. 1, no favorable improvement was obtained after furnace cooling and in fact, ΔT was much greater compared to NTZ and NTH samples aged at $500\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$. This effect of furnace cooling on ΔT as compared to other aging cases is due to the different microstructures that are formed after the various heat treatments.

Densely distributed nanoprecipitates, 7 to 20 nm in length and 3 to 8 nm in width, were observed in the NTH/ $500\text{ }^\circ\text{C}/48\text{ h}$ and NTH/ $550\text{ }^\circ\text{C}/3\text{ h}$ samples, as shown in the bright field TEM images in Figs. 2a and 2b, respectively. These fine precipitates not only increase the resistance to defect formation, through matrix strengthening, and thus lower ΔT , but at the same time do not interfere significantly with the martensitic transformation (MT), resulting in the growth of several hundred nanometer wide martensite variants. As seen in Fig. 2a and 2b, the final martensite variant sizes were different, but both samples have precipitates sufficiently small that could be absorbed by these martensite variants. Therefore,

regardless of the difference in aging temperature and duration, both samples essentially have final generic microstructures defined as “Type A microstructures” for simplicity. On the other hand, large spindle like precipitates, 70 to 250 nm in length and 20 to 70 nm in width, were present in the NTH/FC/48h after furnace cooling from 700°C, as seen in Fig. 2c. These large precipitates, some were labeled with letter “P” in the inset image, limit the martensite growth within the space between precipitates and refine the martensite microstructure leading to a generic microstructure consist of a large number of martensite variants comparable in size with the precipitates (defined as “Type B microstructures”). Therefore, more energy is dissipated during the martensitic transformation in type B microstructures in order to form a large number of constrained martensite variants leading to increased ΔT as compared to the samples with Type A microstructures.

Similar microstructures were also identified in precipitation heat treated $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples and the corresponding bright field TEM images are shown in Figs. 3a-c. Figs. 3a (NTZ/500°C/48h) and 3b (NTZ/550°C/3h) are examples of Type A microstructures, consisting of fine precipitates, 18 to 45 nm in length and 7 to 15 nm in width, absorbed by several hundred nanometer wide martensite variants. Furnace cooling of $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ specimens, like $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$, also leads to the growth of much larger precipitates, 200 to 500 nm in length and 35 to 55 nm in width, which refine the martensite variant size and hence form Type B microstructures as shown in Fig. 3c. Similar to $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$, ΔT is reduced in samples with Type A microstructures as compared to the SHT case, due to the matrix strengthening, while ΔT is increased in samples with Type B microstructures due to the higher energy dissipation during formation of a large number of martensitic variants. Therefore, the same conclusions on the effect of microstructure on ΔT can be drawn for both the Ni-rich NiTiZr and NiTiHf alloys.

4.2. Transformation thermal hysteresis and crystallographic compatibility

In the absence of major microstructural changes or concurrent plasticity during transformation, the crystallographic compatibility of the austenite and martensite phases should be the dominant factor influencing ΔT . In order to study the crystallographic compatibility, the eigenvalues of the transformation stretch matrix ($\lambda_1, \lambda_2, \lambda_3$) were calculated using lattice parameters determined from the transforming phases in this study. Figs. 4a and 4b show the XRD patterns acquired at RT and the corresponding Rietveld refinement fits of the solution heat treated and precipitation heat treated $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples, respectively. Several peaks belonging to B19' martensite were indexed in all samples at RT (Figs. 4a and 4b) and the lattice parameters of B19' were calculated through Rietveld refinement of these peaks. An additional peak in $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples and a shallow peak in

$\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ samples around $2\Theta \sim 33^\circ$ were also observed, which were identified as zirconium carbide and hafnium carbide phase, respectively. These carbides were formed during the vacuum induction melting of the SMA ingots in graphite crucibles. Similar carbide particles were revealed in our previous studies by electron microscopy in $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{15}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{15}$ samples fabricated with the same procedure [17,20]. None of the observed peaks could be attributed to H-phase precipitates even after precipitation heat treatments, which may be due to the overlap with martensite peaks. As expected, the martensite peaks disappeared upon heating of the samples above their A_f , i.e. $A_f + 20^\circ\text{C}$, but only the (110) peak of B2 austenite phase was visible. One example of the phase transformation is shown for the NTH/500°C/48h sample in Fig. 5a and the evolution of this single B2 austenite peak at several different testing temperatures is shown in Fig. 5b. As expected, the austenite peak shifted to lower 2Θ angles representing an increase in the lattice parameter due to thermal expansion of the austenite lattice with an increase in temperature. Therefore, the peak positions (2Θ) were extrapolated to room temperature to calculate the B2 austenite lattice parameter, correcting for thermal expansion for all samples.

The room temperature B19' martensite (a , b , c and β) and B2 austenite (a_0) lattice parameters of $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples along with the calculated eigenvalues of the transformation stretch matrix (λ_1 , λ_2 , λ_3), relative volume change ($\Delta V/V$ (%) = $100 \cdot (\lambda_1 \cdot \lambda_2 \cdot \lambda_3 - 1)$, and the measured ΔT values from DSC experiments are summarized in Table 1. Furthermore, Table 1 also contains these values for some binary NiTi and ternary NiTi-based SMAs showing B2 to B19' (monoclinic) and B2 to B19 (orthorhombic) transformations from the literature. The present Ni-rich $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloy samples have all three eigenvalues (λ_1 , λ_2 , λ_3) deviating the most from unity among all the alloys included in the table. Therefore, it can be stated that the martensite lattice is significantly more deformed (in relation to austenite) in the present NiTi(Hf/Zr) alloys as compared to other alloys showing B2 to B19' transformation and still much more deformed when compared to the alloys undergoing B2 to B19 transformation. The reason for such a large lattice distortion should be attributed to a different interaction of Hf/Zr with Ni and Ti atoms. However, the absolute values of the relative volume change ($\Delta V/V$) observed in the present NiTi(Hf/Zr) samples are comparable to, or even lower than, that of the other alloys, being well below 1% in most cases. Among the NiTi(Hf/Zr) samples, an exception is visible for the furnace cooled samples (NTH/FC/48h and NTZ/FC/48h) where a relative volume change is over 1%. This is probably due to the remarkable refinement of the martensite microstructure induced by the large precipitates resulting in a larger distortion of the martensite lattice.

Fig. 6 shows the relationship between λ_2 and ΔT of the present NiTi(Hf/Zr) alloys and the different alloy systems given in Table 1. As previously mentioned, several studies have recently shown a strong

correlation between λ_2 and ΔT for ternary systems that show B2-austenite to B19-martensite phase transformation. Thus, the data for the NiTi(Cu/Pd/Pt/Au) alloys retrieved from these recent studies [29,32] was also used to populate Fig. 6. It is important to note that the data for the lattice parameters or the eigenvalues of the transformation matrix (except λ_2) were not reported for these NiTi(Cu/Pd/Pt/Au) alloys hence they were not included in Table 1. As seen from Fig. 6, NiTiPd and NiTiCu alloys studied by Cui et al. [32] and Zhang et al. [29] follow a V-shaped curve on both sides of the $\lambda_2 = 1$ condition. However, it is also clear that NiTiCu alloys show a large spread on the left arm of the V-curve, where $\lambda_2 < 1$. Although some deviation on $\lambda_2 > 1$ side is visible, the data for the NiTiPt and NiTiAu ternary alloys [29] also follow the similar V-shaped behavior as NiTiCu and NiTiPd alloys. It is also evident from Fig. 6 that Ni_{50-x}Ti₅₀Cu_x alloys studied by Nam et al. [35, 36] and the Ni_{50-x}Ti₅₀Pd_x alloys studied by Delville et al. [31] comply with the same trend and fall near the V-shaped curve. The common feature of all these NiTi(Cu/Pd/Pt/Au) alloys is that they show a B2 to B19 phase transformation and it can be concluded that when the thermal hysteresis is evaluated as a function of λ_2 , the data collapse onto a nearly universal V-shaped curve as shown in Fig. 6.

Interestingly, when the data for the present Ni-rich NiTi(Hf/Zr) samples (given in Table 1) showing B2 to B19' phase transformation were added to Fig. 6, again a linear relationship (indicated by the new dashed line on the $\lambda_2 < 1$ side) is observed; however, with a **shallower slope** as compared to the universal V-shaped curve of other alloys showing B2 to B19 phase transformation. The λ_2 vs ΔT relationship of samples in the solution heat treated (SHT) state or with Type A microstructures correlates well with the new dashed line with negligible deviation. Although, samples with Type A microstructures have very fine precipitates, which may decrease ΔT independently from λ_2 values due to precipitation hardening, these precipitates, on the other hand, do not interfere with the martensite growth. Therefore, the change in microstructure as compared to solution heat treated samples is apparently not significant in the present case. As a consequence, both the solution heat treated samples and the samples with Type A microstructures essentially follow the same trend and the data fall on the new dashed line. However, as shown in Fig. 6, the samples exhibiting Type B microstructures clearly deviate from the new dashed line and exhibit the highest ΔT values in spite of comparable λ_2 values to some of the other NiTi(Hf/Zr) samples. As explained above, these samples consist of large precipitates, which drastically change the martensite morphology and lead to relatively larger volume change during the MT. Hence, energy dissipation during MT and thus the thermal hysteresis are enhanced prominently in samples with Type B microstructure leading to a deviation from the new relationship shown in Fig. 6.

Furthermore, the data for the $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ alloys [35,36] (summarized in Table 1) showing B2 to B19' transformation also deviate from the universal V-shaped curve of alloys with B19 martensite and fit closer with the new B2-B19' relationship followed by the present Ni-rich NiTi(Hf/Zr) alloys (Fig. 6). These samples were solution heat treated and therefore probably single phase, which would prevent deviations from the B2-B19' trend. Moreover, the two binary NiTi alloys [37-39] showing B2 to B19' transformation in Fig. 6 (with data included in Table 1), also do not follow the V-shaped B2-B19 curve and instead lie a bit above the new B2-B19' dashed line.

Although, the λ_2 vs ΔT relationship of the ternary $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ and binary NiTi alloys follow the general B2-B19' trend of the present NiTi(Hf/Zr) samples, the data for the $\text{Ni}_{49.8}\text{Ti}_{50.2-x}\text{Hf}_x$ alloys [40] (summarized in Table 1), also exhibiting B2 to B19' transformation, deviates both from the universal V-shaped curve and the new B2-B19' relationship. As shown in Fig. 6, the data for these samples lies between the two trend lines with similar λ_2 values, but notably higher ΔT values ($\Delta T > 70$ °C) as compared to the present NiTi(Hf/Zr) alloys. However, these samples were investigated in the form of ribbons and produced via melt-spinning leading to small grain size, retained vacancies and internal stresses from the rapid quenching, which may influence the transformation process and enhance ΔT . Indeed, it was recently shown that the martensite transformation temperatures and thermal hysteresis can notably be influenced by the grain size to thickness ratio of SMA thin films / ribbons [41]. Additionally, these NiTiHf alloys are Ni poor (Ni content lower than 50 at.%) with high transformation temperatures and are relatively soft at high temperatures. Thus, ΔT may be strongly effected by plastic deformation of the matrix during MT. Indeed, the poor ductility and dimensional stability of such Ni-poor NiTiHf HTSMAs have been widely reported in the literature [9-14]. It is also important to note that these $\text{Ni}_{49.8}\text{Ti}_{50.2-x}\text{Hf}_x$ samples were reported to follow the universal V-shaped curve of alloys showing B2 to B19 transformation by Zhang et al. [29]. Yet, in spite of the large spread of the data belonging to the NiTiCu alloys on the $\lambda_2 < 1$ side, the fit is not that good. Instead, the new data presented here demonstrate a different trend for the alloys transforming to the monoclinic B19' martensite and these $\text{Ni}_{49.8}\text{Ti}_{50.2-x}\text{Hf}_x$ samples must be considered to deviate from the new trend (dashed line) as a consequence of the aforementioned microstructural effects caused by melt-spinning and low strength, which naturally lead to an increased hysteresis.

Considering all the previous studies and the present observations on NiTi(Hf/Zr) specimens, it can be concluded that alloys showing B2 to B19' transformation follow an experimental ΔT vs λ_2 linear relationship but with a **shallower slope** as compared to the $\lambda_2 < 1$ line for alloys undergoing B2 to B19 transformation. This relationship seems valid as long as microstructural factors do not overly influence

the thermal hysteresis. For instance, solution heat treated $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ samples, binary NiTi alloys and the present NiTi(Hf/Zr) alloys in the SHT state represent a consistent set of data falling on or around the new B2-B19' dashed line shown in Fig. 6. NiTi(Hf/Zr) samples exhibiting Type A microstructures also follow this trend due to a relatively small change in the martensite microstructure as compared to the SHT case. **It is worth noting here that there could be other aging conditions leading to formation of sufficiently small precipitates which would result in generic Type A microstructures in the present NiTi(Hf/Zr) samples. Although, it is not possible to investigate all possible aging cases for generic Type A microstructures in the present work, it is proposed that all samples with Type A microstructures should follow the dashed line shown in Fig. 6 owing to the relatively small change in their microstructure as compared to solution heat treated cases.** On the other hand, the present samples with Type B microstructures deviate from this relationship due to the drastic change of martensitic microstructure and large volume change during the MT. Ni-poor $\text{Ni}_{49.8}\text{Ti}_{50.2-x}\text{Hf}_x$ melt spun ribbons showing B2 to B19' transformation also deviate significantly from the B2-B19' relationship presumably due to the melt-spun microstructure and the high level of plasticity that might accompany the martensitic transformation in these alloys. Finally, although it is beyond the scope of the present work to develop a theoretical justification for the different slopes of the ΔT vs λ_2 relationship in alloys with different crystallography, several arguments can still be made as discussed below.

4.3 Thermal hysteresis and λ_2 revisited

Zhang et al. [29] relates the width of transformation thermal hysteresis to the energy barriers that the austenite/martensite interface has to overcome during MT and report that such energy barriers consist of three elements: i) interfacial energy of twin boundaries, ii) elastic energy in the transition layer from austenite to twinned martensite, and iii) bulk free energy difference between the phases. These energies are then calculated using the phenomenological theory of MT for B2 to B19 transformation, the linear elasticity theory and thermodynamics and finally lead to an equation that relates the thermal hysteresis width H with λ_2 parameter:

$$H = \frac{2\lambda\theta_c}{L} \sqrt{\frac{2K\mu(1-\lambda)\xi}{l_c}} \quad (1)$$

Here, θ_c is the equilibrium temperature of the MT, L is the latent heat, κ is the interfacial energy per unit area of the twin, μ is the elastic shear modulus, ξ is a geometric factor dependent on the particular twin system, l_c is the critical size of a martensite nucleus with fully developed austenite/martensite interfaces and λ is the volume fraction of one twin in the twinned martensite ($1-\lambda$ is the fraction of the other twin).

Then, λ is calculated from the phenomenological theory of MT and under the approximation of $\lambda_2 \sim 1$, the dominant part of λ turns out to be a function of λ_2 . More details on the derivation of equation (1) and λ can be found in reference [29]. Finally, equation (1) can be rewritten in two terms as:

$$H = F \lambda \sqrt{(1 - \lambda)} \xi \quad (2)$$

where the factor F depends on the parameters θ_c , L , κ , μ and l_c . The remaining part, $\lambda \sqrt{(1 - \lambda)} \xi$, is plotted as a function of λ_2 by Zhang et al. [29] and reproduces the V-shaped curve in the vicinity of $\lambda_2 \sim 1$.

For the present NiTi(Hf/Zr) alloys, it can be argued that since the λ_2 eigenvalues (Table 1) are very far from 1, they do not fulfill the conditions for the validity of Zhang's theory [29] and therefore deviate from the universal V-shaped B2-B19 curve. Furthermore, the thermal hysteresis values measured by DSC are much lower than those predicted by this theory. This could be an indication that for the cases when λ_2 is far from 1, the thermal hysteresis is not controlled only by the λ_2 value but it is also affected by the volume change criterion (present NiTi(Hf/Zr) samples have a volume change nearly zero except the ones with Type B microstructures). However, the data for the $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ alloys [35,36] transforming to B19' martensite also deviate from the V-shaped curve (in spite of having λ_2 values not so far from 1) and fit the new B2-B19' relationship based on the NiTi(Hf/Zr) alloys, with **shallower slope** than the $\lambda_2 < 1$ leg of the V-shaped B2-B19 curve (Fig. 6). This still points out the validity of λ_2 criterion for thermal hysteresis even in the case when λ_2 is rather far from 1, as long as there is also a small transformation volume change. Therefore, the difference in slope between the $\lambda_2 < 1$ leg of the V-shaped curve and the new B2-B19' relationship represented with the dashed line in Fig. 6 can be attributed to the difference in crystallography (B2-B19 versus B2-B19' transformation).

Equation (2) can also be used to justify the difference in slope of the ΔT vs λ_2 relationship for different alloys systems with different crystallography. Here, the slope of the ΔT vs λ_2 relationship depends on two terms: the factor F and the term $\lambda \sqrt{(1 - \lambda)} \xi$. The NiTi-based alloys transforming to monoclinic B19' are similar in nature to those transforming to B19. In some cases like NiTiCu and NiTiHf alloys, the same alloy system can form both martensite crystallographic structures (B19 or B19') depending on composition. Then, as mentioned in the study of Zhang et al. [29], it can be expected that the factor F does not vary remarkably among these alloys. In other words, the variations in F among the different alloys cannot justify the very different slopes of the ΔT vs λ_2 relationships. However, the second term $\lambda \sqrt{(1 - \lambda)} \xi$ is completely crystallographic in origin and hence could be responsible for the different slopes of the B2-B19 and B2-B19' transformations. Although equation (2) is derived for an

orthorhombic martensite and cannot be directly applied to a cubic to monoclinic transformation, the present experimental results on NiTi(Hf/Zr) alloys along with the data on $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ alloys [35,36] point to the existence of a linear ΔT vs λ_2 relationship for the alloys with monoclinic martensite too, but with a significantly different slope than the alloys with orthorhombic martensite.

Considering the theory reported by Zhang et al. [29], it is at first surprising that the present NiTi(Hf/Zr) alloys have relatively low thermal hysteresis although they have λ_2 values far from 1, i.e., they have a very low compatibility between austenite and martensite lattices. However, if the new line in Fig. 6 actually represents a new universal relationship between ΔT vs λ_2 for B2-B19' transforming alloys, then the low hysteresis for the NiTi(Hf/Zr) alloys is simply a consequence of the crystallography, where hysteresis is much less sensitive to deviations in λ_2 . Indeed, the low hysteresis of present alloys with their λ_2 values deviating far from 1, is in accordance with the observations of Bucsek et al. [33]. They reported that besides designing alloys with λ_2 values approaching 1, the thermal hysteresis may also be improved through aging in alloys where a compatibility condition, rationalized as the second cofactor condition (CC2), approaches zero. These cofactor conditions refer to the compatibility between the austenite and martensite phases and correspond to the degeneracies of the crystallographic theory of martensite. According to their study, a low CC2 value along with precipitation may decrease thermal hysteresis independent of λ_2 . It is beyond the scope of the present paper to study the cofactor conditions but it is likely that the present precipitation heat treated NiTi(Hf/Zr) alloys also present low CC2 values which may limit their thermal hysteresis while they still have λ_2 values far from 1.

5. Summary and Conclusions

The present study discusses the relationship between the λ_2 parameter (a measure of crystallographic compatibility) and the transformation thermal hysteresis of Ni-rich NiTiHf and NiTiZr alloys showing B2 to B19' martensitic transformation as a function of microstructure. The experimental observations and the ΔT vs λ_2 relationship of the current work were compared to previous studies on other alloy systems showing B2 to B19' or B2 to B19 martensitic transformations and the differences were discussed in detail. The main conclusions can be summarized as follows:

- (1) Very fine and densely distributed precipitates (< 20 nm in $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ and < 45 nm in $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$) were identified in samples aged at 500 °C for 48 h and at 550 °C for 3 h. These fine precipitates did not limit martensite propagation significantly and were easily absorbed by growing martensite variants (Type A microstructures). Samples subjected to furnace cooling from 700 °C to 100 °C in 48 h exhibited large precipitates, several hundred nanometers in size,

which constrained martensite growth between the precipitates and thus refined the martensite microstructure (Type B microstructures).

- (2) A single experimental linear relationship of ΔT vs λ_2 (indicated by the dashed line in Fig. 6) was observed for the present Ni-rich NiTi(Hf/Zr) alloys in the solution heat treated state or with Type A microstructures. These alloys exhibit a B2 to B19' phase transformation and the slope of the ΔT vs λ_2 relationship was **shallower** as compared to the $\lambda_2 < 1$ leg of the V-shaped universal curve for the NiTi(Pd/Pt/Au/Hf/Cu) alloys undergoing B2 to B19 transformation. On the other hand, samples with Type B microstructures deviated from the newly defined ΔT vs λ_2 relationship as a consequence of the dramatic change in martensite microstructure and large volume change during MT.
- (3) In the absence of microstructural features like large precipitates, the ΔT vs λ_2 relationship of NiTiCu ternary [35,36] and NiTi binary [37-39] alloys, also showing B2 to B19' martensitic transformation, deviated from the universal V-shaped curve for B2-B19 transforming alloys but were found to follow the experimentally obtained relationship of the present NiTi(Hf/Zr) alloys. However, Ni-poor (< 50 at.% Ni) NiTiHf ribbons [40] undergoing B2 to B19' transformation present an exception and the ΔT vs λ_2 data deviated both from the experimental B2-B19' curve or the B2-B19 V-shaped universal curve. The large deviation from the B2-B19' line is probably due to the melt spun microstructure and particularly to the tendency for Ni-lean NiTiHf alloys to undergo significant plasticity concurrent with the martensitic transformation.
- (4) The present experimental results on NiTi(Hf/Zr) alloys along with the data on NiTiCu and NiTi alloys, all showing B2 to B19' martensitic transformation, suggest the existence of a universal ΔT vs λ_2 relationship for monoclinic martensite, with a significantly **shallower slope** as compared to the $\lambda_2 < 1$ leg of the V-shaped curve of alloys undergoing the transformation to orthorhombic martensite.
- (5) A poor crystallographic compatibility between the austenite and martensite lattices was found in the present alloys since the second eigenvalue of the transformation matrix, λ_2 , showed a remarkable deviation from 1. However, the present alloys exhibited much lower ΔT values as compared to what is predicted in the literature [29]. As demonstrated in this work, this may be an inherent property of B2 to B19' transformation **expressed by the slope** of the ΔT vs λ_2 relationship for the alloys that transform to monoclinic martensite, making thermal hysteresis much less sensitive to deviations in λ_2 .

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FIGURES

Figure 1: DSC curves of the solution heat treated and precipitation heat treated $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ HTSMAs. Thermal hysteresis, ΔT , was calculated as the difference between the A_f and M_s temperatures ($A_f - M_s$).

Figure 2: The bright field TEM images for the precipitation heat treated $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ samples; (a) aged at 500 °C for 48 h, (b) aged at 550 °C for 3 h and (c) held at 700 °C for 5 minutes and furnace cooled to 100 °C in 48 h. Conditions (a) and (b) represent Type A microstructures, which have very fine precipitates (< 20 nm in size) easily absorbed by the large martensite variants that grow to several hundred nanometers in size. Condition (c) is representative of Type B microstructures, which consist of precipitates several hundred nanometers in size, which refine the martensite microstructure and limit the variant growth. The inset image in (c) more clearly reveals the large precipitates (some were labeled with letter “P”).

Figure 3: The bright field TEM images for the precipitation heat treated $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples; (a) aged at 500 °C for 48 h, (b) aged at 550 °C for 3 h and (c) held at 700 °C for 5 minutes and furnace cooled to 100 °C in 48 h. Similar to the observations in $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$, Type A microstructures were visible after aging at 500 °C for 48 h and at 550 °C for 3 h. Furnace cooling refines the martensite microstructure in $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ due to the formation of large precipitates (some were labeled with letter “P” in image (c) for clarity).

(a)

(b)

Figure 4: The room temperature XRD patterns and the corresponding Rietveld fits of solution heat treated and precipitation heat treated (a) $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ and (b) $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ samples. Several peaks belonging to the B19' martensite phase were indexed in all samples at room temperature.

Figure 5: (a) XRD patterns of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ sample aged at 500 °C for 48h at room temperature (RT) and at 200 °C ($A_f + 20$ °C). (b) The evolution of the (110) B2 austenite peak during XRD scans at various temperatures of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ sample aged at 500 °C for 48h. All samples undergo martensitic transformation while they are heated inside the XRD instrument and exhibit very similar behavior, therefore their XRD patterns are not shown here.

Figure 6: Thermal hysteresis of NiTi-based ternary SMAs as a function of λ_2 values. Data for the NiTi(Cu/Pd/Pt/Au) ternary alloys [29,31,32] showing B2 to B19 transformation and for the NiTi binary [37-39], NiTi(Hf/Cu) ternary alloys [35,36,40] undergoing B2 to B19' transformation were obtained from the literature and plotted with the data derived from the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloys in the present study. The corresponding microstructural types for the two-phase samples are also labeled. A clear difference in the λ_2 dependence of the transformation thermal hysteresis can be observed between the two types of martensitic transformation.

TABLES

Table 1

The lattice parameters of martensite (a, b, c, β) and austenite (a_0) phases of the present $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ samples as a function of heat treatment, and the calculated λ_2 and measured ΔT values together with the data on some other alloys retrieved from literature.

Alloy	Lattice Parameters					λ_1	λ_2	λ_3	ΔT (°C)	$\Delta V/V$ (%)
	a (Å)	b (Å)	c (Å)	β (°)	a_0 (Å)					
B2 – B19' transformation										
Ni _{50.3} Ti _{29.7} Zr ₂₀ (Present Study)										
NTZ/SHT	3.076	4.079	4.946	103.689	3.112	0.9059	0.9268	1.1913	46	0.03
NTZ/500°C/48h	3.070	4.095	4.881	103.292	3.110	0.9057	0.9311	1.1772	40	-0.73
NTZ/550°C/3h	3.084	4.072	4.920	104.032	3.102	0.9060	0.9280	1.1940	41	0.401
NTZ/FC/48h	3.061	4.086	4.879	102.910	3.109	0.9070	0.9290	1.1740	65	-1.042
Ni _{50.3} Ti _{29.7} Hf ₂₀ (Present Study)										
NTH/SHT	3.052	4.089	4.887	103.072	3.100	0.9070	0.9327	1.1787	34	-0.29
NTH/500°C/48h	3.051	4.104	4.858	103.123	3.095	0.9063	0.9376	1.1757	27	-0.09
NTH/550°C/3h	3.047	4.099	4.854	103.244	3.095	0.9042	0.9365	1.1754	28	-0.48
NTH/FC/48h	3.051	4.088	4.871	103.016	3.107	0.9044	0.9304	1.1727	63	-1.32
Ni _{49.8} Ti _{50.2-x} Hf _x [40]										
Hf _{9.5}	2.987	4.095	4.750	99.99	3.052	0.9265	0.9487	1.1444	69	0.59
Hf ₁₅	3.025	4.096	4.826	102.04	3.075	0.9145	0.9419	1.1673	74	0.55
Hf ₂₀	3.063	4.083	4.889	103.06	3.098	0.9102	0.9321	1.1809	102	0.19
NiTi [37,38]	2.889	4.120	4.622	96.8	3.015	0.9321	0.9663	1.1065	29	-0.34
	2.883	4.117	4.623	96.800	3.015	0.9304	0.9656	1.1064		-0.60
	2.898	4.108	4.646	97.780	3.015	0.9285	0.9634	1.1176		-0.02
NiTi [39]	2.880	4.120	4.620	96.800	3.010	0.9311	0.9679	1.1075	31	-0.20
Ni _{50-x} Ti ₅₀ Cu _x [35,36]										
Cu ₅	2.903	4.147	4.613	96.220	3.027	0.9358	0.9686	1.0977	21	-0.50
Cu _{7.5}	2.907	4.170	4.596	95.487	3.030	0.9404	0.9733	1.0895	8	-0.27
Cu ₁₀	2.872	4.192	4.577	95.204	3.031	0.9312	0.9781	1.0821	8	-1.44

**B2 – B19
transformation**

Ni_{50-x}Ti₅₀Cu_x [35,36]

Cu_{7.5}	2.911	4.228	4.517	90	3.030	0.961	0.989	1.056	12	0.36
Cu₁₀	2.901	4.249	4.515	90	3.031	0.958	0.993	1.055	11	0.36
Cu_{12.5}	2.896	4.252	4.514	90	3.034	0.956	0.992	1.053	7	-0.14
Cu₁₅	2.899	4.260	4.516	90	3.043	0.954	0.992	1.052	7	-0.44
Cu₂₀	2.900	4.264	4.512	90	3.046	0.954	0.993	1.050	4	-0.53

Ni_{50-x}Ti₅₀Pd_x [31]

Pd₉	2.846	4.304	4.583	90	3.047	0.9341	0.9988	1.0635	18	-0.78
Pd₁₁	3.830	4.314	4.604	90	3.050	0.9280	1.0001	1.0674	13	-0.93
Pd₁₈	3.820	4.343	4.628	90	3.056	0.9227	1.0050	1.0710	22	-0.68
Pd₂₀	3.820	4.340	4.613	90	3.051	0.9244	1.0060	1.0691	26	-0.58
Pd₂₅	3.807	4.361	4.667	90	3.063	0.9167	1.0070	1.0775	32	-0.53

Martensitic transformation thermal hysteresis vs. the middle eigenvalue of the transformation stretch tensor exhibits a different relationship based on the martensitic transformation type in NiTi-based shape memory alloys. B2 to B19' (monoclinic) martensitic transformation hysteresis seems to have a less steep dependence as compared to B2 to B19 (orthorhombic) martensitic transformation hysteresis