The effect of precipitates on the superelastic response of [100] oriented FeMnAlNi single crystals under compression

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ABSTRACT

FeMnAlNi shape memory alloys were recently discovered to have a small temperature dependence of the superelastic critical stress in a large superelastic temperature window from -196°C to 240°C. We investigate the effect of B2 nanoprecipitates on the superelastic characteristics of [100] oriented $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystals under compression, and found that the size, volume fraction and composition of precipitates strongly influence the transformation temperature, superelastic strain, critical stress for stress-induced martensitic transformation and stress hysteresis of the single crystals. The single crystal aged at 200°C for 3 hours show 7.2% superelastic strain with the precipitate size of about 6-10 nm. Longer aging times or higher aging temperature reduce superelastic recovery due to the coarsening of the precipitates.

Keywords: Superelasticity; Fe-based shape memory alloys; B2 precipitates; atom probe tomography;

1. Introduction

Fe-based shape memory alloys (SMAs) have attracted attention due to low material cost and ease of processing as compared to NiTi SMAs. Therefore, there have been many studies on Fe-based SMAs since the 1970s. Unfortunately, most Fe-based SMAs exhibit poor superelastic recovery or small superelastic strains, due to non-thermoelastic martensitic transformation [1-7], which also results in large temperature and stress hysteresis. Recently, a pair of newly discovered Fe-based SMAs: $\text{Fe}_{41.95}\text{Ni}_{28}\text{Co}_{17}\text{Al}_{10.5}\text{X}_{2.5}\text{B}_{0.05}$ (X: Ta, Nb and Ti) polycrystalline alloy [8-10], $\text{Fe}_{40.5}\text{Ni}_{28}\text{Co}_{17}\text{Al}_{11.5}\text{X}_{2.5}$ (X: Ta, Nb and Ti) single crystals [11-23], $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ polycrystalline alloy [24] and single crystals [25], have shown large superelastic strain at room temperature. One of the most interesting findings for the $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ SMA was the small tensile stress-temperature slope about 0.53 MPa/°C in polycrystalline samples and 0.54 MPa/°C in single crystals, with the [100] orientation, over a large temperature window [24-25].

In our previous study, we characterized the superelastic response of the $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystals along the [100] orientation under tension and compression since this orientation possesses the highest theoretical transformation strain in both tension (26.5%) and compression (10.5%) [25]. Although both tension and compression samples showed small values of stress-temperature slope (0.54 MPa°C⁻¹ in tension and 0.41 MPa°C⁻¹ in compression) [25], the recoverable superelastic strain in both tension and compression were considerably smaller than theoretical predictions, with the compression sample showing significantly better superelastic recovery than the

tension sample. The asymmetry is caused by the differences in the variant selection during the stress-induced martensite formation and associated need for the plastic deformation mechanisms in order to accommodate the transformation shear. Two martensite variants are readily activated when the sample is compressed along the [100] orientations and the deformation can be easily accommodated. On the other hand, only one martensite variant can accommodate the tensile deformation along [100] orientation, and as a result, high density of parallel and hairpin shaped dislocations are generated at the austenite-martensite interface and in the austenite matrix, causing widespread retained martensite and poor superelastic recovery [25]. In any case, a maximum superelastic strain of only 4.2% was obtained in the aged compression sample, which was still much smaller than the theoretical values.

In the FeNiCoAlTa single crystal studies, Ma *et al.* [11,12] investigated the effect of aging heat treatment on superelasticity in both tension and compression. The superelasticity experiments revealed that recoverable strain was strongly dependent on the precipitate size, which increased with increasing the aging time from 7 hours to 90 hours at 600°C. However, the volume fraction of the precipitates in all aging conditions at 600°C was very similar. Furthermore, change in precipitate size also altered other shape memory characteristics such as transformation hysteresis, stress-temperature slope, and tension-compression asymmetry. Studies on FeCoNiTi SMAs by Sehitoglu *et al.* [26-28] show that increasing aging times reduce the transformation temperature, enlarge temperature hysteresis, and increase the recoverable strain in both superelasticity and shape memory experiments. Similar effects of precipitation on shape memory response were also reported in Ni-Ti SMAs [29-39].

Despite the important influence of the precipitates on the superelastic characteristics, there have been no previous studies on this topic on FeMnAlNi shape memory alloys. Therefore, this work aims to present the effect of aging on the size, composition and volume fraction of the precipitates and in turn, the effect of precipitate size and volume fraction on the transformation temperature, superelastic characteristics such as stress hysteresis, superelastic strain, critical stress for stress-induced martensitic transformation, and stress-temperature slope in the [100] oriented $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystals.

2. Experimental Procedures

Ingots with the nominal composition of $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ were melted under argon environment. The single crystal samples were fabricated using the Bridgman method under a helium atmosphere. The compression specimens with the dimensions of 4 mm x 4 mm x 8 mm were cut with the compression axis nearly parallel to the [100] crystal orientation of the sample using wire electro-discharge machining. The single crystals were sealed in quartz tubes under high purity argon and solution treated at 1200°C for 1 hour followed by quenching in ice water. The homogenized samples were then aged at 200 °C and 300 °C for different durations in argon atmosphere to obtain B2 precipitates and quenched in water. For the sake of brevity, we will refer to the $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystals aged at 200°C and 300°C for x hours as “200°C-xh” and “300°C-xh”.

Vickers microhardness values were measured on the {100} faces of the single crystals at room temperature. In order to investigate the effect of aging heat treatment

on the transformation temperature, a Quantum Design Superconducting Quantum Interference Device (SQUID) was used to determine the stress-free phase transformation temperatures under 0.5 kilogauss field level.

Microstructure characteristics such as precipitate size were investigated using an FEI Tecnai G² F20 transmission electron microscope. Single crystals with different aging treatments were first mechanically ground to approximately 30 μm in thickness. The thin samples were then ion-milled until a hole appeared in the center of the specimens. All the transmission electron microscopy (TEM) images were taken at room temperature.

Due to the small size of the precipitates, it was difficult to determine their composition and volume fraction using TEM. As a result of this, atom probe tomography (APT) was used to determine the volume fraction and composition, while providing a 3D reconstruction of the precipitates. The APT was performed using a Cameca Local Electrode Atom Probe (LEAP) 3000XSi. The atom probe specimens were lifted-out from the bulk sample, and placed onto pre-fabricated Si posts using a FEI Quanta 200 3D Dual Beam scanning electron-focused ion beam microscope equipped with a probe micromanipulation lift-out system. Once attached to the Si post, the specimens were annular milled to yield the appropriate geometric needle shape with a radius of ~ 100 nm required for field evaporation. More in-depth details of the FIB-based atom probe preparation can be found elsewhere [40, 41]. The specimens were held at a base temperature of 30K (-243°C), scanned in laser mode with a pulse rate of 200 kHz, pulse energy 0.2 nJ, and a target evaporation set at 0.5. The atom probe data was reconstructed using the IVAS 3.6.6 software package.

The superelastic response of the single crystal samples along the [100] orientation was characterized by two sets of experiments under compression: constant-strain tests at different temperatures and cyclic strain tests at room temperature. The first test is used to determine the stress-temperature phase diagram. The second test is used to find the maximum superelastic strains at room temperature. Both sets of mechanical experiments were conducted at a nominal strain rate of $5 \times 10^{-4} \text{s}^{-1}$. The compressive strain was measured using an extensometer attached to the grips of the test frame at roughly $\sim 2 \text{mm}$ above and below the sample. Specimen temperature was measured using a thermocouple attached directly to the samples. Heating and cooling of the samples were achieved through the grips by heating bands and liquid nitrogen flowing through copper coils wrapped around the grips.

In order to determine the superelastic characteristics used for comparison in this study, the properties such as σ_c , $\Delta\sigma$, ϵ_{irrec} , ϵ_{SE} and ϵ_e are defined in Figure 1. σ_c is the critical stress for stress-induced martensitic transformation and determined using the 0.2% strain offset method. $\Delta\sigma$ is the stress hysteresis and calculated as the stress difference between the loading and unloading curves. ϵ_{irrec} , ϵ_{SE} and ϵ_e represent the irrecoverable strain, superelastic strain and the elastic strain, respectively.

3. Results and Discussions

3.1 Effects of aging on the microhardness and transformation temperatures

Figure 2 summarizes the effect of aging temperatures and duration on the Vickers microhardness at room temperature for the FeMnAlNi single crystals oriented along the [100] direction. It is clear that the hardness values of the samples increase

with increasing aging times, although the increase in the samples aged at 300°C is much more pronounced than those aged at 200°C.

Figure 3 displays the thermo-magnetization result of the solution-treated single crystals. In this test, the sample was first heated up from room temperature to 130°C. After the test temperature reached 130°C, a magnetic field of 0.5 kG was applied and the sample was cool down to -260°C and again heated up to 130°C under the applied field. Magnetization decreased during cooling and increased during heating under this field. We used the tangent line method to determine the transformation temperatures as indicated in the figure. For the solution treated sample, the martensitic transformation temperatures were determined as: austenite finish temperature (A_f) = 45°C, austenite start temperature (A_s) = -84°C, martensite start temperature (M_s) = -82°C, and martensite finish temperature (M_f) = -210°C. The same test was conducted for the single crystals aged at 200°C for 15 minutes, and the results are also shown in Figure 3. The transformation temperatures of the aged single crystal were: A_f = 30°C, A_s = -97°C, M_s = -90°C and M_f = -212°C. The temperature hysteresis is defined as $A_f - M_s$, and was calculated to be 120°C.

3.2 Effect of aging on the size, volume fraction and composition of precipitates

3.2.1 TEM investigation of precipitates

Figure 4a shows the selected area diffraction (SAD) pattern of the single crystal solution treated at 1200°C for 1 hour. The diffraction pattern indicates that the austenite, precipitates and martensite are of the disordered bcc (A2) structure, ordered bcc (B2) structure and disordered fcc structure, respectively. The diffraction pattern also shows

the $[001]_{\text{BCC}} \parallel [001]_{\text{FCC}}$ Kurdjumov-Sachs (K-S) relationship. It is important to note that the signs of precipitates are observed in a solution-treated sample, indicating a rapid formation during the quenching process. However, it is difficult to see the precipitates in the bright field and dark field TEM images due to their small size, and their existence could only be detected from the diffraction patterns. Figure 4b shows the high resolution bright field TEM images at different aging times, and Figure 4c summarizes the relationship between the average precipitate size and aging times at 200°C. When the aging time is 1 hour, the precipitate size is around 3 to 6 nm and increases to 6 to 10 nm at 3 hours and 12 to 18 nm at 10 hours. Comparatively, the precipitate size for the 300°C-1h aged sample is about 28-40 nm. The results indicate that the size of the precipitates increase with increasing the aging times and temperature as expected. These values are comparable to the reported values of ~10 nm for FeMnAlNi polycrystals aged at 200°C for 15 minutes [42].

3.2.2 Atom probe tomography analysis of precipitates

Atom probe tomography was performed on the samples with three separate aging conditions: 200°C-1h, 200°C-3h, and 300°C-1h. The 200°C-3h case was selected because as shown below, it appears to be the “peak-aged” condition as it demonstrates the best combination of large superelastic strain and high rate of superelastic recovery. On the other hand, much higher hardness were measured in the 300°C-1h sample and the sample is quite brittle, and the hardness level is quite low in the 200°C-1h sample and it exhibits significant irrecoverable strain representing an underaged condition. Both of these latter cases show much different superelastic response (shown below),

thus our rationale in selecting these conditions were 1) peak aged condition (200°C-3h), 2) somewhat “overaged” condition showing brittleness (300°C-1h), and 3) underaged condition showing larger irrecoverable strain (200°C-1h).

Figure 5a and b show the Fe ions along with Ni iso-concentration surfaces used to delineate the precipitates from the matrix for the 200°C-1h and 200°C-3h samples. The precipitate volume fraction of the 200°C-1h sample was determined to be 29.8% using the procedure outlined in Ref. [43] with an approximate precipitate number density of $3.43 \pm 0.69 \times 10^{23} \text{ m}^{-3}$. The precipitates appear to be spherical in shape. Applying the same analysis technique to the 200°C-3h sample, its precipitate volume fraction was determined to be 34.3% with an approximate precipitate number density of $2.07 \pm 0.24 \times 10^{23} \text{ m}^{-3}$. For this condition, the precipitate shape appears to be more plate-like with one axis becoming elongated. The increase in volume fraction and decrease in number density from the 1 hour to 3 hours aged sample indicates that the growth of the precipitates is still ongoing and the nucleation has concluded. Figure 5c shows the Fe ions along with Ni iso-concentration surfaces used to delineate the precipitates from the matrix for the 300°C-1h samples. Analysis of this condition yielded a precipitate volume fraction of 30.6% with an approximate precipitate number density of $3.05 \pm 0.61 \times 10^{23} \text{ m}^{-3}$. Additionally, the precipitates are of an oblate spindle type shape opposed to the spherical precipitates seen in the 200°C-1h sample. Figure 5a, b, and c are constructions based on the composition profiles shown in Figure 6. The green areas represent regions of relatively high nickel content, while the red regions show areas of relative high iron concentration.

The corresponding proximity histogram for the 200°C-1h, 200°C-3h, and 300°C-1h specimens were generated from 36.20% Fe, 37.85%Fe and 39.00% Fe iso-concentration surfaces respectively, and an example of the results is shown in Figure 6 for the 200°C-1h sample. The proximity histograms for both conditions clearly show an enrichment of Ni and Al in the precipitate from their respective levels in the matrix, while Fe is strongly segregated to the matrix and Mn to a lesser degree. This observation of Ni-rich precipitates has been observed several other material systems: FeNiCoAlTaB and FeNiCoTi [12, 44]. The numeric values for the precipitate compositions are reported in Table 1.

From the results presented in Table 1, changes in the aging heat treatment times and temperature slightly alters the composition of the precipitates: the Ni and Al contents in the precipitate decrease with increasing aging times and temperature, while the Fe content increases. The change in the composition of the precipitates alters the composition of the matrix, which may affect the transformation temperatures.

3.3 Effect of aging on superelastic strain and stress hysteresis under compression

3.3.1. Constant-strain superelastic experiments and stress-temperature phase diagram

In order to investigate the effect of aging times and temperature on the stress-temperature phase diagram, the single crystal samples with [100] orientation were aged at 200°C for different times and also at 300°C for 1 hour. The compression specimens were loaded to 2% strain at various temperatures between -80°C and 160°C. Further

increase in the test temperature causes precipitation during the experiment, which increases the critical stress values. A representative experiment set (200°C-3h) is shown in Figure 7.

Linear relationships between critical stress for the onset of martensitic transformation under compression and test temperature are demonstrated in Figure 8 for the single crystal samples aged at 200 °C for 0, 1, 3, 6 and 10 hours and at 300 °C for 1 hour. The linear stress-temperatures relationship can be described using the Clausius-Clapeyron relationship:

$$\frac{d\sigma_c}{dT} = -\frac{\Delta S}{\epsilon \cdot V_m}$$

where $d\sigma/dT$ represents the critical stress-temperature slope; ΔS is the transformation entropy; V_m is the molar volume, and ϵ is the transformation strain. From the compression test results, the slopes for the solution heat treated, 200°C-3h and 200°C-10h samples are 0.52, 0.38 and 0.3 MPa/°C, respectively. For 300°C-1h sample, the slope is about 0.3 MPa/°C. It is clear that at the same test temperature, the critical stresses increase with increasing aging time, which indicates that transformation temperatures of the alloy are decreased with increasing aging time. At the same test temperature (ex. -80°C), the critical stress for 300°C-1h sample (about 1100MPa) is significantly higher than that in the 200°C-1h sample (about 200MPa). Since the precipitate volume fraction of the sample is not appreciably increased from 200°C-1h to 300°C-1h, it is likely that transformation temperatures are primarily influenced by the size of the precipitates and the composition of the matrix.

Similar trend in aging time vs. transformation temperature was reported in FeNiCoTi SMAs. Increasing the aging times at 550°C or at 600°C caused the

transformation temperature to increase, which corresponded with an increase in the superelastic critical stress under compression [44]. In contrast, the superelastic critical stresses and the values of stress-temperature slope of the FeNiCoAlTa SMAs decreases in both tension and compression when the aging times increase from 7 hours to 90 hours at 600°C [12].

3.3.2. Incremental strain superelastic experiments

In the incremental strain tests, the experiments were carried out at room temperature under compression. The samples were loaded to 2% strain and unloaded. Subsequently, the applied strain was increased at 1% increments until the specimen showed significant hardening after the transformation plateau region. Figures 9a, b and c show the stress-strain curves of the specimens aged at 200°C for 1 hour, 200°C for 3 hours, and 300°C for 1 hour, respectively. For the 300°C-1h sample, cracks appeared in the sample during the 6% applied strain cycle and the test was stopped. The superelastic and irrecoverable strain values extracted from the incremental strain tests were plotted as a function of applied strain in Figure 10a. At low applied strain levels, the maximum superelastic strain increases with increasing applied strain, gradually reaching a peak value beyond which the superelastic strain decreases with increasing applied strain. The maximum values of the superelastic strains, ε_{SE}^{MAX} , were determined from the plots in Figure 10a, as shown in the figure, and other similar plots, for each aging case, and the results are summarized in Figure 10b. ε_{SE}^{MAX} are about 5%, 7.2% and 2.2% for 200°C-1h, 200°C-3h, and 300°C-1h cases, respectively. The results in

Figure 10b show that the maximum superelastic strain is obtained after aging at 200°C for 3 hours.

Based on the previously shown TEM, APT, and superelasticity test results, larger precipitates were formed in the 300°C-1h aging case as compared to the 200°C-1h and 200°C-3h cases. The largest superelastic strain is obtained in the 200°C-3h sample with the precipitate size about 6 to 10 nm and the volume fraction of the precipitates around 34.3%. The volume fraction of the precipitate in the 200°C-1h sample is about 29.8%, which is closed to the 30.6% in the 300°C-1h sample. However, the superelastic strain is considerably higher in the 200°C-1h sample than that of the 300°C-1h sample. Since the volume fraction of the precipitates in all three of these samples does not differ significantly (<5%), and the differences in the precipitate compositions are small and not expected to create large differences in mechanical response, it is likely that the differences in the superelastic strain levels and the mechanical responses could be explained by the differences in the average size of non-transforming precipitates in the samples.

The effect of average precipitate size is also apparent in the microhardness of the samples. Figure 11 summarizes Vickers microhardness values as a function of precipitate size for different aging times and temperatures. It is clear that an increase in the precipitate size drastically increases the hardness of the material without a concomitant increase in volume fraction for the 200°C-1h and 300°C-1h samples. This again suggests that the size of precipitates has a significant effect on the mechanical and superelastic response of the alloy.

3.3.3 Precipitate effect on superelastic and recoverable strains

It is possible that the portions of the irrecoverable strain observed in the experiments shown in Figure 9 are caused by unrecovered martensite. This component is also a portion of total transformation strain and should be considered when comparing the experimentally measured superelastic strain levels to the theoretical values. For the three aforementioned aging conditions (200°C-1h, 200°C-3h, 300°C-1h), the specimens after the incremental strain experiments were heated to 100°C. Total strain recovery (ϵ_{SME} SME: Shape Memory Effect) during heating was recorded and added to the superelastic strains (ϵ_{SE}) as a measure to the total recoverable strain ($\epsilon_{tr\ experiment}$) of the specimen, and plotted as a function of the average precipitate size in Figure 12a. The result shows that the $\epsilon_{tr\ experiment}$ values are about 6.2%, 7.3% and 3% for 200°C-1h, 200°C-3h and 300°C-1h cases, respectively.

We use a simple rule of mixture calculation to find out the expected experimental transformation strain on these samples considering the relatively large volume fractions of the non-transforming precipitates. The equation can be expressed as

$$\epsilon_{tr\ experiment} = \epsilon_{tr\ theory} (1 - V_p)$$

$\epsilon_{tr\ experiment}$, $\epsilon_{tr\ theory}$, and V_p represent the expected experimental total recoverable strain, theoretical transformation strain and volume fraction of the precipitates. For the 200°C-1h sample, the $\epsilon_{tr\ theory} = 10.5\%$ [25] and $V_p = 0.298$, we can obtain $\epsilon_{tr\ experiment}$ as $10.5\% (1 - 0.298) = 7.37\%$. For the 200°C-3h sample, $\epsilon_{tr\ experiment}$ is $10.5\% (1 - 0.343) = 6.9\%$ using $V_p = 0.343$. For the 300°C-1h sample, $\epsilon_{tr\ experiment}$ can be calculated as ϵ_{tr}

$experiment = 10.5\% - 0.306 = 7.29\%$. The results indicate that the maximum expected superelastic strain should be comparable in all three samples. However, the experimental results show that the 200°C-3h sample has a significantly higher superelastic strain than the 200°C-1h sample. The reason could be related to the precipitate size and its influence on the deformation plasticity. For the 200°C-1h sample, the size of the precipitates is about 3 to 6 nm. The small precipitates may not be strong enough to strengthen the austenite matrix to resist the plastic deformation. As a result, the plastic deformation may occur at higher applied strain levels when martensite variant interactions dramatically increase the magnitude of internal stresses within the sample. By comparison, the size of the precipitates is around 6 to 10 nm in the 200°C-3h sample, which may provide improved strengthening and better recoverability.

On the other hand, further increase in the precipitate size, as in the case of the 300°C-1h sample, may result in a loss in coherency and reduced effects of precipitation hardening. In a study on the FeMnAlNi polycrystals, Omori *et al.* [42] reported that the precipitates with the diameters around 10 nm are coherent with the matrix. The range of 5 to 10 nm also resulted in coherent precipitates in aged FeNiCoAlTa [11,12] and FeNiCoAlTi [23] single crystals. Geng *et al.* [45] reported in aged FeNiCoAlTaB polycrystals that as aging time increases at 700°C, the martensitic transformation changes from thermoelastic to non-thermoelastic due to coherency loss between the precipitates and the matrix. The precipitate size is around 40 nm in 700°C–240h aged samples where the transformation becomes non-thermoelastic. Similar effect may be the reason for the present results. Additionally, the increase in the precipitate size appears to significantly reduce the ductility of the sample, causing fracture at 6%

applied strain. Similar embrittlement was also reported by Omori *et al.* [24] as aging temperature increased.

3.3.4 Precipitate effect on stress hysteresis

In order to determine the relationship between the precipitate size and stress hysteresis in different aging conditions, the stress hysteresis values at various applied strain levels was extracted from Figure 9 and summarized in Figure 12b. The hysteresis values at 5% applied strain are shown in Figure 12a. As expected, stress hysteresis increased with increasing applied strain as greater portion of the material is transformed. It is interesting to note, however, that at any applied strain level, the stress hysteresis in the 300°C-1h sample was consistently the highest, and in the 200°C-3h sample the lowest. The rate at which stress hysteresis increased with increasing applied strain followed a similar comparable trend: the fastest in 300°C-1h and the slowest in 200°C-3h.

Interestingly, there appears to be an inverse relationship between maximum recoverable strain and stress hysteresis. When the aging time increases from 1 hour to 3 hours at aging temperature 200°C, the stress hysteresis decreases and recoverable strain increases, and the smallest hysteresis and highest recoverable strain both occur in the 200°C-3h sample. This suggests that superelastic recovery and stress hysteresis may be governed by similar sets of mechanisms. On the smaller end of the precipitate size spectrum, such as in the 200°C-1h sample, plastic deformation that becomes active due to insufficient precipitation strengthening increases the energy dissipation during a transformation cycle, resulting in a larger hysteresis. In contrast, when the

precipitates are large as in the case for 300°C-1h, large critical stress is required to induce the martensitic transformation and the frictional resistance to phase boundary motion increases due to a hardening effect [46, 47]. The increase in the frictional resistance, in turn, amplifies the hysteresis loop.

4. Summary and Conclusions

In this study, we showed that aging heat treatment affects the size, volume fraction and composition of the nano-precipitates, which in turn affect transformation temperature and superelastic characteristics such as superelastic strain, stress hysteresis, critical stress and critical stress temperature slope in $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystal samples with the [100] orientation. We summarize the major findings as follows:

- 1) Increasing the aging times at 200°C increases the size and slightly increases the volume fraction of the B2 precipitates. Precipitation coarsening occurs much more quickly at 300 °C compared to 200 °C, but precipitate volume fraction appears to be unaffected. Precipitates are enriched in Ni and Al, and with increasing aging time and temperature, the chemical segregation is magnified.
- 2) Transformation temperatures of the FeMnAlNi single crystals decrease with increasing the aging time and temperature.
- 3) Mechanical properties such as hardness and superelastic properties such as recoverable strain and stress hysteresis are most directly influenced by the size of the precipitates. Larger precipitates monotonically increase hardness,

but its influence on recoverable strain and hysteresis show maxima/minima behavior.

- 4) Optimal superelastic properties are found for samples with precipitate sizes around 6 to 10 nm, which represents a balance between sufficient precipitation hardening and avoidance of loss of coherency or excessive embrittlement.

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References

- [1] A. Sato, E. Chishima, K. Soma, T. Mori, Shape memory effect in $\gamma \rightleftharpoons \varepsilon$ transformation in Fe-30Mn-1Si alloy single crystals, *Acta Metall.* 30 (1982) 1177-1183.
- [2] S. Kajiwara, K. Ogawa, Mechanism of improvement of shape memory effect by training in FeMnSi, *Material Science Forum* 327 (2000) 211-214.
- [3] A. Sato, E. Chishima, Y. Yamaji, T. Mori, Orientation and composition dependences of shape memory effect in FeMnSi alloys, *Acta Metall.* 32 (1984) 539-547.
- [4] T. Maki, Ferrous shape memory alloys, in: K. Otsuka, C.M. Wayman (Eds.), *Shape memory materials*, Cambridge University Press, United Kingdom, 1998, pp. 117-132.

- [5] T. Maki, K. Kobayashi, M. Minato, I. Tamura, Thermoelastic martensite in an assuaged FeNiCoTi alloy, *Scripta Metall.* 18 (1984) 1105-1109.
- [6] T. Maki, S. Furutani, I. Tamura, Shape memory effect related to thin plate martensite with large thermal hysteresis in assuaged FeNiCoTi alloy, *The Iron and Steel Institute of Japan International* 29 (1989) 438-445.
- [7] S. Kajiwar, Characteristic features of shape memory effect and related transformation behavior in Fe-based alloys, *Materials Science & Engineering A* 273 (1999) 67-88.
- [8] Y. Tanaka, Y. Himuro, R. Kainuma, Y. Sutou, K. Ishida, Ferrous polycrystalline shape-memory alloy showing huge superelasticity, *Science* 327 (2010) 1488-1490.
- [9] T. Omori, S. Abe, Y. Tanaka, D.Y. Lee, K. Ishida, K. Kainuma, Thermoelastic martensitic transformation and superelasticity in FeNiCoAlNbB polycrystalline alloy, *Scripta Materialia* 69 (2013) 812-815.
- [10] D. Lee, T. Omori, R. Kainuma, Ductility enhancement and superelasticity in FeNiCoAlTiB polycrystalline alloy, *Journal of Alloys and Compounds* 617 (2014) 120-123.
- [11] J. Ma, B. Kockar, A. Evirgen, I. Karaman, Z.P. Luo, Y.I. Chumlyakov, Shape memory behavior and tension-compression asymmetry of a FeNiCoAlTa single-crystalline shape memory alloy, *Acta Materialia* 60 (2012) 2186-2195.
- [12] J. Ma, B.C. Hornbuckle, I. Karaman, G.B. Thompson, Z.P. Luo, Y.I. Chumlyakov, The effect of nanoprecipitates on the superelastic properties of FeNiCoAlTa shape memory alloy single crystals, *Acta Materialia* 61 (2013) 3445-3455.
- [13] A. Evirgen, J. Ma, I. Karaman, Z.P. Luo, Y.I. Chumlyakov, Effect of aging on the superelastic response of a single crystalline FeNiCoAlTa shape memory alloy, *Scripta Materialia* 67 (2012) 475-478.
- [14] I.V. Kireeva, Y.I. Chumlyakov, V.A. Kirillov, E. Cesari, Orientation and temperature dependence of superelasticity caused by reversible γ - α' martensitic transformations in FeNiCoAlTa single crystals, *Technical Physics Letters* 37 (2011) 487-490.
- [15] I.V. Kireeva, Y.I. Chumlyakov, V.A. Kirillov, I. Kretinina, Y. Danil'son, I. Karaman, E. Cesari, Thermoelastic γ - α' martensitic transformations in FeNiCoAlTa aging single crystals, *Russian Physics Journal* 53 (2011) 1103-1106.

- [16] Y.I. Chumlyakov, I.V. Kireeva, E.Y. Panchenko, E.E. Timofeeva, I. Kretinina, O. Kuts, I. Karaman, H.J. Maier, Shape memory effect and superelasticity in single crystals of high-strength ferromagnetic alloys, *Advance Materials Research* 1013 (2014) 15–22.
- [17] Y.I. Chumlyakov, I.V. Kireeva, I.V. Kretinina, K.S. Keinikh, O.A. Kuts, V.A. Kirillov, I. Karaman, H.J. Maier, Shape memory effect and superelasticity in the [001] single crystals of a FeNiCoAlTa alloy with γ - α' thermoelastic martensitic transformations, *Russian Physics Journal* 56 (2013) 920-929.
- [18] P. Krooß, C. Somsen, T. Niendorf, M. Schaper, I. Karaman, Y.I. Chumlyakov, G. Eggeler, H.J. Maier, Cyclic degradation mechanisms in aged FeNiCoAlTa shape memory single crystals, *Acta Materialia* 79 (2014) 126-137.
- [19] P. Krooß, M.J. Holzweissig, T. Niendorf, C. Somsen, M. Schaper, Y.I. Chumlyakov, H.J. Maier, Thermal cycling behavior of an aged FeNiCoAlTa single-crystal shape memory alloy, *Scripta Materialia* 81 (2014) 28-31.
- [20] P. Krooß, H.J. Maier, I. Karaman, Y.I. Chumlyakov, T. Niendorf, Cyclic Deformation behavior of aged FeNiCoAlTa single crystals, *Functional Materials Letters*, 05 (2012) 1250045.
- [21] Y.I. Chumlyakov, I.V. Kireeva, O.A. Kuts, D.A. Kuksgauzen, Thermoelastic Martensitic Transformations and Superelasticity in the [001]-Oriented FeNiCoAlNb Single Crystals, *Russian Physics Journal* 57 (2015) 1328-1335.
- [22] Y.I. Chumlyakov, I.V. Kireeva, V.V. Poklonov, Z.V. Pobedennaya, I. Karaman, The shape memory effect and superelasticity in single crystal ferromagnetic alloy FeNiCoAlTi, *Technical Physics Letters* 40 (2014) 747-750.
- [23] L.W. Tseng, J. Ma, I. Karaman, S.J. Wang, Y.I. Chumlyakov, Superelastic response of the FeNiCoAlTi single crystals under tension and compression, *Scripta Materialia* 101 (2015) 1-4.
- [24] T. Omori, K. Ando, M. Okano, X. Xu, Y. Tanaka, I. Ohnuma, R. Kainuma, K. Ishida, Superelastic effect in polycrystalline ferrous alloys, *Science* 333 (2011) 68-71.
- [25] L.W. Tseng, J. Ma, I. Karaman, S.J. Wang, M. Kaya, Z.P. Luo, Y.I. Chumlyakov, Superelastic response of a single crystalline FeMnAlNi shape memory alloy under tension and compression, *Acta Materialia* 89 (2015) 374-383.
- [26] H. Sehitoglu, C. Efstathiou, H.J. Maier, Y. Chumlyakov, Magnetization, shape memory and hysteresis behavior of single and polycrystalline FeNiCoTi, *Journal of Magnetism and Magnetic Materials* 292 (2005) 89-99.

- [27] H. Sehitoglu, C. Efstathiou, H.J. Maier, Y. Chumlyakov, Hysteresis and deformation mechanisms of transforming FeNiCoTi, *Mechanics Materials* 38 (2006) 538-550.
- [28] H. Sehitoglu, I. Karaman, X.Y. Zhang, Y. Chumlyakov, H.J. Maier, Deformation of FeNiCoTi shape memory single crystals, *Scripta Materialia* 44 (2001) 779-784.
- [29] K. Otsuka, X. Ren, Physical metallurgy of Ti-Ni based shape memory alloys, *Progress in Materials Science* 50 (2005) 511-678.
- [30] E.Y. Panchenko, Y.I. Chumlyakov, I.V. Kireeva, A.V. Ovsyannikov, H. Sehitoglu, I. Karaman, H.J. Maier, Effect of disperse Ti_3Ni_4 particles on the martensitic transformations in titanium nickelide single crystals, *The Physics of Metals and Metallography* 106 (2008) 577-589.
- [31] K. Gall, H. Sehitoglu, Y.I. Chumlyakov, I.V. Kireeva, Tension-compression asymmetry of the stress-strain response in aged single crystal and polycrystalline NiTi, *Acta Materialia* 47 (1999) 1203-1217.
- [32] K. Gall, H. Sehitoglu, Y. Chumlyakov, Y.L. Zuev, I. Karaman, The role of coherent precipitates in martensitic transformations in single crystal and polycrystalline Ti-50.8 at% Ni, *Scripta Materialia* 39 (1998) 699-672.
- [33] H. Sehitoglu, I. Karaman, R. Anderson, X. Zhang, K. Gall, H.J. Maier, Y. Chumlyakov, Compressive response of NiTi single crystals, *Acta Materialia* 48 (2000) 3311-3326.
- [34] J. Zhang, W. Cai, X. Ren, K. Otsuka, M. Asai, The nature of reversible change in M_s temperature of Ti-Ni alloys with alternating aging, *Materials Transactions* 40 (1999) 1367-1375.
- [35] S. Miyazaki, K. Otsuka, Y. Suzuki, Characteristics of deformation and transformation pseudoelasticity in Ti-Ni alloys, *Journal of Physics* 43 (1982) C4255-C4260.
- [36] T. Saburi, T. Tatsumi, S. Nenno, Effect of heat treatment on mechanical behavior of Ti-Ni alloys, *Journal of Physics* 43 (1982) C4261-C4266.
- [37] J. Kahlil-Allafi, A. Dlouhy, G. Eggler, NiTi-precipitation during aging of Ni_4Ti_3 shape memory alloys and its influence on martensitic phase transformations, *Acta Materialia* 50 (2002) 4255-4274.
- [38] G.L. Fan, W. Chen, S. Yang, J.H. Zhu, X.B. Ren, K. Otsuka, Origin of abnormal multi-stage martensitic transformation behavior in aged Ni-rich Ti-Ni shape memory alloys, *Acta Materialia* 52 (2004) 4351-4362.

- [39] J. Michutta, C. Somsen, A. Yawny, A. Dlouhy, G. Eggler, Elementary martensitic transformation processes in Ni-rich NiTi single crystals with Ni_4Ti_3 precipitates, *Acta Materialia* 54 (2006) 3525-3542.
- [40] K. Thompson, D. Lawrence, D.J. Larson, J.D. Olson, T.F. Kelly, B. Gorman, In situ site-specific specimen preparation for atom probe tomography, *Ultramicroscopy* 107 (2007) 131-139.
- [41] L.A. Giannuzzi, Reducing FIB damage using low energy ions, *Microscopy and Microanalysis* 12 (2006) 1260-1261.
- [42] T. Omori, M. Nagasako, M. Okano, K. Endo, R. Kainuma, Microstructure and martensitic transformation in the FeMnAlNi shape memory alloy with B2-type coherent fine particles, *Applied Physics Letters* 101 (2012) 2319071-2319074.
- [43] D. Blavette, P. Caron, T. Khan, Superalloys, in: S. Reichman, D.N. Duhl, G. Maurer, S. Antolovich, C. Lund (Eds.), *The Mineral Metals and Materials Society*, Warrendale, Pennsylvania, 1988, pp. 305-314.
- [44] H. Sehitoglu, X.Y. Zhang, T. Kotil, D. Canadinc, Y. Chumlyakov, H.J. Maier, Shape memory behavior of FeNiCoTi single and polycrystals, *Metallurgical and Materials Transactions A* 33A (2002) 3661-3672.
- [45] Y. Geng, D. Lee, X. Xu, N. Makoto, X. Jin, T. Omori, R. Kainuma, Coherency of ordered γ' precipitates and thermoelastic martensitic transformation in FeNiCoAlTaB alloys, *Journal of Alloys and Compounds* 628 (2015P) 287-292.
- [46] R.F. Hamilton, C. Efsthathiou, H. Sehitoglu, Y. Chumlyakov, Thermal and stress-induced martensitic transformations in NiFeGa single crystals under tension and compression, *Scripta Materialia* 54 (2006) 465-469.
- [47] R.F. Hamilton, H. Sehitoglu, Y. Chumlyakov, H.J. Maier, Stress dependence of the hysteresis in single crystal NiTi alloys, *Acta Materialia* 52 (2004) 3383-3402.

FIGURES:

Figure 1. A schematic demonstrating the determination of the critical stress for martensitic transformation (σ_c), stress hysteresis ($\Delta\sigma$), irrecoverable strain (ϵ_{irrec}), superelastic strain (ϵ_{SE}), and elastic strain (ϵ_e).

Figure 2: Room temperature Vickers microhardness values of the $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ [001] single crystals aged at 200°C and 300°C for various durations.

(a)

(b)

Figure 3: Magnetization response of the Fe_{43.5}Mn₃₄Al₁₅Ni_{7.5} SMA single crystals as a function of temperature under a magnetic field of 0.5 kG for (a) the solution treated sample and (b) the sample aged at 200°C for 15 minutes.

(a)

1200°C , 1h + 200°C , 1h

1200°C , 1h + 200°C , 3h

(b)

(c)

Figure 4: (a) The selected area diffraction pattern of the [001] oriented $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystals solution heat treated at 1200°C for 1 hour followed by water quenching. (b) The high resolution TEM images of the B2 precipitates after different aging times. The size of the precipitates was marked with the circles. (c) The relation between the average precipitate size and aging temperature and time.

(a) 1200°C , 1h + 200°C , 1h

(b) 1200°C , 1h + 200°C , 3h

(c) 1200°C , 1h + 300°C , 1h

● Ni - rich

● Fe - rich

Figure 5: Atom probe tomography analysis of the B2 precipitates in the $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ SMAs aged at 200°C and 300°C. Atom probe reconstruction image for the (a) 200°C-1h (b) 200°C-3h and (c) 300°C-1h samples.

Figure 6: Proximity histogram taken across the precipitate and matrix boundary for the 200°C-1h sample.

Figure 7: A representative constant strain superelastic experiment: the [100] oriented $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystal specimens were solution heat treated at 1200°C for 1 hour and aged at 200°C for 3 hours. The specimens were loaded in compression at various temperatures to approximately 2% strain.

Figure 8: Summary of the critical compressive stress for stress-induced martensitic transformation vs. temperature response of the [100] oriented $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystals heat treated at 200°C for different times and 300 °C for 1 hour. The results were determined from the constant strain superelastic experiments at different temperatures shown in Figure 7.

(a)

(b)

(c)

Figure 9: Incremental strain superelastic experiments in the [100] $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystal specimens aged at (a) 200°C for 1 hour, (b) 200°C for 3 hour and (c) 300°C 1 hours. The experiments were conducted at room temperature.

(a)

(b)

Figure 10: (a) Superelastic and irrecoverable strain levels as a function of the applied strain in the [100] oriented $\text{Fe}_{43.5}\text{Mn}_{34}\text{Al}_{15}\text{Ni}_{7.5}$ single crystals with various aging temperatures and times, determined from the incremental strain experiments shown in Figure 9. (b) The maximum superelastic strains for the single crystals aged at 200 °C for different durations, determined from the results similar to those shown in (a).

Figure 11: Change in hardness as a function of the average precipitate size determined from the TEM images in Figure 4.

(a)

(b)

Figure 12 (a) The relationship between the superelastic strain + shape memory strain $((\epsilon_{tr})_{\text{experiment}})$ and stress hysteresis as a function of precipitate size in three different aging conditions. The stress hysteresis is determined from the 5% applied strain shown in Figure 9. (b) The relation between the stress hysteresis and applied strain for various aging conditions.

TABLES:

Table 1: Precipitate compositions determined from the atom probe tomography measurements for the 200°C-1h, 200°C-3h and 300°C-1h samples.

Precipitate composition (at.%)			
	200 °C 1 hr	200 °C 3 hr	300 °C 1 hr
Fe	22.03 ± 1.48	25.05 ± 3.05	26.07 ± 1.97
Mn	25.69 ± 1.45	27.54 ± 1.02	25.92 ± 0.98
Al	27.20 ± 1.19	23.70 ± 1.54	21.04 ± 1.44
Ni	25.11 ± 1.50	23.70 ± 2.72	19.29 ± 2.04

*Graphical Abstract
1200°C , 1h + 200°C , 3h

1200°C , 1h + 200°C , 3h

● Ni - rich

● Fe - rich

1200°C , 1h + 300°C , 1h

Large tensile
superelastic strain
in the inexpensive
FeMnNiAl shape
memory alloy with
optimum
precipitate size

1200°C , 1h + 300°C , 1h

Reasonable
superelastic
response under
very high stresses
but brittle behavior
due to the large
precipitate size