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Shape memory effect and superelasticity of NiMnCoIn metamagnetic shape memory alloys under high magnetic field

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ABSTRACT

The effects of the magnetic field on the shape memory behavior of [001]-oriented metamagnetic NiMnCoIn shape memory single crystals were investigated. Thermal cycling under constant stress and magnetic field, and stress cycling under constant magnetic field tests were conducted to understand their magneto-thermo-mechanical behavior. It was observed that critical stress during the superelastic behavior increased and transformation temperatures decreased with the applied field. Under 9 T applied field, compared to all magnetic shape memory alloys, an ultrahigh magnetostress level of 71 MPa was observed during the stress cycling experiments and transformation temperatures were decreased by 16 °C during the thermal cycling under stress.

Magnetic shape memory alloys have been widely investigated in the past decade due to their ability to produce large magnetic field induced strain and show high frequency response [1–4]. NiMnGa alloys are the workhorse of magnetic shape memory alloys that show high magnetic field induced strain (5–10%) by variant reorientation, and have high thermal stability in single crystalline form [4–7]. The main magnetic energy source of variant reorientation mechanism is the magnetocrystalline anisotropy energy (MAE), which is limited and does not increase with applied field after a critical value, resulting in low magnetostress values. It should also be noted that NiMnGa alloys are intrinsically brittle and they can only be utilized in single crystalline or textured forms since MAE is highly orientation dependent [8,5]. Field induced phase transformation in NiMnGa is only possible under special conditions such as at temperatures very close to A_s or when X-phase is observed [9,10]. However, the available magnetic energy for phase transformation is still limited, resulting in low magnetostress values. Thus, these factors limit the potential applications of NiMnGa alloys as magnetic actuators.

NiMn-based metamagnetic shape memory alloys such as NiMnIn [11], NiMnSn [12] and NiMnCoSb [13] have the ability to exhibit magnetic field induced phase transformation. In general, austenite is ferromagnetic and martensite is weakly magnetic (paramagnetic or antiferromagnetic) in these alloys. Thus, the difference between the magnetization values of transforming phases creates Zeeman energy which is the main source of field induced phase transformation. It should be noted that Zeeman energy increases with applied field and it is orientation independent. Appropriately, metamagnetic shape memory alloys could work in polycrystalline form and provide higher actuation stress values than conventional NiMnGa alloys. Earlier studies conducted by Karaca et al. observed a high magnetostress value of approximately 30 MPa under 1.6 T in NiMnCoIn alloys which is nearly five times higher than that observed in NiMnGa alloys (6 MPa) [14]. High actuation stress levels in metamagnetic shape memory alloys are essential for magnetic actuation applications.

In order to determine transformation strain in shape memory alloys, it is necessary to observe the formation of reoriented (detwinned) martensite variants instead of self-accommodated martensite variants. Since ferromagnetic austenite and weakly magnetic martensite have negligible MAEs, self-accommodating martensite variants are not biased with magnetic field. Krenke et al. reported that in the absence of applied stress, $Ni_{50}Mn_{34}In_{16}$ polycrystalline alloy exhibits only 0.12% strain with magnetic superelasticity due to magnetic field induced phase transformation [15]. Liu et al. also studied the effects of temperature and training of a textured $Ni_{45.2}Mn_{36.7}In_{13}Co_{5.1}$ and reported a maximum magnetostrain of 0.25% under 5 T after training [16]. Therefore, either

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external stress or training to show two-way shape memory effect is necessary to produce large magnetic field induced strain.

In this study, effects of magnetic field (up to 9 Tesla) on the shape memory and superelastic responses of [001]-oriented NiMnCoIn single crystals were systematically determined under compression. Thermal cycling under stress and superelasticity experiments at selected magnetic fields were conducted to reveal the change in transformation temperatures and critical stress with magnetic field.

The ingots with nominal composition of $Ni_{45}Mn_{36.5}Co_5In_{13.5}$ (at. %) were fabricated by induction melting under vacuum. The Bridgman technique, in He atmosphere, was used to grow single crystals from the ingots. Compression specimens ($4 \times 4 \times 8\ mm^3$) were cut with their long axes along the [001] orientation of the austenite phase. Transformation temperatures were determined by Perkin Elmer PYRIS 1 differential scanning calorimetry (DSC). In order to analyze the microstructure, each specimen was dropped in etchant solution, which contains 75 ml HCl, 75 ml ethanol, 15 g $CuSO_4$ and 10 ml distilled water, and taken out immediately. A KEYENCE VH-S5 digital microscope was used to determine microstructure. Chemical composition analysis was obtained with EDS by a Hitachi S3200 Scanning Electron Microscope (SEM). QUANTUM DESIGN (QD) 14 T Physical Properties Measurement System (PPMS) was used for magnetization experiment to determine martensitic phase transformation during heating and cooling under applied magnetic field. A 100 kN MTS servohydraulic test frame was used for compression tests. Magnetic field was applied by a Cryogenic Limited 9 Tesla PID controlled cryogen free superconducting magnet which was attached to the MTS servohydraulic test frame. Transformation strain was measured by a capacitec sensor. 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 for heating–cooling under magnetic field and compressive stress experiment.

Fig. 1a shows the DSC response of the NiMnCoIn single crystal. The exothermic peak corresponds to the forward transformation upon cooling and the endothermic peak corresponds to the back transformation during heating. During cooling, the martensite transformation start temperature (M_s) and finish temperature (M_f) were found to be 91.2 °C and 37.2 °C, respectively. The reverse transformation start temperature (A_s) and finish temperature (A_f) were determined to be 56.9 °C and 104.1 °C. The small peak observed at 115 °C indicates the Curie temperature of austenite. Fig. 1b shows the microstructure of as-grown sample at room temperature where the sample was martensite. In addition martensite variants, formation of secondary phases are observed in the optical micrograph. The chemical composition of matrix and other phases were determined by SEM/EDS. Composition of the martensite matrix was found as $Ni_{44.6}Mn_{36.6}Co_{4.8}In_{14}$, whereas the dark region and white small particles in the secondary phases were determined as $Ni_{44}Mn_{36.1}Co_{5.7}In_{14.2}$ and $Ni_{40.1}Mn_{38.6}Co_{20.2}In_{1.1}$, respectively. It should be noted that the transformation temperatures of the alloy studied here were relatively higher than what was reported previously on $Ni_{45}Mn_{36.5}Co_5In_{13.5}$ alloys due to slightly different matrix composition and second phase formation during fabrication [17]. By XRD analysis (results are not shown), the lattice structures of austenite and martensite were determined to be cubic $L2_1$ and monoclinic 14M, respectively.

Phase transformation behavior of the single crystals was monitored by the change in magnetization during temperature cycling under constant magnetic field experiments, as shown in Fig. 2. Selected magnetic fields from 0.05 T to 12 T were applied in austenite phase and temperature was cycled between 127 °C and −173 °C. Under 0.05 T, forward transformation began at 79 °C and ended at 12 °C while back transformation began at 33 °C and completed at 95 °C. Under 12 T, austenite transformed to martensite between 25 °C and −69 °C while the reverse martensitic transformation started at −30 °C and ended at 57 °C. It is clear that transformation temperatures shifted to lower temperatures by increasing the magnetic field. On the contrary, the maximum difference of magnetization between the austenite and martensite phases was determined to be 32.4 emu/g under 0.05 T, 41.1 emu/g under 3 T and 30.4 emu/g under 12 T. Ito et al. reported that martensitic transformation is arrested during field cooling and is not continued with further cooling in metamagnetic shape memory alloys due to the disappearance of a driving force [18]. Thus, we can conclude that in NiMnCoIn single crystals, austenite stabilizes at low temperatures upon field cooling under magnetic fields of 3 T or higher, resulting in incomplete phase transformation and decreased magnetization difference.

It should be noted that although magnetization as a function of temperature under constant magnetic field or magnetic field at selected temperatures provides useful information about the magnetization behavior and transformation temperatures, it does not provide any information about the shape memory properties such

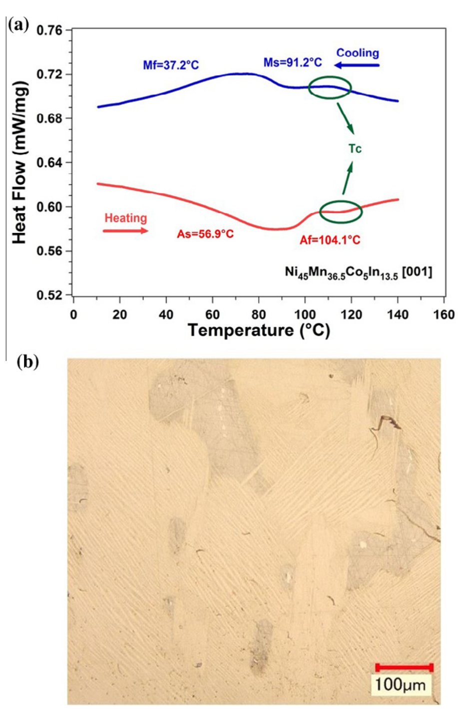

Fig. 1. (a) DSC response of NiMnCoIn single crystal and (b) optical image of the microstructure at room temperature.

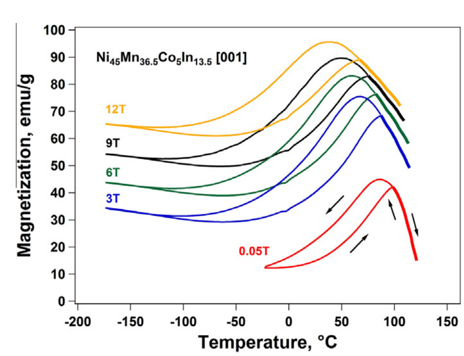

Fig. 2. Magnetization vs. temperature response of NiMnCoIn single crystal under selected magnetic fields.