Martensitic transformation and magnetic domains in Mn$_{50}$Ni$_{40}$Sn$_{10}$ studied by in-situ transmission electron microscopy

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The structural features, martensitic transformation, and magnetic domains in the Mn$_{50}$Ni$_{40}$Sn$_{10}$ Heusler alloy are investigated by in-situ transmission electron microscopy and Lorentz microscopy. A rich variety of microstructural phenomena arising from structural and magnetic transitions are demonstrated at low temperatures. The “5M” or “6M” superstructure modulations and needle-shaped martensites have been clearly observed in the martensitic phase. Structural evolutions of magnetic domains are revealed under in-situ applied magnetic fields using Lorentz microscopy. The structural domains and reversibility of the phase transitions are analyzed based on our experimental observations and discussed in comparison with results of low-temperature magnetization. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4740458]

I. INTRODUCTION

Ferromagnetic (FM) shape memory alloys have attracted considerable attention because of their potential applications as fast-response sensors and compact actuators. In past decades, a variety of notable materials have been extensively investigated, including Ni-Mn-Ga, Co-Ni-Al, Fe-Pd, and Fe-Pt. Recently, remarkable exchange bias features arising from antiferromagnetic and ferromagnetic exchange interaction have been observed in Heusler alloys Ni-Mn-X (X = Sb, Sn, In), and a large exchange bias field of 1170 Oe was observed in Mn$_{50}$Ni$_{40}$Sn$_{10}$ as prepared by a deep cooling method. The large exchange bias field could have important applications in novel devices, e.g., ultrahigh-density magnetic recorders, sensors, and spintronic devices. In addition, the coexistence of reentrant spin glass (RSG) and ferromagnetic martensitic phase was reported to be responsible for the giant exchange bias in the martensitic phase below 117 K. Experimental investigations demonstrated that both magnetic and martensitic transitions (MT) in this kind of alloy can be controlled by Sn concentration. Crystal structural analyses revealed that Mn$_{50}$Ni$_{50-x}$Sn$_x$ shape memory alloys in general adopt an off-stoichiometric Hg$_2$CuTi-type structure at room temperature (RT), i.e., a highly-ordered bcc structure with the space group of F-43m. The Mn$_{50}$Ni$_{50}$Sn$_{10}$ material undergoes a ferromagnetic transition at around $T_c = 270$ K and a martensitic transition at around 214 K. In previous studies, certain fundamental properties for the MT and magnetic domains have been studied in some typical materials. Nevertheless, the evolution of microstructure associated with MT remains an open problem in Mn$_{50}$Ni$_{50-x}$Sn$_x$. In present paper, we report our in-situ TEM and Lorentz microscopy observations of the structural changes following the MT and magnetic transition in a sample with nominal composition of Mn$_{50}$Ni$_{50}$Sn$_{10}$. The evolution of magnetic domains under an applied field was also examined at the temperature of 255 K.

II. EXPERIMENTAL

Samples used in the present study were prepared by arc melting high purity (99.99%) powers of Mn, Ni, and Sn in an argon atmosphere. Annealing were carried out at 1073 K for 72 h in an evacuated quartz ampoules followed by quenching into liquid nitrogen. Ribbon samples were prepared by spinning the melt of the precursor ingot with a nominal composition of Mn$_{50}$Ni$_{40}$Sn$_{10}$, which undergoes a ferromagnetic transition at about 270 K and then a MT at $\sim$214 K. In order to avoid stress that grinding would induce during the TEM sample preparation, the 40 $\mu$m thick ribbons were selected and polished mechanically to about 20 $\mu$m, then ion-milled by a Gatan-691 PIPS. Microstructure analyses were performed on Tecnai F20 (200 kV) field-emission TEM equipped with Lorentz lens. The specimens were cooled from room temperature to 100 K in a Gatan double-tilt liquid nitrogen cooling holder in order to observe the MT and the evolution of magnetic domains.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows a typical selected-area electron diffraction (SAED) pattern taken along the [1-10] zone-axis direction for a Mn$_{50}$Ni$_{40}$Sn$_{10}$ ribbon at room temperature. The appearance of sharp [111] and [113] diffraction spots suggests that this sample has an off-stoichiometric Hg$_2$CuTi structure. The main diffraction spots as indicated by stars can be well indexed by a cubic cell with the lattice parameter of $a = 6.01$ Å. The most notable microstructural feature revealed in our observations is the presence of additional reflection spots and diffuse streaks along the $\langle -2, -2, 4 \rangle$ direction as indicated by a white arrow. Similar structural features have also been observed in Ni$_2$FeGa. Actually, this structural phenomenon originates from complex microdomains commonly existing in such materials.

In order to better understand the microstructural features in correlation with MT in the present system, we performed extensive in-situ TEM observations at low temperatures.
Figures 1(b)–1(d) show a few SAED patterns taken from a number of crystals along the [001] zone axis direction, illustrating the structural features of the low-temperature martensitic phase at 100 K. It is recognizable that, in addition to the main diffraction spots, superlattice spots and diffused streaks along the \(h_{110}\) direction commonly appear in the low-temperature diffraction patterns. In addition, notable monoclinic structural distortions also appear in certain crystals. Figure 1(b) shows a SAED pattern containing clear “5M” superstructure spots. This modulation goes along the [1–10] direction with a monoclinic angle 87.4°. We can also see another un-modulated variant which tends to adopt a distorted face-centered square with an angle of \(~85\)° between two reciprocal vectors, this structural feature can be well interpreted by twinning of domains in the low-temperature martensitic phase as discussed in one of our previous publications.16 Figure 1(c) shows a “5M” modulated diffraction pattern with a monoclinic angle of 85.3°. Note the presence of diffuse streaks accompanying the “5M” superlattice spots, suggesting the existence of complex domain structures arising from the martensitic phase transition. Figure 1(d) shows an electron diffraction pattern taken from an area with two clear sets of “6M” modulations, and these two sets of “6M” modulations are rotated 85.9° with respect to one another, indicating the orientation relationship between the two martensite variants.

Micro-domain structures and local structural distortions are also concerned in our \textit{in-situ} TEM observations from 300 K down to 100 K. In particular, the microstructural features associated with the formation of martensitic variants have been carefully analyzed. Figure 2(a) shows a bright-field TEM image taken from a crystal at 300 K, in which no domain contrasts are clearly visible. The inset shows the corresponding SAED pattern taken along the [001] zone axis direction, demonstrating the presence of weak diffraction streaks along the \(h_{110}\) direction. The white square indicates the area for electron diffraction observations in our \textit{in-situ} TEM experiments. Figures 2(b)–2(e) show the bright-field images demonstrating the notable evolution of the martensitic structural domains with lowering temperature. Careful analysis of the experimental data suggests that the lamellar martensitic structures in general appear progressively at about 172 K with decreasing temperature. Figure 2(f) shows a TEM image taken at 100 K, illustrating the presence of needle-shaped martensites. Also note that the large martensitic domains at around 135 K and divide gradually into small needle-shaped domains at low temperatures. The needle-shaped martensites in general go along the \(h_{100}\) direction. Our high-resolution TEM observations at 100 K reveal that the needle-shaped martensites are composed of small micro-twinning variants similar to what we observed in NiFeGa.16 The white square indicates an area with clear 90° twinning domains. Inset of Fig. 2(f) shows a diffraction pattern taken at 100 K, in which sharp superlattice reflections appear at the position of \([1/5, 1/5, 0]\) along with fundamental reflection spots.

The formation and evolution of magnetic domains in association with MT can be observed by using \textit{in-situ} Lorentz microscopy at low temperatures. In our experiments, the observations of magnetic domains were performed in the
Fresnel mode, in which the incident electron beam penetrates through a specimen in parallel with its domain walls, and the electrons are deflected by the Lorentz force. As a result, the bright and dark lines appear in Lorentz microscopy images corresponding to the domain walls, so called convergent and divergent wall-images, respectively. Our observations of the evolution of magnetic domain walls were carried out on a single crystal grain of about $5\mu m^2$ which has been well characterized in measurements of physical properties.

Figure 3 exhibits a series of Lorentz TEM images of magnetic domain walls taken from an in-situ cooling-heating cycle. In these images, magnetic domain walls, as expected, are visible as alternating appearance of bright and dark lines. Importantly, our analysis suggests that the magnetic contrast in all Lorentz images can be well interpreted in comparison with experimental magnetization. The Mn$_{50}$Ni$_{40}$Sn$_{10}$ sample used in the present study has a paramagnetic state at RT, so no characteristic magnetic contrasts are visible in Fig. 3(a)—rather, only a faint contrast due to thickness appears under the defocused condition. As the temperature is decreased below the critical temperature ($T_c$) for the ferromagnetic transition, magnetic domains shown as parallel lamella become clearly visible in the crystal, with an average width of about $1\mu m$. Figure 3(b) shows the Lorentz TEM image of domain lamellar taken at 250 K, indicating the presence of 180° domains/walls nearly parallel to (100) direction. At this temperature, the average structure of the sample remains austenitic. With lowering temperature to 150 K, another notable change of microstructure can be observed, and a number of needle-shaped small martensites become progressively visible in correlation with the MT as discussed above (see Fig. 3(c)). Moreover, we can clearly see the coexistence of the magnetic and martensitic micro-domains in the examined area. It should also be mentioned that the appearance of martensitic domains significantly affects magnetic properties and magnetic domain structures. According our TEM observations, complex micro-domain contrasts of martensites often appear along with the MT and yield notable complex contrasts in the TEM images. Figure 3(d) shows a typical pattern.

In order to examine the characteristics and reversibility of this martensitic transformation, we have also performed a heating-run observation from 100 K to 300 K. The experimental results demonstrate that there are no significant changes in the martensitic micro-domains as the temperature increases from 100 K to 190 K. However, when the temperature exceeds 200 K, these micro-domains gradually become invisible. On the other hand, the magnetic domains gradually appear in the Lorentz TEM images, and the 180° domains walls become plainly visible at $\sim 240$ K indicating the sample is in a ferromagnetic state as shown in Fig. 3(f). As the temperature increases above 270 K, the magnetic domain...
walls disappear in the paramagnetic state as shown in Fig. 3(g). We also noted in our in-situ cooling/heating TEM observations that transitions of microstructure and magnetic domains occur at slightly lower temperatures than the corresponding ferromagnetic and martensitic transformations measured by others in ribbon samples. This distinction can been considered to be an expected difference between bulk material (such as the ribbons) and the thin foil samples used.
in TEM observations.\textsuperscript{16} According to the measurements of magnetization in the present compound as shown in Fig. 3(h), the volume fraction of ferromagnetic phase increases notably when temperature is lowered below 270 K. However, occurrence of the MT at a lower temperature suppresses partially the ferromagnetic order in the sample—a phenomenon which is fundamentally in agreement with what we observed in our \textit{in-situ} TEM investigations. The difference between the FC (Field Cooling) and ZFC (Zero Field Cooling) curves at temperature \( T_b \) (\( \sim 130 \) K) suggests that complex magnetic phases, such as a super paramagnetic phase, appear in \( \text{Mn}_{50}\text{Ni}_{40}\text{Sn}_{10} \) at the temperature of \( T_b \).\textsuperscript{13} Actually, AC measurements reveal that a RSG phase and the long-range FM order martensitic phase can coexist in the \( \text{Mn}_{50}\text{Ni}_{40}\text{Sn}_{10} \) system, and the RSG phase enters into a spin frustrated state at 130 K.\textsuperscript{13}

We now go on to examine the magnetizing process and field effects on the magnetic domain structure as revealed by \textit{in-situ} Lorentz microscopy observations. In our experiments, the TEM objective lens was weakly excited to produce a magnetic field at sample position. As a result, the clear changes of magnetic domains can be directly observed in our \textit{in-situ} observations. Figure 4(a) shows a Lorentz microscopy image for the austenitic ferromagnetic phase taken at 255 K, exhibiting the presence of magnetic lamella and domain walls in the observed area. Figure 4(b) shows the image of magnetic domains when a 0.05 T magnetic field is applied. It is recognizable that a number of domains become much larger, suggesting the occurrence of magnetization. It is also noted that an applied magnetic field of about 0.1 T makes all magnetic domains merge into a single large one as shown in Fig. 4(c). Figures 4(d) and 4(e) show the re-emergence and alterations of the magnetic domains following the decrease of magnetic field from 0.06 T down to 0.03 T, respectively. Note that the orientation of magnetic domain lamella shows visible reversibility. However, the detailed domain configuration, in particular the domain sizes in Fig. 4(f), shows visible changes in comparison with that in Fig. 4(a). This fact is in good agreement with the measurements of magnetization, which reveal clear hysteretic features associated with the ferromagnetic transition.

\section*{IV. CONCLUSION}
In summary, \textit{in-situ} TEM and Lorentz TEM observations of \( \text{Mn}_{50}\text{Ni}_{40}\text{Sn}_{10} \) reveal a rich variety of structural phenomena in correlation with the MT and ferromagnetic transition at low temperatures. Microstructure analyses demonstrate that \( \text{Mn}_{50}\text{Ni}_{40}\text{Sn}_{10} \) adopts a cubic structure at room temperature and transforms into “5M” or “6M” superstructures along with the low-temperature MT. \textit{in-situ} Lorentz microscopy investigations indicate that magnetic domains in the ferromagnetic phase often have a lamellar structure and go along the \( \langle 100 \rangle \) direction. These magnetic domains are significantly affected by the MT, in good agreement with the experimental measurements of magnetization. Notable alterations of magnetic domains are revealed under \textit{in-situ} applied magnetic fields in the Lorentz TEM.

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