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Shape memory and pseudoelasticity response of NiMnCoIn magnetic shape memory alloy single crystals

H.E. Karaca,[a] I. Karaman,[a,*] A. Brewer,[a] B. Basaran,[a] Y.I. Chumlyakov[b] and H.J. Maier[c]

[a]*Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA*
[b]*Siberian Physical-Technical Institute, Tomsk 634050, Russia*
[c]*Lehrstuhl für Werkstoffkunde, University of Paderborn, 33095 Paderborn, Germany*

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The shape memory characteristics of $Ni_{45}Mn_{36.5}Co_5In_{13.5}$ single crystals, which exhibit magnetic field-induced phase transformation (FIPT), were investigated under compression along the [1 0 0] orientation. The effects of temperature and bias stress on the pseudoelastic response and the shape memory effect were explored. The crystals demonstrated large stress and temperature hysteresis with a fully reversible transformation strain of 5.4%, the ramifications of which on the field requirement for FIPT are discussed.

Keywords: Magnetic shape memory alloys; Phase transformation; NiMnCoIn; Thermal hysteresis; Magnetic field induced strain

In magnetic shape memory alloys (MSMAs), the main mechanism utilized for magnetic field-induced shape change has been martensite variant reorientation triggered by a magnetic field [1]. In NiMnGa alloys, this mechanism results in recoverable magnetic field-induced strains (MFIS) up to 10% but with actuation stresses less than 5 MPa [1]. Alternatively, we have recently shown the possibility of magnetic field-induced phase transformation (FIPT) in these alloys [2]. Utilizing reversible FIPT, almost an order of magnitude increase in actuation stress (~20 MPa) was achieved with the MFIS level of 0.5% under low magnetic fields [3]. A necessary condition for FIPT was identified as the pseudoelastic stress hysteresis being lower than the magnetostress, which is defined as the amount of change in the critical stress for phase transformation under a given field [3]. Similarly, transformation thermal hysteresis should be lower than the change in transformation temperatures under the field.

In the last few years, a new family of MSMAs, called meta-magnetic SMAs such as the NiMnX alloys ($X = \mathrm{In, Sn, Sb}$), was discovered where FIPT was observed between a ferromagnetic austenite and an antiferromagnetic martensite [4]. In this mechanism, the Zeeman energy is employed as the main source for the required energy as opposed to the magnetocrystalline anisotropy energy (MAE), which triggers the field-induced martensite reorientation. Zeeman energy is less sensitive to crystal orientation than MAE, thus providing an opportunity to utilize polycrystals in actuators [3]. In contrast to the fixed maximum MAE levels, Zeeman energy increases continuously with the field and so can actuation stress. To intensify the available magnetic energy further in these meta-magnetic SMAs, the effects of quaternary cobalt addition have been investigated [5]. Co increases the Curie temperature and saturation magnetization in these alloys [6]. In turn, this increases the Zeeman energy and decreases the required critical magnetic field for FIPT.

Kainuma et al. [5] recently reported the aforementioned FIPT mechanism in a few NiMnCoIn alloys and noted a decrease in their transformation temperatures with the field. They have also reported a magnetoelastic magnetization response where martensite transforms to austenite above a certain field, and then transforms back upon reducing the field. One-way 3% MFIS was obtained in a predeformed single crystal under a field of 4 T. Later, Wang et al. [7] observed reversible FIPT in a $Ni_{45}Mn_{36.6}Co_5In_{13.4}$ alloy with the application of 5 T under 50 MPa.

Obviously, the required magnetic field for FIPT in NiMnCoIn alloys is still high for applications. This is partially because of the large transformation hysteresis. There are some microstructural factors influencing

* Corresponding author. Tel.: +1 979 862 3923; fax: +1 979 862 2418; e-mail: ikaraman@tamu.edu

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conventional shape memory properties [8] that can be engineered to decrease the hysteresis of these alloys. However, this initially requires a systematic work on the shape memory and pseudoelastic response of MSMAs to assess hysteretic transformation behavior. Without a proper understanding of the SMA characteristics, it is not possible to fully comprehend their magnetic shape memory response.

Thus, in this study, the shape memory response of a NiMnCoIn alloy single crystal was characterized along the [1 0 0] orientation. The effects of stress and/or temperature on the transformation temperatures, strain and hysteresis were investigated, along with the critical stress for transformation. The [1 0 0] orientation was chosen since, in similar alloys, transformation strain and resistance against plastic deformation are relatively high in this orientation under uniaxial loading [9].

An ingot of $Ni_{45}Mn_{36.5}Co_5In_{13.5}$ was prepared using vacuum induction melting. Single crystals were grown using the Bridgman technique in He atmosphere. Compression samples ($4 \times 4 \times 8\ mm^3$) were cut with their long axes along the [1 0 0] orientation of the parent phase. The samples were homogenized at 900 °C for 24 h in vacuum. The mechanical experiments were conducted using an MTS servohydraulic test frame. A capacitive displacement sensor was used to measure the strain. The heating/cooling of the samples was achieved by conduction through compression plates with a rate of 10 °C min^{-1}.

Compositional analysis of the samples was carried out on a four-spectrometer Cameca SX50 electron microprobe at an accelerating voltage of 15 kV. Figure 1 shows a back-scattered electron image of a heat-treated crystal. Second-phase particles are evident which were inherited from the as-grown crystals and could not be eliminated by the selected heat treatment. Wavelength-dispersive spectroscopy revealed the composition of the matrix and the second phase as $Ni_{45.7}Mn_{35.6}Co_{4.8}In_{13.8}$ and $Ni_{42.0}Mn_{40.3}Co_{16.0}In_{1.6}$, respectively. Some sulfur contamination (dark spots in Figure 1) was present, but the total content was only 0.005 wt.%.

Figure 2 shows the thermal cycling response under various constant compressive stress levels. The stress was isothermally applied to the austenite and the sample

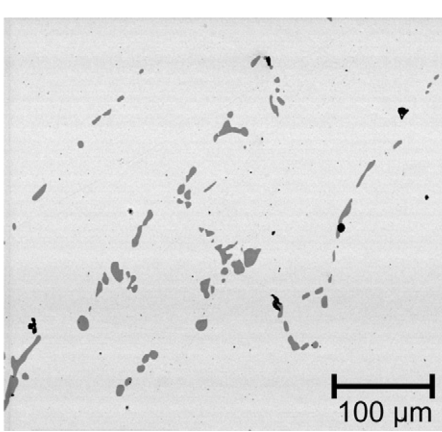

Figure 1. Back-scattered electron image of a $Ni_{45}Mn_{36.5}Co_5In_{13.5}$ single crystal heat treated at 900 °C for 24 h in vacuum.

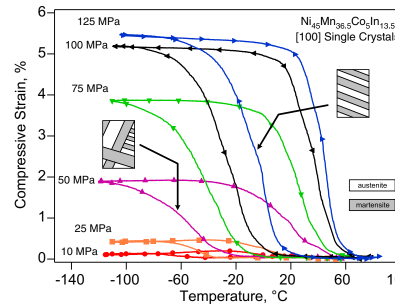

Figure 2. The strain vs. temperature response of $Ni_{45}Mn_{36.5}Co_5In_{13.5}$ single crystals under constant compressive stress levels applied along the [1 0 0] orientation. The insets show the possible microstructural evolution under the different stress levels, as discussed in the main text.

was thermally cycled between a temperature below the martensite finish temperature (M_f) and a temperature above the austenite finish temperature (A_f) at this stress. After the cycle was completed, the stress was increased further and the thermal cycling was repeated. Clearly, the transformation strain (ε_{tr}) increases with stress, concomitantly with the transformation temperatures, from 0.2% under 10 MPa to 5.4% under 125 MPa. Note that the second-phase particles do not transform.

Figure 3 shows the pseudoelastic response of the [0 0 1] crystals at 0, 20 and 50 °C. As the stress increases, austenite ($L2_1$ cubic phase) deforms elastically and then transforms to martensite (14M modulated structure [5]) with notable hardening in the plateau region, followed by further transformation of remnant austenite and simultaneous elastic deformation of martensite. Upon unloading, martensite relaxes elastically and transforms back to austenite before the elastic relaxation of austenite takes place. ε_{tr} is determined to be 5.2% in the plateau region at 0 °C, which is in good agreement with ε_{tr} detected in Figure 2. The stress hysteresis is approximately 110 MPa at 0 °C and increases with temperature.

Figure 4 presents the M_s temperature as a function of applied stress, determined from the thermal cycles in Figure 2 and the critical stress for the forward transformation (σ_{SIM}) as a function of test temperature, extracted from Figure 3. The results from these separate experiments are in good agreement with each other, indicating that the critical stress and temperature for the transformation increases linearly with each other. This linear dependence can be expressed following the Clausius–Clapeyron (CC) relation, i.e.

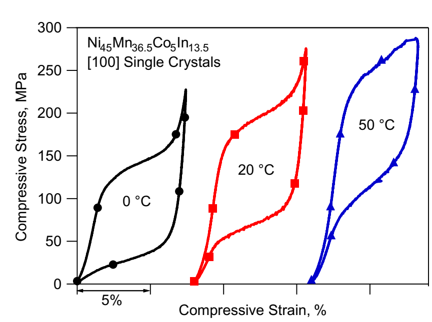

Figure 3. Pseudoelastic response of the $Ni_{45}Mn_{36.5}Co_5In_{13.5}$ single crystals as a function temperature under compression.