Superelasticity of [001]-oriented Fe_{42.6}Ni_{27.9}Co_{17.2}Al_{9.9}Nb_{2.4} Ferrous Shape Memory Alloys

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The shape memory properties of a ferrous single crystalline alloy, FeNiCoAlNb, were investigated along the [100] orientation by superelasticity tests in both tension and compression. Aging was used to form nano-size precipitates to demonstrate and tailor their shape memory properties. After aging at 700 °C for 3 hours, [001]-oriented FeNiCoAlNb shows high compression-tension asymmetry and shape recovery of about 4.5 % in tension and 8.8 % in compression. The superelastic behavior of [001]-oriented FeNiCoAlNb is weakly temperature dependent due to large transformation strain. FeNiCoAlNb has great potential for temperature independent and large scale actuator applications.

Keywords: Shape memory effect; Tension-compression asymmetry; Iron-based shape memory alloys; Magnetic shape memory alloys; Martensitic transformation.

Ferrous shape memory alloys (FeSMAs) such as Fe-Ni-C [1], Fe-Mn-Si [2, 3], Fe-Mn-Al [4] and Fe-Ni-Co-Ti [5-7] have received considerable attention due to their better workability, weldability and lower cost than the commercially available NiTi based SMAs. They have the potential to be utilized in many industries, such as construction, that requires the employment of large quantities of materials. Foremost, the main disadvantages of FeSMAs were that they exhibit non-thermoelastic transformation that resulted in very large temperature hysteresis (>300 °C) and no superelasticity [8]. However, composition alteration and precipitation were successfully employed in some FeSMAs to obtain thermoelastic transformation with lower temperature hysteresis [9, 10]. However, their recoverable strains were lower than 3 % which limits their applications to special cases such as large diameter pipe couplings [11, 12].

Although FeSMAs have been known about for a long time, the breakthrough for the alloy design has been achieved by the discovery of FeNiCoAlTaB [12] and FeMnAlNi [13] alloys. FeNiCoAlTaB alloys exhibit high strength (1 GPa), huge superelasticity (13 %), high damping ability and good plasticity in the polycrystalline form [12]. However, it should be noted that they showed these remarkable properties only after they were alloyed with Boron for grain refinement, textured along the [100] orientation by cold rolling and then precipitation hardened [12]. Later, the thermoelastic martensitic transformation and the orientation dependence of superelasticity in single crystalline FeNiCoAlTa was studied by I. Kireeva et al.[14, 15] and they found that these alloys show a superelastic strain of 6.8 %, stress hysteresis of 130 MPa and a large superelastic temperature interval of 130 °C in the [001]-oriented single crystalline form while in tension [14, 15]. Ma et al. [16] investigated the tension-compression asymmetry along

the [100] orientation of FeNiCoAlTa and observed a transformation strain of 3.5 % in tension and 2 % in compression. Evirgen et al. studied the effects of aging on FeNiCoAlTa single crystals and revealed superelasticity with 3.4 % tensile strain [17]. The experimental superelastic strains are observed to be lower than theoretical strain levels which can be attributed to the higher volume fraction of precipitates and lower tetragonality. In addition, they have reported that FeNiCoAlTa has magnetization difference between its transforming phases where it could demonstrate field induced strain as other magnetic shape memory alloys [18-20].

Omori et al. studied the shape memory properties of FeNiCoAlNbB alloys and observed that the alloy has high ductility and shows superelasticity with 5 % strain after texture formation [21]. Recently, Kireeva et al. revealed large reversible tensile strain of 15.3 % in [001]-oriented FeNiCoAlNb single crystal [22]. It should be noted that shape memory and superelastic behaviors are functions of a large number of factors that include microstructural features such as grain size, orientation and precipitation characteristics, as well as external influences such as applied stress and temperatures [23].

In this study, we will present the shape memory response of precipitation hardened [001]-oriented $\text{Fe}_{41}\text{Ni}_{28}\text{Co}_{17}\text{Al}_{11.5}\text{Nb}_{2.5}$ (at.%) (hereafter notated as FeNiCoAlNb) single crystals that show large transformation strain, tension-compression asymmetry, and low temperature dependence.

The single crystal samples were grown by the Bridgman technique in He atmosphere by using a material with nominal composition of $\text{Fe}_{41}\text{Ni}_{28}\text{Co}_{17}\text{Al}_{11.5}\text{Nb}_{2.5}$ (at.%). Dog-boned tension samples with a working section of $2 \times 1 \times 12 \text{ mm}^3$ and compression specimens ($4 \times 4 \times 8 \text{ mm}^3$) oriented along [001] direction and with {110} surface plane were cut with an electrospark discharge machine. The single crystals were solutionized at 1200 °C for 5 hours in a vacuum and quenched with water. Then, they were heat treated at 700 °C for 3 hours to form fine precipitates. Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDX) composition analysis was performed to determine actual composition in a Zeiss EVO MA 10 instrument. The composition of the alloy was found to be $\text{Fe}_{42.6}\text{Ni}_{27.9}\text{Co}_{17.2}\text{Al}_{9.9}\text{Nb}_{2.4}$ (at.%). Transmission electron microscope (TEM) observations were conducted in a JEOL-2010F instrument operated at an acceleration voltage of 200 kV. A 100 kN MTS servohydraulic test frame was used for compression tests and strain measurements were attained by high temperature extensometer (MTS). The loading rate was applied in the strain control with a rate of 10^{-4} sec^{-1} while unloading was applied in the force control with a rate of 100 N/sec. An Omega CN8200 series temperature controller was used to govern a heating rate of 10 °C/min and a cooling rate of 5 °C/min during thermal cycling experiments.

Figure 1a shows the dark field TEM image and the corresponding diffraction pattern was taken from the circled diffraction spot of 700 °C-3h aged FeNiCoAlNb single crystal. It was found that after 700 °C-3h aging, the alloy is austenite (γ , FCC) at room temperature and precipitates (γ' , L_{12}) of about 5 nm in diameter are formed in the matrix. The DSC tests (not

shown) confirmed that no transformation is observed in aged samples when they are cooled to -150 °C. Thus, even after aging, the transformation temperatures are still very low.

In order to observe martensite at TEM and XRD, [001]-oriented FeNiCoAlNb single crystal was compressed to a strain of 8% (stress induced phase transformation was observed) and then unloaded at room temperature. Figure 1b shows the dark field TEM image and the corresponding diffraction pattern from the [110] zone axis (Figure 1c and 1d) of 700°C-3h aged and deformed single crystal. The precipitates improved the strength of the austenite and increased tetragonality of martensite that resulted in thermoelastic martensitic transformation in this alloy. When the images were analyzed, it was found that austenite, martensite (α' , BCT) and nanosize precipitates (γ') were available in the microstructure. The lattice parameters of γ and α' phases were determined as $a_0=0.3625\text{nm}$, $a=0.2761\text{ nm}$ and $c=0.3047\text{nm}$ at room temperature. Also, the XRD response of the deformed single crystal (not shown) confirmed the formation of martensite.

Figure 2a and 2b presents the tensile and compressive responses of [001]-oriented FeNiCoAlNb single crystal after aging at 700 °C for 3 hours. Transformation strain was determined at the critical stress of phase transformation by the intersection method as the difference between the strain values during loading and unloading. The tensile test was conducted at -196 °C and the alloy showed reversible superelastic strain up to 4.5 % with a low stress hysteresis of 72 MPa, as shown in figure 2a. The stress hysteresis did not change with applied strain in tension. During compression tests at -130 °C, almost perfect superelasticity was observed initially. Further loading resulted in a substantial increase in hysteresis and irrecoverable strain upon unloading. When the sample was loaded until 11%, there was a retained strain of 6.5% which was recovered upon heating as shown in figure 2b. Thus, the irrecoverable strain upon unloading can be attributed to retained martensite. As a result, transformation strain of compression was determined to be 8.8 %. It should be noted that there was a drop in stress during loading at a compressive strain of about 7.9 %. The reasons for this load drop will be discussed in the next section.

Figure 3a and 3b shows the superelastic responses of 700 °C -3h aged samples at selected temperatures in tension and compression. In tension, perfect superelasticity with low stress hysteresis was observed from -130 °C to -20 °C under stress levels reaching to 900 MPa. In compression, superelasticity was also observed for a large temperature window but at high temperatures there was some retained strain upon unloading. Stress hysteresis in compression was higher than the stress hysteresis observed tension. It should also be noted that stress hysteresis is strain dependent in compression while it is stress-independent in tension. It is clear that superelasticity is observed for a very large temperature window of about 150 °C in both cases.

It is well-known that transformation strain of SMAs is strongly dependent on the lattice parameters of transforming phases. Transformation strains can be theoretically estimated by the Energy Minimization [24] and the Lattice Deformation Theories [25]. The energy minimization

theory considers the existence of the invariant plane (habit plane) between austenite and martensite phases. The martensite plates consist of twin-related correspondence variants pairs (CVPs) which form habit planes. In the energy minimization theory, active CVPs are selected depending on the resolved shear stress on the most favorable CVPs under stress. The details of the calculation procedure of transformation strains can be found in work done by Sehitoglu et al. [26].

For the [001] orientation, the CVP and single variant (detwinned CVP) strains were both calculated to be 8.31 % in tension by using the Energy Minimization Theory. In compression, the CVP and detwinned CVP strains were determined to be 7.9 % and 14.3 %, respectively.

The lattice deformation theory does not consider the existence of habit planes. The theory assumes that the austenite transforms into a single crystal of martensite without twins. The transformation strain along the [001] orientation can be calculated in compression and tension as;

$$\varepsilon^C = \frac{(\sqrt{2} \times c) - a_0}{a_0} \times 100 = -15.5 \% \text{ and } \varepsilon^T = \frac{c - a_0}{a_0} \times 100 = 8.3 \% \quad (1)$$

The calculated compression strain is almost two times larger than it is for tension strain. Thus, it is in good agreement with the experimental findings shown in Figure 2a. The experimental values are lower than theoretical values since they are determined at the plateau region where the difference of the elastic moduli of transforming phases affects the transformation strain and further loading might be needed to obtain full martensitic transformation.

Figure 4 shows the critical stress for transformation as a function of the temperature of FeNiCoAlNb in tension and compression. Critical stresses with respect to testing temperature were depicted from figure 3a and 3b. It is clear that the critical stress for transformation increases linearly with temperature in both compression and tension. This linear behavior satisfies the Clausius-Clapeyron (C-C) relation, i.e.

$$\frac{\Delta\sigma}{\Delta T} = - \frac{\Delta H}{T_0 \varepsilon_{tr}^{max}} \quad (2)$$

where $\Delta\sigma$ is the change in the critical stress, ΔT is the change in temperature, ΔH is the transformation enthalpy, T_0 is the equilibrium temperature, and ε_{tr}^{max} is the transformation strain. The C-C slopes of [001]-oriented FeNiCoAlNb single crystals were determined to be 2.8 and 1.4 MPa/°C in tension and compression, respectively. It should be noted that C-C slope is inversely proportional to transformation strain. Therefore, it is expected that the transformation strain while in tension should be half of the transformation strain while in compression. This is in good agreement with the theoretical findings where the transformation strain was calculated to be 8.5 % in tension, and 15.5% in compression. For comparison, the C-C curves of selected alloys are also added to figure 4. The C-C slope of FeNiCoAlNb is 1.4-2.8 MPa/°C which is lower than the C-C slopes of NiTi (12 MPa/°C in compression and 8 MPa/°C in tension), comparable to FeNiCoAlTa (3.1 MPa/°C) and higher than (0.5 MPa/°C) alloys [13, 16, 27]. A low C-C slope is useful for applications that require stable superelastic behavior for a large temperature window.

[001]-oriented FeNiCoAlNb alloys provides large strain, low C-C slope and large superelastic temperature window which would be very beneficial for actuator applications.

Large tension-compression asymmetry has been reported for FeNiCoAlX (X=Ti, Ta) single crystalline alloys which can be attributed to the changes in deformation mechanisms and compatibility between the transforming phases [16, 28]. FCC structured parent phase transforms to BCT structured martensite phase during martensitic phase transformation in FeNiCoAl alloys. During deformation along the [001] orientation, formation of correspondent variant pairs (CVP) accommodates in two martensite variants in tension while it accommodates in one martensite variant in compression. The number of martensite variant difference between tension and compression affects the compatibility between transforming phases and challenges the CVP formation in compression resulting in large tension-compression asymmetry [29].

It should be noted that in Figure 2b, there was a stress drop during loading at around 7.5% compressive strain. Additionally, during heating, the remaining strain was recovered very steeply at around -40 °C. This behavior could be attributed to the burst-type transformation. Since loading was performed with strain control, the grips did not allow the fast transformation and force was dropped since the stress needed to move the transformation front is less than the stress needed for nucleation. Another reason for the load drop might be the fact that the stress required to detwin the martensite variants could be less than the stress required to form CVPs. As it was mentioned before that according to the energy minimization theory, the CVP strain along the [001] orientation is 7.9 % in compression which corresponds to the strain where the load drop was observed. The third and the least likely possibility for the load drop could stem from the multi phase transformation, where austenite might transform to one type of martensite and then that formed martensite can undergo intermartensitic transformation.

Although single crystals along the [100] orientation of FeCoNiAlNb alloys were used in this study, it is well known that polycrystals can be textured to mimic their single crystalline behavior. Previously, FeNiCoAlTaB was cold rolled to have a texture along the [100] orientation to show good superelasticity. Thus, it is expected that polycrystalline of FeCoNiAlNb alloys can also be textured to mimic the results presented here. Ferrous FeCoNiAlNb alloys have many advantages when compared to NiTi alloys. FeCoNiAlNb alloys have low temperature dependent superelastic behavior, and higher strain and strength than NiTi alloys. They can be used as an inexpensive replacement of NiTi alloys for large scale applications, or utilized as compact actuators.

The main disadvantage of FeCoNiAlNb alloys is the low transformation temperatures. With this in mind, it should be noted that shape memory properties of FeCoNiAlNb alloys can be adjusted with aging treatments and composition alterations. Therefore, in the future, composition and thermomechanical treatments can be optimized to use these alloys at higher temperature ranges.

Shape memory properties of [001]-oriented FeNiCoAlNb single crystalline ferrous shape memory alloys were characterized under tension and compression in this study. After the

homogenization process, aging at 700 °C for 3 hours was employed to form precipitates (γ' , $L1_2$) of about 5 nm in diameter to observe thermoelastic martensitic transformation from austenite (γ , FCC) to martensite (α' , BCT). Superelasticity experiments revealed that FeNiCoAlNb single crystals showed high compression-tension asymmetry and shape recovery of about 4.5 % in tension and 8.8 % in compression. Moreover, they were weakly temperature dependent and showed low C-C slopes which were 2.8 MPa/°C in tension and 1.4 MPa/°C in compression due to large transformation strain. The findings of this study show that FeNiCoAlNb alloys have promising shape memory properties for temperature independent and large scale actuator applications.

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- [1] S. Kajiwar, T. Kikuchi, *Acta Metall Mater*, 38 (1990) 847-855.
- [2] A. Sato, E. Chishima, Y. Yamaji, T. Mori, *Acta Metallurgica*, 32 (1984) 539-547.
- [3] A. Sato, E. Chishima, K. Soma, T. Mori, *Acta Metallurgica*, 30 (1982) 1177-1183.
- [4] K. Ando, T. Omori, I. Ohnuma, R. Kainuma, K. Ishida, *Appl. Phys. Lett.*, 95 (2009).
- [5] O.M. Shevchenko, G.V. Gavriluk, V.V. Kokorin, V.A. Chernenko, *Powder Metall Met C+*, 36 (1997) 71-76.
- [6] T. Maki, K. Kobayashi, M. Minato, I. Tamura, *Scripta Metallurgica*, 18 (1984) 1105-1109.
- [7] T. Kakeshita, K. Shimizu, T. Maki, I. Tamura, S. Kijima, M. Date, *Scripta Metallurgica*, 19 (1985) 973-976.
- [8] V.V. Kokorin, L.P. Gunko, O.M. Shevchenko, *Scr. Metall. Materialia*, 28 (1993) 35-40.
- [9] H. Sehitoglu, I. Karaman, X.Y. Zhang, Y. Chumlyakov, H.J. Maier, *Scripta Materialia*, 44 (2001) 779-784.
- [10] E. Hornbogen, N. Jost, *J. Phys. IV*, 1 (1991) 199-210.
- [11] H. Sehitoglu, X.Y. Zhang, T. Kotil, D. Canadinc, Y. Chumlyakov, H.J. Maier, *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, 33 (2002) 3661-3672.
- [12] Y. Tanaka, Y. Himuro, R. Kainuma, Y. Sutou, T. Omori, K. Ishida, *Science*, 327 (2010) 1488-1490.
- [13] T. Omori, K. Ando, M. Okano, X. Xu, Y. Tanaka, I. Ohnuma, R. Kainuma, K. Ishida, *Science*, 333 (2011) 68-71.
- [14] I.V. Kireeva, Y.I. Chumlyakov, V.A. Kirillov, I. Karaman, E. Cesari, *Tech Phys Lett+*, 37 (2011) 487-490.
- [15] I.V. Kireeva, Y.I. Chumlyakov, V.A. Kirillov, I.V. Kretinina, Y.N. Danil'son, I. Karaman, E. Cesari, *Russ Phys J+*, 53 (2011) 1103-1106.
- [16] J. Ma, B. Kockar, A. Evirgen, I. Karaman, Z.P. Luo, Y.I. Chumlyakov, *Acta Materialia*, 60 (2012) 2186-2195.
- [17] A. Evirgen, J. Ma, I. Karaman, Z. Luo, Y. Chumlyakov, *Scripta Materialia*, 67 (2012) 475-478.
- [18] A. Turabi, H. Karaca, H. Tobe, B. Basaran, Y. Aydogdu, Y. Chumlyakov, *Scripta Materialia*, 111 (2016) 110-113.
- [19] H.E. Karaca, I. Karaman, B. Basaran, Y. Ren, Y.I. Chumlyakov, H.J. Maier, *Advanced Functional Materials*, 19 (2009) 983-998.
- [20] H. Karaca, I. Karaman, B. Basaran, Y.I. Chumlyakov, H. Maier, *Acta Materialia*, 54 (2006) 233-245.

- [21] T. Omori, S. Abe, Y. Tanaka, D.Y. Lee, K. Ishida, R. Kainuma, *Scripta Materialia*, 69 (2013) 812-815.
- [22] Y.I. Chumlyakov, I.V. Kireeva, O.g.A. Kutz, A.S. Turabi, H.E. Karaca, I. Karaman, *Scripta Materialia* in press (2016).
- [23] J. Ma, I. Karaman, R.D. Noebe, *Int. Mater. Rev.*, 55 (2010) 257-315.
- [24] J.M. Ball, R.D. James, *Arch. Ration. Mech. Anal.*, 100 (1987) 13-52.
- [25] T. Saburi, S. Nenno, *Solid to Solid Phase Transformations*, (1981) 1455-1479.
- [26] H. Sehitoglu, I. Karaman, R. Anderson, X. Zhang, K. Gall, H.J. Maier, Y. Chumlyakov, *Acta Materialia*, 48 (2000) 3311-3326.
- [27] L. Orgas, D. Favier, *Acta Materialia*, 46 (1998) 5579-5591.
- [28] L. Tseng, J. Ma, I. Karaman, S. Wang, Y. Chumlyakov, *Scripta Materialia*, 101 (2015) 1-4.
- [29] J. Ma, B. Hornbuckle, I. Karaman, G. Thompson, Z. Luo, Y. Chumlyakov, *Acta Materialia*, 61 (2013) 3445-3455.

Figure 1: a) The dark field TEM image and the corresponding diffraction pattern taken from the circled diffraction spot of 700C-3h aged FeNiCoAlNb single crystal. b) The dark field TEM image on pre-deformed sample until 8 % at room temperature. c and d) corresponding diffraction patterns from the [110] zone axis on deformed sample.

Figure 2: The tensile and compressive responses of [001]-oriented FeNiCoAlNb single crystal after aging at 700C for 3 hours

Figure 3: Superelastic responses of [001]-oriented and 700C-3h aged FeNiCoAlNb single crystal at selected temperatures in **a)** tension and **b)** compression.

Figure 4: The critical stress for transformation as a function of temperature of FeNiCoAlNb in tension and compression. For comparison, the C-C curves of NiTi, FeMnAlNi and FeNiCoAlTa are added [13, 16, 27].

Figure 1

Figure 2

Figure 3

Figure 4

Graphical Abstract