Shell-ferromagnetism in Ni-Mn-based Heuslers in view of ductile Ni-Mn-Al

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Shell-ferromagnetism in Ni-Mn-based Heuslers in view of ductile Ni-Mn-Al

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The present work deals with magnetic and structural phase instabilities in Ni-Mn-based Heusler alloys especially Ni-Mn-Al. The temper-annealed $Ni_{50}Mn_{45}Al_5$ Heusler alloy decomposes into the full stoichiometric Ni_2MnAl and NiMn phases. The decomposed stoichiometric Heusler forms precipitates in an anti-ferromagnetic NiMn matrix and exhibits shell-ferromagnetic properties when the temper-annealing is performed under magnetic field. The shell-ferromagnetism results from the magnetic proximity effect and is observed as vertically shifted magnetization loops. The presence of this property in $Ni_{50}Mn_{45}Al_5$ adds the possibility of having a ductile material while preserving the shell-ferromagnetic properties. [http://dx.doi.org/10.1063/1.4975792]

After their discovery in the beginning of the 20th century, Heusler alloys were intensively investigated because of their ferromagnetism, and later, at the turn of the 21st century, they reattracted interest because of their emerging multifunctional properties such as magnetic shape-memory (MSM), magneto-caloric effect (MCE), spintronic applications, and giant magneto-resistance (GMR).[1] Especially, Ni-Mn-based type Heuslers with 3A-5A group elements Al, Ga, In, Sn, and Sb have been found to exhibit functionalities opening new application areas.[2–4] The origin of these functionalities lie in the strong coupling between magnetic and structural degrees of freedom through the martensitic transitions and the accompanied large change of the magnetization. Also, the magnetic and martensitic transition temperatures can be tailored by varying the composition choosing various combinations of the main group elements, thereby adjusting the temperature range of the functionality.

Ni_2MnGa exhibits a martensitic transition below room temperature and is ferromagnetic (FM) in both austenitic and martensitic phases.[5] These alloys exhibit the MSM effect showing magnetic-field-induced strain (MFIS) up to 10% depending on the martensite structure.[2,6] Furthermore, Ni-Mn-*X*-type (*X*: In Sn, and Sb) Heusler alloys are found to be important for their MCE and GMR properties.[7] Recent studies have also shown the presence of zero-field-cooled and spin-reoriented exchange-bias properties in these alloys which can be employed in applications related to spintronics.[8] *X* as Al is a case in its own. Ni_2MnAl, isoelectronic to Ni_2MnGa and Ni_2MnIn, is antiferromagnetic (AF) and does not transform martensitically.[9] Very long-time heat treatments within the $L2_1$ phase bring in only partial FM exchange, and the martensitic transition begins to occur at slight off-stoichiometry. The virtue of Ni-Mn-Al is that it is ductile. However, the strong AF coupling in this compound hinders the development of possible functional properties.

In spite of these favorable functionalities, recent experimental and theoretical studies have shown that Ni-Mn-based Heusler alloys are not necessarily stable in their martensitic structures at low temperatures.[10] On decreasing temperature, modulated martensitic phases tend to transform to the non-modulated martensite structure which is more favorable energetically.[11,12] Additionally, the same materials also exhibit metastable behavior when temper-annealed at high temperatures.[4,13–15]

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Recently, it was found that AF tetragonal Mn-rich Ni-Mn-*X* Heusler alloys, with *X* as Ga, In, and Sn, decompose into a FM Heusler component as precipitates embedded in an AF NiMn matrix when annealed around 650-750 K. When the annealing takes place under a magnetic field, the precipitates form a shell-FM structure with a paramagnetic (PM) core giving rise to vertically shifted magnetization loops.[4] These structures are particularly relevant to non-volatile magnetic memory, being both magnetic-field-proof and heat resistant.

In the present work, the properties shell-FM precipitates of a Mn-rich Ni-Mn-Al Heusler alloy is investigated prepared by temper-annealing under magnetic field. This gives the possibility in making use of the favorable ductility of Ni-Mn-Al as relatively more durable material than the other Ni-Mn-based Heuslers for use in non-volatile memory applications.

$Ni_{50}Mn_{45}Al_5$ was prepared by arc melting high purity elements. For attaining homogeneity, it was annealed under Ar at 1073 K in sealed quartz tubes for 5 days. A part of the sample was pulverized, and the powder sample was used for magnetization measurements. The compositions were determined by energy dispersive x-ray analysis for both powder and bulk. Magnetization measurements as a function of time M(time), temperature $M(T)$, and magnetic field $M(H)$ were carried out using a superconducting quantum interference device magnetometer with fields up to 5 T and in the temperature range $300 \leq T \leq 750$ K.

$M(T)$ measurements were taken under a 5 T magnetic field on sequential thermal cycling as shown in fig. 1. The sample is first warmed from 300 K up to 500 K then cooled back down to 400 K. A deviation of the 500-400 K-path from the initial 300-500 K path is already seen. Subsequent warming up to 600 K and cooling back to 550 K also causes a change in path. Each path-change is an indication of decomposition. This becomes more obvious when the cycling is carried up to 750 K and back to 300 K. When the sample is taken again up to 750 K and allowed to remain at this temperature for 1 hour, $M(T)$ shows even a more rapid increase with decreasing temperature indicating that FM exchange has generated in the sample.

M(time) and $M(H)$ measurements were carried out to observe the temper-annealing properties of a $Ni_{50}Mn_{45}Al_5$ Heusler alloy. M(time) taken at 650 K annealing temperature and under 5 T is given in fig. 2. M(time) increases steadily with increasing annealing time and exhibits a fine structure at about 1.5 h; the origin of this effect being presently not known. Increasing M with progressing time demonstrates that $Ni_{50}Mn_{45}Al_5$ is magnetically not stable at the temper-annealing temperature 650 K. Analogous to the arguments in our previous studies on Ni-Mn-*X* (*X*: Ga, In, and Sn), $Ni_{50}Mn_{45}Al_5$ tends to decompose into Ni_2MnAl and and NiMn.[4,13,16] NiMn is AF, and consequently, it remains for Ni_2MnAl to become FM. Therefore, we find that ferromagnetism can indeed be stabilized in Ni_2MnAl precipitates, contrary to the fact that it is difficult to introduce FM interactions in this material when prepared in bulk form.

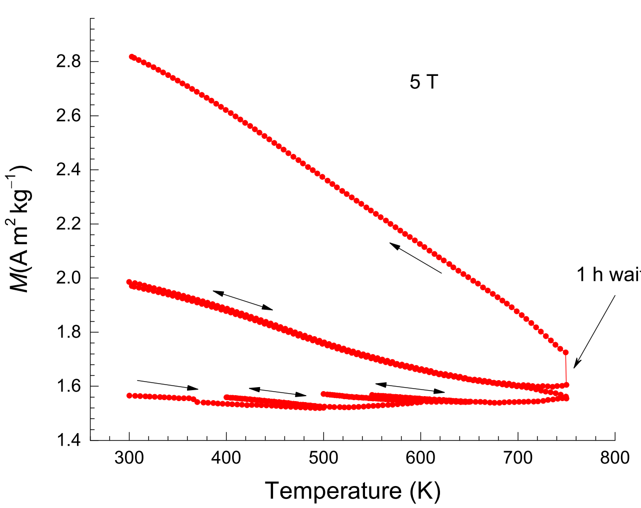

FIG. 1. Temperature dependent cycling magnetization change under 5 T magnetic field.

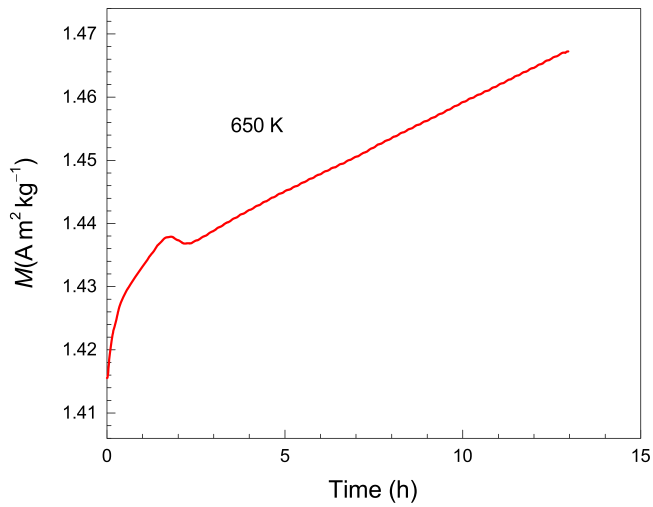

FIG. 2. Time dependent magnetization measurement of $Ni_{51.87}Mn_{43.73}Al_{4.40}$ Heusler alloy at 650 K annealing temperature and under 5 T magnetic field.

Vertically shifted $M(H)$-loops in fig. 3a–d suggests the occurrence of shell-ferromagnetic decomposition when annealing takes place under a magnetic field. $M(H)$ measurements of the 650 K annealed sample is given in fig. 3a–d at at 450 K, 400 K, 350 K and 300 K, respectively. A vertical shift is observed at the 450 K hysteresis loop in fig. 3a. The vertical shifts can be similarly noticed in the lower temperature $M(H)$ data at 400, 350, and 300 K in fig. 3b–d, respectively.

Additionally, $M(H)$ measurement of the 750 K annealed sample is given in fig. 4 at 450 K. Although the decomposition is more progressed at this temperature (fig. 1), it is seen that the vertical shift is more evident in the $M(H)$ measurement of the 650 K annealed sample (fig. 3). When annealed at 750 K, the volume gets too large, and the vertical shift effect arising from the surface is masked.

Ni-Mn-based Heusler systems Ni-Mn-X (X: Ga, Sn, In, Al) are metastable and decompose when temper-annealed. The decomposition leads to shell-FM precipitates embedded in an AF matrix when the decomposition is carried out under a magnetic field. The FM pining is along the direction of

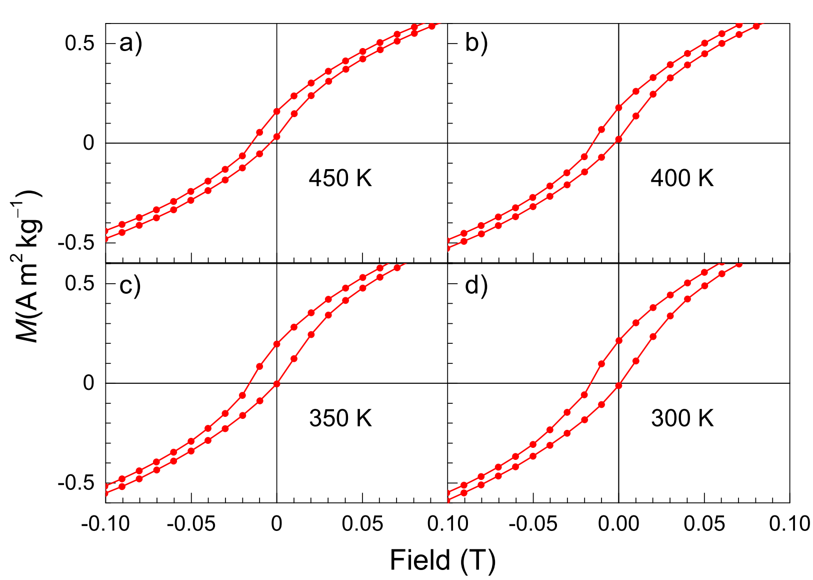

FIG. 3. $M(H)$ measurements of the 650 K annealed sample at a) 450 K, b) 400 K, c) 350 K, and d) 300 K.

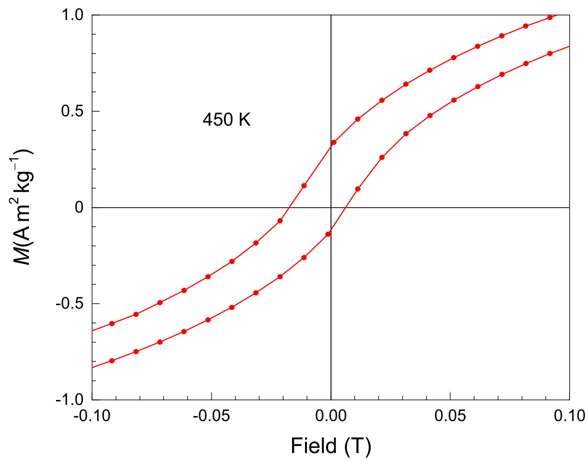

FIG. 4. $M(H)$ measurements of the 750 K annealed sample at 450 K.

the magnetic field. The occurrence of shell-ferromagnetism particularly in Ni-Mn-Al provides the possibility to prepare such functional materials with better ductility.

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