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Microstructure and Superelastic Properties of FeNiCoAlTi Single Crystals with the <100> Orientation under Tension

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Abstract: The microstructure and superelastic response of an $Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ti_{2.5}$ (at.%) single crystal along the <100> orientation was investigated under tension at room temperature after aging at 600 °C for 24 h. From the superelastic results, the samples aged at 600 °C for 24 h exhibited 4.5% recoverable strain at room temperature. The digital image correlation (DIC) method was used to observe the strain distribution during the 6.5% applied strain loading. The DIC results showed that the strain was uniformly distributed during the loading and unloading cycles. Only one martensite variant was observed from the DIC results. This was related to the aging heat treatment times. The martensite morphology became a single variant with a longer aging time. The thermo-magnetization results indicated that the phase transformation and temperature hysteresis was around 36 °C. Increasing the magnetic field from 0.05 to 7 Tesla, the transformation temperatures increased. The maximum magnetization was 160 emu/g under the magnetic field of 7 Tesla. From the transmission electron microscopy results, the $L1_2$ precipitates were around 10 nm in size, and they were high in Ni content and low in Fe content.

Keywords: superelasticity; FeNiCoAlTi; shape memory alloys

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1. Introduction

Shape memory alloys (SMAs) possess two unique properties: the shape memory effect and superelasticity. Commercial Nickel–Titanium (NiTi) SMAs have a high cost in terms of material and difficulty to manufacture, which limits the wide application of these alloys. In contrast to NiTi alloys, iron-based SMAs have a low material cost and good workability, and they have drawn attention and interest in both industry and academia.

Recently, FeNiCoAlXB (X: Ta, Nb, Ti) alloys have been reported to have greater than 4% superelastic strain [1–3] and 1.6% shape memory strain [4], and single crystals have exhibited at least a 5% recoverable strain [5–8]. The martensitic transformation (MT) of the FeNiCoAlXB (X: Ta, Nb, Ti) alloy system is face-centered cubic (fcc) (austenite) to body-centered tetragonal (bct) (martensite). Iron-based SMAs are required to undergo aging heat treatment to introduce the $L1_2$ precipitates into the austenite matrix. The purposes of $L1_2$ precipitates are to strengthen the austenite matrix, change iron-based SMAs from non-thermo-elastic to thermo-elastic transformation, and assist martensitic transformation during the superelastic tests [1].

Previous aging heat-treatment studies of FeNiCoAlXB (X: Ta, Nb, Ti) alloys have reported that the optical aging temperatures of these alloys, to obtain superelastic properties, ranged from 600 to 700 °C [1–8]. Tanaka et al. [1] found that $Fe_{40.95}Ni_{28}Co_{17}Al_{11.5}Ta_{2.5}B_{0.05}$

(at.%) alloys aged at 600 °C for 72 h show a 13.5% superelastic strain at room temperature, and the diameter of the precipitate was 3 nm. Ma et al. [5] reported that 3.5% superelastic strain at 0 °C under tension was achieved in $Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ta_{2.5}$ (at.%) single crystals with the <100> orientation aged at 600 °C for 90 h. The precipitate size was around 3–5 nm. In addition, FeNiCoAlTa single crystals aged, for the first stage of aging, at 700 °C for 0.5 h and then at 700 °C for 3 h, exhibiting 15% superelastic strain at −196 °C [9]. The size of precipitates was 2–6 nm.

Tseng et al. [6] found that replacing Ta with Ti could reduce the aging heat treatment times. FeNiCoAlTi single crystals with <100> orientation aged at 600 °C for 4 h possessed 6% superelastic strain at −80 °C. The precipitate size was around 5 nm. Chumlyakov et al. [7] used a two-stage aging heat treatment (600 °C for 4 h and 600 °C for 2 h) and achieved a 3% superelastic strain at −100 °C. In previous studies, good superelastic properties could only be obtained at low temperatures. When the test temperature was at room temperature, the superelastic strain was deteriorated due to very low transformation temperatures [5,6,9]. As a result, the motivation of this study was to obtain the aging condition to show good superelastic properties at room temperature. In this study, $Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ti_{2.5}$ (at.%) single crystals, with the <100> orientation after aging heat treatment, were investigated to determine their microstructure, thermo-magnetization, and superelastic properties under tension.

2. Materials and Methods

$Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ti_{2.5}$ (at.%) single crystals were grown using the Bridgman technique. Tensile samples with gauge dimensions of 1.5 mm × 3 mm × 8 mm were cut by wire electro-discharge machining (EDM) from single crystal alloys with the tension axis parallel to the <100> crystal orientation. The single crystals were first sealed in a quartz tube under an argon atmosphere. The single crystals were solution heat treated at 1300 °C for 24 h to homogenize the sample and then quenched in water. Subsequently, the homogenized samples were aged at 600 °C for 24 h to allow precipitation.

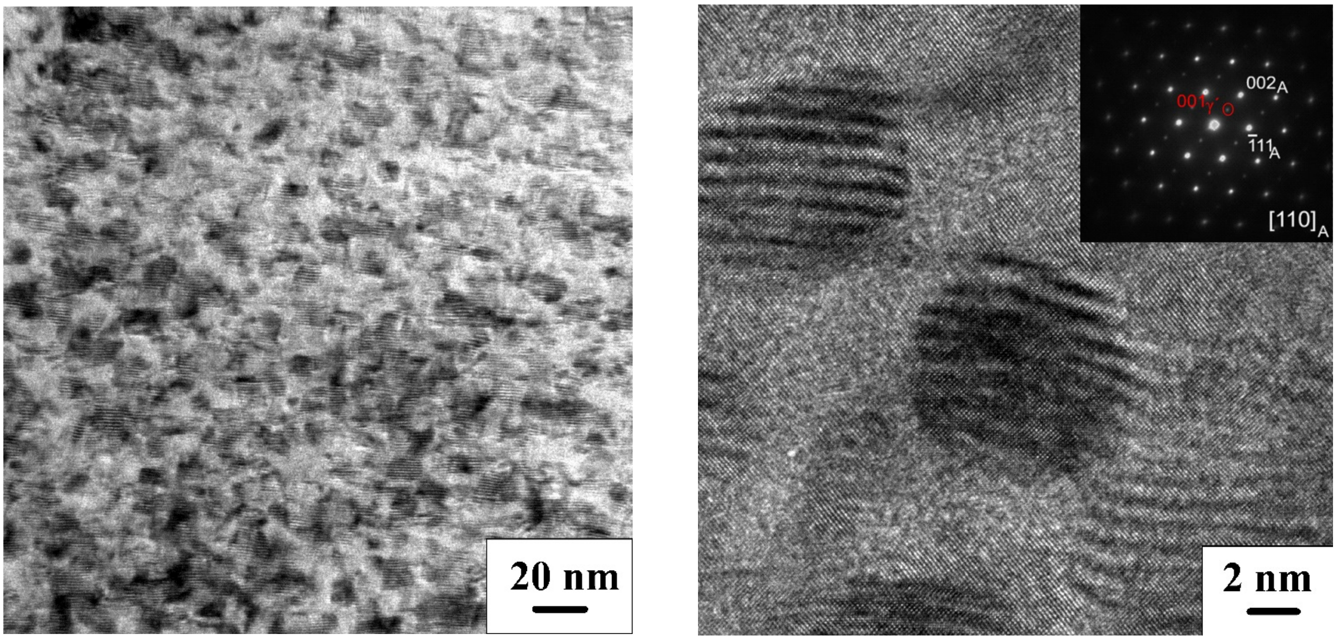
The crystal structure and size of the precipitates were analyzed by transmission electron microscopy (TEM) at room temperature. TEM samples were prepared using a focused ion beam (FIB). TEM observations were conducted with a JEOL JEM-F200 electron microscope. The composition of the precipitates was analyzed by energy dispersive spectroscopy (EDS). The martensitic transformation temperatures were measured with a Superconducting Quantum Interference Device (SQUID) magnetometer under magnetic fields of 0.05 and 7 Tesla (T). The heating and cooling rates for this experiment were 5 °C/min. The magnetic results were used to determine the thermo-martensitic transformation temperatures for calculation of the temperature hysteresis. A sample was first heated to 120 °C under zero magnetic field. Then, it was cooled to 260 °C and subsequently heated to around 120 °C under a constant magnetic field of 0.05 T. After the 0.05 T, the magnetic field was increased to 7 T. The sample was then cooled from 120 °C to −260 °C and heated to 120 °C again to complete another cycle.

The superelastic responses of the aged single crystals were characterized by a superelastic experiment under tension. A tensile test was performed with a universal tensile testing machine (AG-IS 50KN, Shimadzu, Kyoto, Japan). The tensile test was conducted in strain-controlled mode with a strain rate of 2×10^{-4} s^{-1}. The sample was cyclic deformed to reach different successive target strains. A virtual optical extensometer (Vic-Gauge 2D, Correlated Solutions, Irmo, SC, USA) tracked the in situ strain during the tensile cycles. A single crystal was tested at room temperature in an incremental superelastic experiment. In this experiment, the sample was loaded to a 0.5% strain and then unloaded. This process was then repeated at increasingly higher strain levels until the sample fractured. A speckle pattern was applied on the sample surface for digital image correlation (DIC) analyses. During the superelastic experiments, the deformation of the sample was recorded with a Complementary Metal-Oxide-Semiconductor (CMOS) at a frame rate of 5 Hz. The strain distribution of the sample during the superelastic cycle was analyzed in commercial VIC-2D software. The optical microscope of the fractured tensile sample was observed by using an Olympus digital optical microscope. The sample was etched with 93% C_2H_5OH + 7% HNO_3 solution for 1 min.

3. Results and Discussion

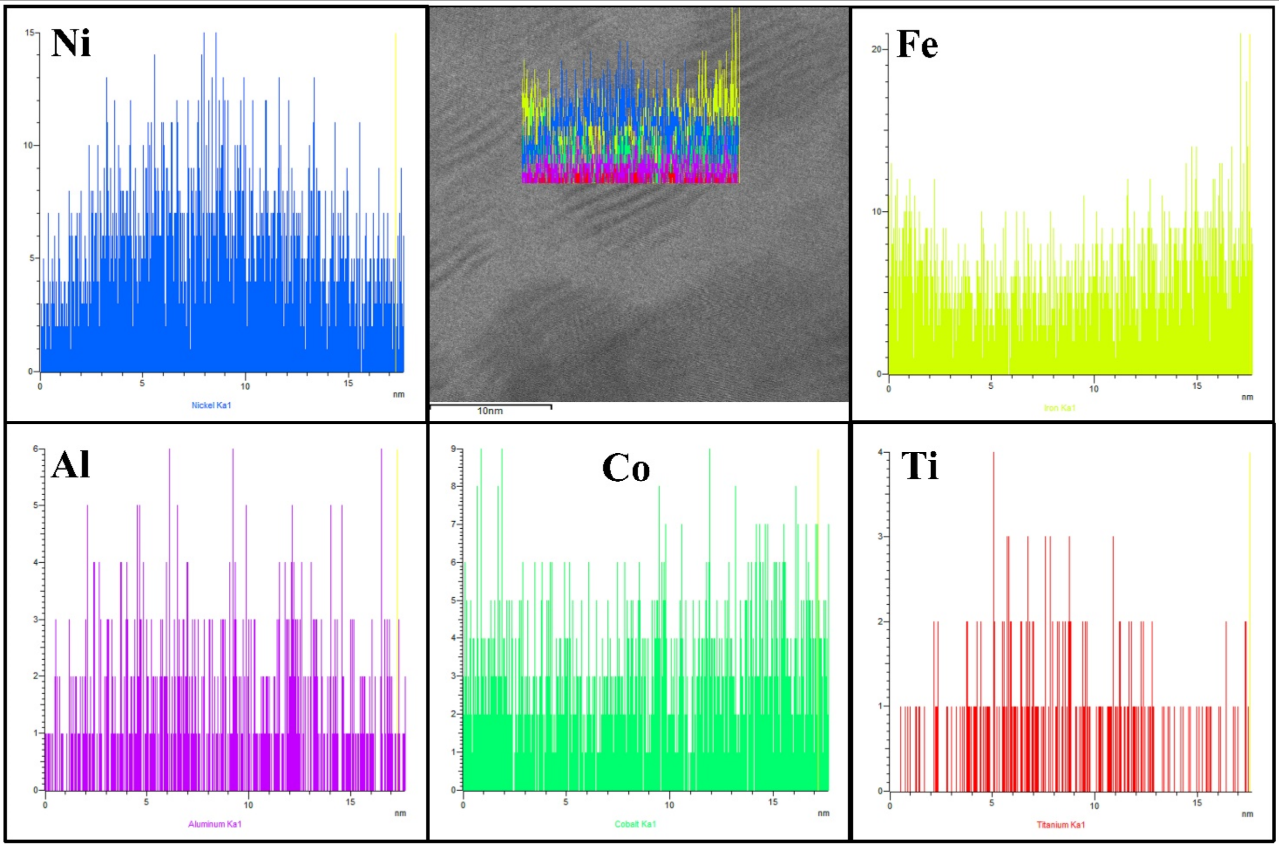
3.1. TEM Results

Figure 1a presents a room temperature bright field TEM image of a $Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ti_{2.5}$ single crystal with <100> orientation aged at 600 °C for 24 h. The high density of precipitates in this aging condition can clearly be observed. The TEM result shows the high density of precipitates. Figure 1b shows a high-resolution TEM image and corresponding selected-area electron diffraction (SAED) pattern of a sample aged at 600 °C for 24 h. In this sample, the diameters of the precipitates were around 8–10 nm. Insert Figure 1b shows the diffraction pattern of austenite and precipitates. The major diffraction spots are from the austenite matrix and are identified in the fcc phase. The spot with the red circle is the diffraction pattern of a precipitate. The diffraction pattern shows that the precipitates had the $L1_2$ structure. The diameters of the precipitates were 5 nm for a sample aged at 600 °C for 4 h [6]. The results indicate that the size of the precipitates increased from 5 to 10 nm when the aging times were increased from 4 to 24 h. The results of the high-magnification STEM examination combined with EDS line scanning for the spherical precipitates are shown in Figure 1c. Its composition via EDS analysis is also tabulated in Table 1. It is found that the main element of the composition for the spherical precipitates were enriched in Ni and Al and had lower Fe content. Therefore, it can be inferred that the spherical precipitation is in the Ni-rich precipitates phase. Such Ni-rich precipitates have been observed in several alloys systems such as FeNiCoAlTa and FeMnAlNi [5,10].



(**a**) (**b**)

Figure 1. *Cont.*



(**c**)

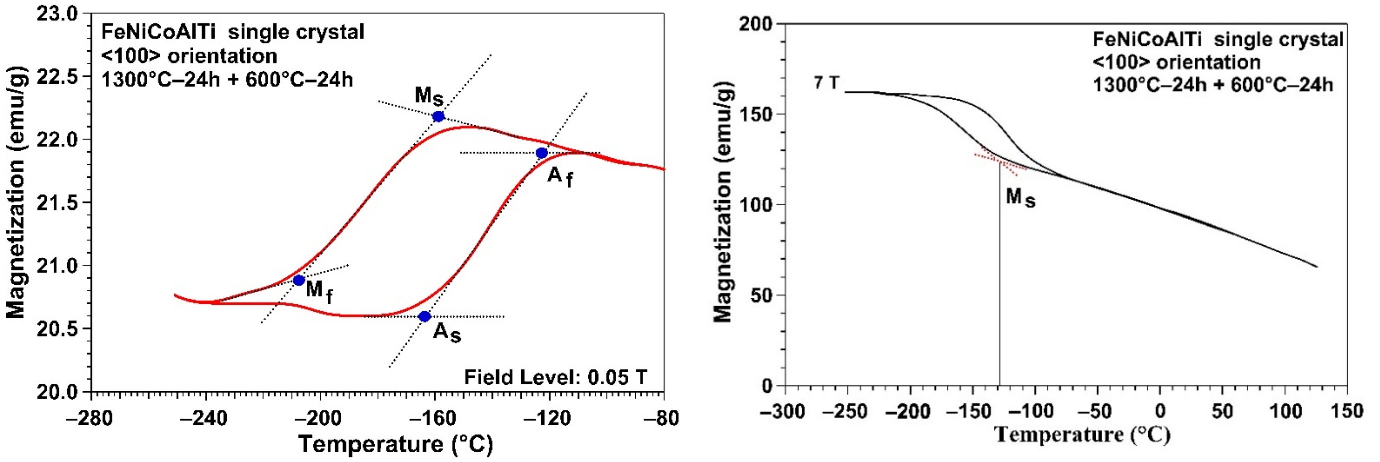
Figure 1. TEM images of the precipitates in a FeNiCoAlTi single crystal aged at 600 °C for 24 h: (**a**) bright field TEM image, (**b**) high resolution TEM image of the precipitates and the corresponding selected-area electron diffraction pattern, and (**c**) TEM mapping results.

Table 1. Composition of the precipitates found by EDS.

	Al (at.%)	Ti (at.%)	Fe (at.%)	Co (at.%)	Ni (at.%)
Measured	12.5	2.67	37.1	16.57	31.16
Nominal	11.5	2.5	41	17	28

3.2. Thermo-Magnetization Results

Figure 2a,b display the thermo-magnetization results of an $Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ti_{2.5}$ single crystal aged at 600 °C for 24 h under magnetic fields of 0.05 and 7 T. The thermo-elastic martensitic transformation temperatures of the samples were determined from the magnetic field results of the 0.05 T test. The tangent line method was used to determine the transformation temperatures as indicated in Figure 2a. From the results, the martensitic transformation temperatures were determined to be as follows: austenite finish temperature (A_f) = −122 °C, austenite start temperature (A_s) = −163 °C, martensite start temperature (M_s) = −158 °C, and martensite finish temperature (M_f) = −207 °C. The temperature hysteresis was defined as $|A_f - M_s|$ and calculated to be 36 °C. The thermo-martensitic transformation was not observed in the previous single crystal aged at 600 °C for 4 h because the transformation temperatures of this aging condition were too low, and the phase transformations were not observed during the heating and cooling cycles by SQUID measurement [6]. From the magnetic results of the 7 T magnetic field test, the magnetization in this aging condition was 160 emu/g. The M_s was around −128 °C. The results showed that the martensitic transformation temperatures increase with the increase in the magnetic field from 0.05 T to 7 T. In Figure 2a, it can be seen that As was close to Ms. Based on the theory of thermo-elastic martensitic transformation [8], we can conclude that the elastic energy generated because the transformation was equal to twice the dissipation energy. Therefore, the heat treatment created the conditions for martensitic transformation.

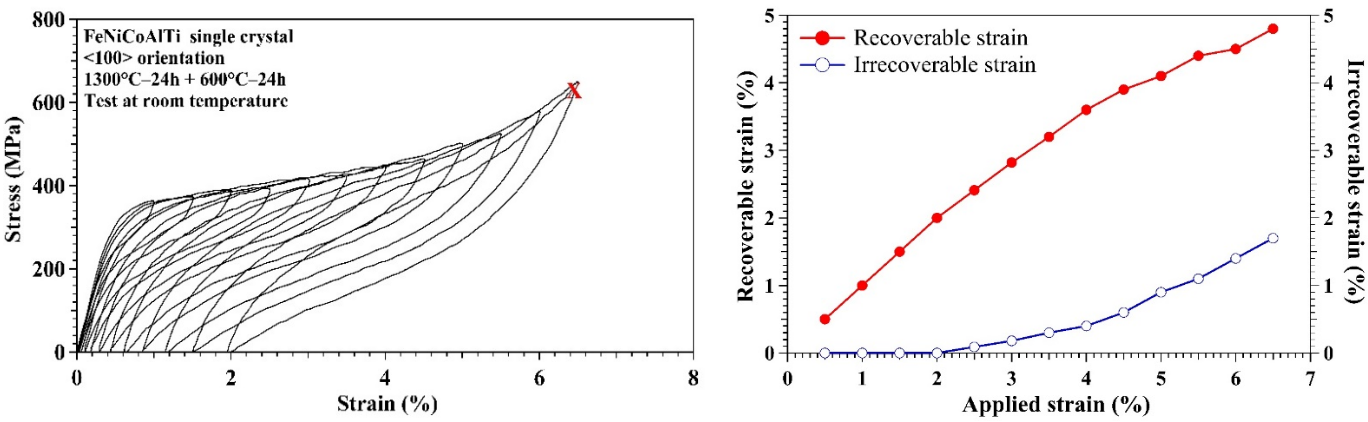


(**a**) (**b**)

Figure 2. Magnetization responses of the FeNiCoAlTi single crystals as a function of temperature under magnetic fields of (**a**) 0.05 T and (**b**) 7 T for single crystals aged at 600 °C for 24 h.

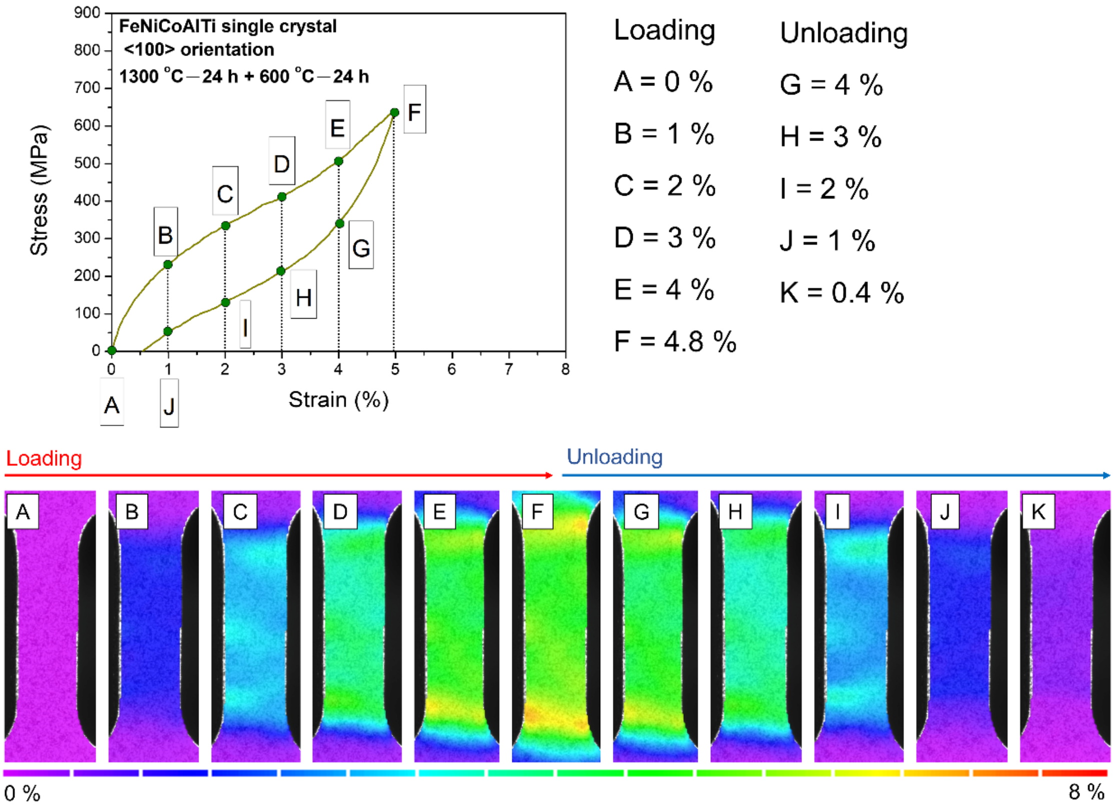
3.3. Superelastic Results

Figure 3a shows the stress–strain curves of $Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ti_{2.5}$ single crystals. The critical stress was determined, by the tangent line method, to be around 323 MPa. The tensile sample fractured during the 7% applied strain test. The fracture stress was around 635 MPa. The recoverable and irrecoverable strains extracted from incremental strain tests were plotted as a function of applied strain in Figure 3b. The maximum values of superelastic strain were about 4.8%. The recoverable strain was limited due to the next stress level being close to the fracture stress.

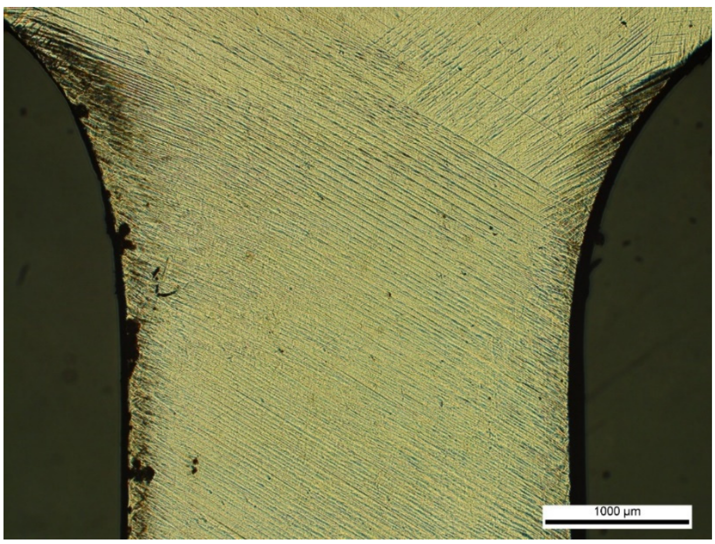


(**a**) (**b**)

Figure 3. *Cont.*



(**c**)



(**d**)

Figure 3. (**a**) Incremental strain superelastic experiment at room temperature in <100> oriented FeNiCoAlTi single crystal aged at 600 °C for 24 h and (**b**) variation of recoverable strain and irrecoverable strain as a function of the applied strain. "X" marks the point of fracture. (**c**) Contour plot of the strain field during 6.5% applied strain loading/unloading determined by DIC method. (**d**) Optical image of a fractured FeNiCoAlTi tensile sample.

The digital image correlation (DIC) method was used to observe the strain distribution during the 6.5% applied strain loading. In the preceding 6% applied strain test, the residual strain was around 1.5%. To clearly show the loading/unloading process, the residual strain was subtracted from the applied strain of 6.5%, leaving 5% strain, as shown in

Figure 3c. The DIC results indicate that the strain was uniformly distributed, and no severe localized strain concentrations were found in the gauge section. These results indicated that the deformation was uniform during the loading and unloading cycles. These DIC results were different from those reported by Abuzai and Sehitoglu [11]. Their DIC results indicated the presence of three martensite variants during the superelastic test. In the current study, only one martensite variant was observed from the DIC results. This difference is attributed to the different precipitate morphologies resulting from the different aging conditions. In their study, the sample was aged at 600 °C for 3 h. Their result suggests that the martensite adopts a twinned morphology in a short aging time during tensile deformation. In contrast, the sample in the current study was aged at 600 °C for 24 h, and only one variant was observed during the tensile deformation. Figure 3d shows the optical micrograph of the fractured $Fe_{41}Ni_{28}Co_{17}Al_{11.5}Ti_{2.5}$ tensile sample aged at 600 °C for 24 h. From the optical microscope results, traces of martensitic bands were declined about 60° to the tensile direction. This result suggests that, with a longer aging time, the martensite morphology becomes a single variant. Moreover, the critical stress of the sample aged at 600 °C for 3 h was around 800 MPa [11], whereas the critical stress of our sample aged at 600 °C for 24 h was 323 MPa. These results imply that the transformation temperature increases with an increase in aging time from 3 to 24 h, so less stress is required to induce martensitic transformation. The undirected role of variant–variant interactions on mechanical hysteresis is demonstrated by the comparison of the mechanical hysteresis in crystals aged for 3 h [11] and the crystals aged for 24 h in the current study. In the sample aged for 24 h, one variant of martensite created conditions for very low mechanical hysteresis of about 150 MPa at 2% transformation deformation. In those aged for 3 h, when three variants were created under stress, the mechanical hysteresis was three times higher than that of the crystals aged for 24 h.

4. Conclusions

In summary, the microstructure and superelastic properties of FeNiCoAlTi single crystals with the <100> orientation aged at 600 °C for 24 h under tension were investigated in this study. The main conclusions are listed as follows:

1. The precipitates were around 10 nm in size. The precipitate structure was the $L1_2$ structure, and the precipitates had high Ni and Al contents.
2. The thermo-magnetization results indicated phase transformations, and the temperature hysteresis was 36 °C.
3. The superelastic test results showed the recoverable strain to be around 4.5% at room temperature. The DIC results showed that the sample was uniformly deformed, and one martensite variant was observed during the loading/unloading.

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Conflicts of Interest: The authors declare no conflict of interest.

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