Stability of a Ni-rich Ni-Ti-Zr high temperature shape memory alloy upon low temperature aging and thermal cycling

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Abstract

The thermal stability of $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ with aging in austenite at 250 °C has been studied for three distinctive microstructures obtained after selected thermal treatments: precipitate free and containing two different sizes and densities of H-phase nanoprecipitates. The martensitic transformation is suppressed after 1-3 weeks aging, depending on the initial microstructure, due to a B2 phase instability in the form of short range atomic reordering within the Ti+Zr sublattice, considered to be precursor to the H-phase precipitation. Thermal cycling leads to notable changes in the transformation temperatures, which strongly depends on the starting microstructure.

Keywords: Martensitic phase transformations, Shape memory alloys, Precipitation, Aging, Phase instability.

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Ni-Ti shape memory alloys are used in a large number of applications owing to their good functional properties related to the thermoelastic martensitic transformation (MT). However, these properties are restricted to relatively low temperatures, as binary Ni-Ti alloys do not have a MT above 100 °C [1]. Many efforts have been focused on macro-alloying additions to increase the transformation temperatures (TTs) while retaining, as much as possible, the beneficial properties of the binary alloy. As a result, Ni-Ti-X alloys with X = Pd, Pt or Au have been developed as high temperature shape memory alloys (HTSMAs) [2]. More recently, the attention has moved to Ni-rich Ni-Ti-Hf and Ni-Ti-Zr as economical alternatives to the alloys containing precious metals. The functional properties of Ni-rich Ni-Ti-Hf/Zr can be modified by selected thermal treatments, particularly those inducing the precipitation of a new Ni-rich phase [3-15]. This precipitate phase, denoted as “H-phase” [16], is a superstructure of the B2 phase obtained from a recombination of the Hf/Zr and Ti atoms in their sublattice followed by a shuffling of all the atoms [16,17].

The Ni-Ti-Hf system so far has received the most attention, showing good thermal stability and excellent shape memory behavior under high loads, enabled by H-phase nanoprecipitation [3,6-15]. To the best of the authors’ knowledge, only a few works dealing with Ni-rich Ni-Ti-Zr can be found in the literature. Sandu *et al.* studied the effects of aging on superelasticity tested under compression in alloys containing 6at%Zr and reported the precipitation of a new phase which was not fully identified at the time [4,5]. Santamarta *et al.* characterized the precipitated phase in several Ni-rich Ni-Ti-Zr/Hf alloys, identifying the same H-phase in both alloy families [17]. Finally, Evirgen *et al.* obtained good shape memory and superelasticity in tension in $\text{Ni}_{50.3}\text{Ti}_{34.7}\text{Zr}_{15}$ and $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloys as a result of nanoscale H-phase precipitation [13,18,19]. However, the optimal microstructures and functionalities of a potential HTSMA device, especially a HTSMA actuator, could be modified by long exposure of the material around the working temperatures, due to diffusive effects. Therefore, the aim of this paper is to study the stability of the MT under prolonged aging in austenite, close to the TTs, in the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloy with different initial distributions of H-phase precipitates. Furthermore, the stability of the transformation under thermal cycling is also investigated.

High-purity elemental Ni (99.98%), Ti (99.95%) and Zr (99.9%) constituents were vacuum induction melted under a protective partial pressure of argon in a graphite crucible and cast into a copper mold. The ingot of nominal composition $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ was subsequently homogenized at 1050 °C for 72 h, sealed in a mild steel can and hot extruded at 900 °C with an area reduction of 7:1. Samples were spark-cut from the extruded rod, encapsulated in quartz ampoules under argon and solution heat treated (SHT) at 900 °C for 1 hour followed by water quenching (WQ) by breaking the ampoule. Some specimens were subjected to additional thermal treatments to generate two characteristic distributions of H-phase precipitates [13,17,18]: *i*) 3h aging at 550 °C followed by WQ (denoted as 550C) and *ii*) a 5 min hold at 700 °C followed by controlled furnace cooling to 100 °C in 48 h and finally WQ (denoted as FC). The 550C treatment produces a high density of homogeneous spindle like nanometric precipitates providing the best alloy functionality, whereas the FC treatment results in elongated particles of hundreds of nanometers in length [13,17,18]. Finally, samples with both distributions of H-phase precipitates, together with precipitate-free SHT specimens for reference, were aged for extended times in the austenite state at 250 °C in air to investigate their thermal stability. DSC measurements were performed in TA Instruments DSC 2920 and METTLER TOLEDO DSC823e units at 10 K/min cooling/heating rate. Conventional TEM (HITACHI H600 at 100kV) was used for microstructural characterization. The TEM samples were double jet electropolished in a solution of 30% HNO_3 in methanol at -20 °C.

Figure 1 shows the DSC thermograms of the different samples after aging at 250 °C compared with the initial state. Long term aging causes a complete suppression of the transformation peaks in the range of temperatures available by DSC (down to -150 °C), irrespective of the initial microstructure. After 1 week of aging, the transformation is already suppressed for SHT and 550C samples, whereas the FC alloy is more resistant to aging and still shows the MT peaks, but with a significant decrease in the transformation temperatures and transformation enthalpy change. The transformation is completely suppressed in the FC material after 3 weeks at 250 °C. Moreover, the behavior of the SHT material was found to be strongly dependent on the effective quenching rate, as different samples treated separately showed different transformation behavior (not shown here), depending on the rapidity of the ampoule breaking process. In some cases, like that shown in Fig. 1, the initial thermogram after SHT indicates

some inhomogeneity in the material, evidenced by a double transformation peak. Also, delays in breaking the ampoules and slow quenching rates were observed to lead to a complete suppression of the MT even without any additional low temperature aging treatment.

TEM observations performed after prolonged aging at 250 °C (7 weeks) only revealed subtle microstructural changes. The aged SHT material showed a very fine mottled contrast in the bright field images accompanied by diffuse streaks in the diffraction patterns, as seen in Figs. 2(a) to 2(c). The fundamental spots in these patterns agree with the B2 phase, while the diffuse streaks have a linear shape connecting the fundamental spots in the $\langle 110 \rangle$ directions and a more rounded shape along the $\langle 100 \rangle$ directions. For the 550C and FC samples, aging at 250 °C did not cause significant changes in the preexisting H-phase particles. The main effects are diffuse streaks in the diffraction patterns similar to the SHT material, as shown in Figs. 2d to 2f. In this case, the B2 spots are accompanied by $1/2\langle 111 \rangle$, $n/3\langle 110 \rangle$ and $n/4\langle 210 \rangle$ satellites characteristic of the H-phase [17]. For the current alloy composition, formation of well-defined H-phase precipitates with such characteristic satellites was observed only after aging at 450 °C or higher temperatures [17].

The H-phase crystal structure arises from a redistribution of the Zr and Ti atoms within their sublattice of the B2 structure, which brings about the 3-fold and 4-fold periodicities along the $\langle 110 \rangle$ and $\langle 210 \rangle$ directions, corresponding to the characteristic satellites in the diffraction patterns [17]. Thus, the diffuse streaks observed after prolonged aging at 250 °C in the three microstructures seem to be related to the preliminary stages of such Zr and Ti atomic redistribution in the B2 matrix towards the H-phase. The present results indicate that the limited diffusion at 250 °C only permits short range atomic reordering and it is not enough for the complete development of the 3-fold and 4-fold periodicities characteristic of the H phase, leading to diffuse streaks in the diffraction patterns instead of well-defined satellites. In fact, diffuse streaks similar to those shown in Fig. 2 were reported by Sandu *et al.* in $\text{Ni}_{52}\text{Ti}_{42}\text{Zr}_6$ and were related to short range ordering of the Zr atoms as a previous step to the formation of precipitates by aging at 500 °C [4,5]. Very recently, Couglin *et al.* reported similar diffuse streaks in a $\text{Ni}_{51}\text{Ti}_{29}\text{Hf}_{20}$ alloy after hot extrusion at 900 °C and observed nanometric areas of enhanced intensity in high resolution High Angle Annular Dark Field (HAADF) images

showing $n/4\langle 111 \rangle$ satellites in the Fast Fourier Transform, which were referred to as a new H' phase and considered as a precursor of the H phase [20]. The present diffraction patterns of $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ after prolonged 250 °C aging do not show any trace of $n/4\langle 111 \rangle$ satellites, indicating a state still previous to the H' precursor phase suggested in NiTiHf alloys, but not reported so far in Zr containing alloys.

Suppression of the MT after low temperature aging is well documented for Ni-rich Ni-Ti binary alloys (see, for instance [21-24]). Kompatscher *et al.* detected ~ 1 nm sized Ni_4Ti_3 precipitates in SHT alloys with high Ni excess (51 to 54 at% Ni) by means of small-angle neutron scattering, which formed during quenching. The precipitates grew to a size of ~ 1.5 nm after additional aging at 280 °C for 1 h [21]. Ji *et al.* also reported nanometric Ni_4Ti_3 precipitates in the $\text{Ni}_{51.3}\text{Ti}_{48.7}$ alloy aged at 200 °C for 3 h, which were responsible for strain-glass behavior of the alloy [23]. In these works, the MT suppression is attributed to the early stages of Ni_4Ti_3 precipitation [21-24].

Previous studies on Ni-rich Ni-Ti-Hf and Ni-Ti-Zr alloys have ruled out the precipitation of Ni_4Ti_3 phase and confirmed the formation of the H-phase in these ternary systems [4,5,16,17]. Thus, in analogy to the binary alloys and taking into account the effects observed by TEM (Fig. 2), the MT suppression observed in the present $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloy after aging at 250 °C (and, in some cases, just after a relatively slow quenching process) should be attributed to diffusive precursor effects of the H-phase precipitation. As the H phase is richer in Zr and lean in Ti compared to the B2 matrix [17], the process at low temperatures probably starts with a short range segregation of Zr and Ti atoms leading to the formation of very small domains (roughly nanometric in size) with “modified” and “normal” compositions, which explains the finely mottled contrast observed in conventional bright field TEM images. In this state, the ultrafine domains with “normal” composition would be smaller than the critical size needed for nucleation and growth of martensite, preventing the transformation, whereas the domains with “modified” composition are still too small for the complete development of the H phase superstructure (note that one lattice parameter of the H phase unit cell is as large as ~2.6 nm [17]). Further detailed characterization of the new state issued from low temperature aging is in progress to understand the mechanism underlying the complete MT suppression.

The stability of the MT of $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ under thermal cycling has also been studied for the three initial microstructures produced by SHT, 550C and FC treatments to evaluate the effect of short term exposures to relatively high temperatures in austenite. Fig. 3a presents the DSC curves of the first 20 cycles for two SHT samples cycled to two different upper cycle temperatures: 100 °C (upper curves in black) and 150 °C (bottom curves in red). It is worth noting the different transformation temperatures of these two samples in the first cycle and the fact that they show a single transformation peak, in contrast to the sample shown in Fig. 1. These results illustrate the variability in the behavior of the SHT condition for the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloy, as mentioned previously. Fig. 3b shows the peak temperatures of the forward and reverse transformations (M_p and A_p , respectively) for an SHT sample plotted as a function of the cycle number. There is a progressive decrease of M_p by ~ 30 °C after 20 cycles when the upper cycle temperature is 100 °C (slightly higher than the austenite finish temperature), which increases to ~ 50 °C when the upper temperature is raised to 150 °C.

A decrease of TTs upon thermal cycling is also well documented in SHT binary Ni-Ti alloys (e.g. [25-29]) and it is generally attributed to the formation of dislocations with cycling. Fig. 4 shows the typical dislocation arrays generated after 20 cycles in the present $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ SHT material, which are relatively moderate in density and may partially contribute to the observed decrease of TTs with cycling. However, the observed upper temperature effect on the cycling evolution reflects the existence of diffusive effects in the form of short range atomic reordering during the time spent in the austenite phase during each thermal cycle, which also contributes to the decrease of TTs with cycling. This is confirmed by additional experiments consisting of holding another SHT sample in the DSC at 100 °C for 40 min before the 2nd thermal cycle and 80 min before the 5th cycle. The results are marked as blue diamonds in Fig. 3b, where it becomes clear that such dwell times at 100 °C cause a larger drop in M_p compared to the normal cycling sequence. A similar behavior has been recently observed in the binary $\text{Ni}_{50.6}\text{Ti}_{49.4}$ alloy with subambient TTs, for which the effect of thermal cycling is notably enhanced when the sample is aged at room temperature between each consecutive cycle [30]. Nevertheless, the authors propose a different microscopic origin in terms of interaction between dislocations and point defects generated from high temperature (1000 °C) quenching [30].

The shift of DSC peak temperatures is less pronounced for the reverse MT than for the forward transition, which results in an increase of MT hysteresis of the SHT samples after 20 cycles by 27 °C and 20 °C for upper cycle temperatures of 100 °C and 150 °C, respectively. The increase in the MT hysteresis is mostly attributed to the dislocation activity and is actually less severe when cycled to a higher temperature. Therefore, increasing the upper cycle temperature and thus reordering effects are much more detrimental to the M_p temperature than the overall hysteresis in the material.

The 550C and FC samples (containing well developed H-phase precipitates) were thermally cycled up to 250 °C due to their higher TTs. As seen in Fig. 3c, the 550C sample experiences a continuous drop in peak temperatures by ~ 30 K after 20 cycles. In this case, the dislocation generation during MT cycling should be notably reduced due to the strengthening effect of the nanoprecipitates introduced with the 550C treatment, which is reflected in a lower MT hysteresis and better superelasticity in relation to the SHT condition [18]. Consequently, for the 550C material, the evolution of MT with cycling is mostly dominated by the short range atomic reordering effect in the B2 matrix. For the FC state, the M_p temperature decreases slightly in the first 8 cycles and then remains constant, while the A_p temperature shows a small continuous increase (Fig. 3c), which causes an increase of ~ 12 K in the MT hysteresis after 20 cycles. After slow furnace cooling, the B2 matrix composition is closer to equilibrium at low temperatures due to the intense H-phase precipitation process and, thus, the short range reordering effect should be strongly diminished. This is consistent with the longer aging times needed to suppress the MT in the FC samples in the prolonged aging experiments at 250 °C (Fig. 1). Similar to the SHT case, the slight increase in hysteresis during thermal cycling in the FC state should be attributed to moderate dislocation generation. In fact, our previous work indicates a notably lower strengthening effect of the large H-phase precipitates in the FC material compared to the 550C case [18].

In conclusion, the present results show that the selected distributions of H-phase precipitates resulting from 550C and FC thermal treatments are not noticeably modified after prolonged aging at 250 °C. However, the B2 phase of $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ is unstable at low temperatures and undergoes short range atomic reordering processes producing diffuse streaks in the diffraction patterns. These processes are interpreted in terms of a short range redistribution of the Ti and Zr atoms as a precursor state to the H-phase

precipitation. This B2 phase instability results in dramatic effects on the functional properties of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloy, with a complete suppression of the martensitic transformation after prolonged aging at 250 °C. Because of a moderate generation of dislocations, the B2 phase instability is also predominantly responsible for the observed shift in MT temperatures with thermal cycling.

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FIGURE CAPTIONS

Figure 1: DSC thermograms of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloy after different aging times at 250 °C for (a) SHT, (b) 550C and (c) FC initial thermal treatments.

Figure 2: Electron diffraction patterns ([001], $[1\bar{1}0]$ and $[1\bar{1}1]$ zone axes) of the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ alloy after aging at 250 °C for 7 weeks. (a), (b), (c): SHT condition ; (d), (e), (f): 550C treatment.

Figure 3: (a) Evolution of the DSC transformation peak with thermal cycling for two upper cycle temperatures (UCT): 100 °C (upper curves in black) and 150 °C (lower curves in red). (b) M_p and A_p temperatures for SHT samples cycled up to 100 °C (circles) and 150 °C (triangles) upper temperatures. (c) M_p and A_p temperatures for 550C (circles) and FC (triangles) samples cycled up to 250 °C.

Figure 4: TEM micrograph of dislocation arrays formed after 20 thermal cycles in $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Zr}_{20}$ SHT material.

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