Title

Observation of magnetic-field-induced transformation in $\text{MnCo}_{0.78}\text{Fe}_{0.22}\text{Ge}$ alloys with colossal strain output and large magnetocaloric effect

Authors

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Abstract

The thermal, structural and magnetic properties were studied for the hexagonal $\text{MnCo}_{0.78}\text{Fe}_{0.22}\text{Ge}$ alloys, which undergoes a first-order phase transformation from paramagnetic hexagonal phase into ferromagnetic orthorhombic martensite on cooling. Owing to the magnetostructural coupling, large magnetocaloric effect ($\Delta S_{\text{M}} = -10.97 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) was obtained at 254 K. In-situ synchrotron high-energy X-ray diffraction experiments were conducted to reveal the detailed change in crystallographic structure of phases and the effect of applied magnetic field on phase transformation behaviors. An anomalously huge strain of 11.89% and volume expansion of 4.35% in unit-cell was obtained between martensite and parent phase across the transformation. Furthermore, the magnetic field-induced martensitic transformation was directly evidenced at 250 K, which eventually demonstrates the possibility to achieve magnetic-field-induced strain and large magnetocaloric effect simultaneously.

Keywords: in-situ synchrotron high-energy X-ray diffraction; magnetic field-induced phase transformation; magnetocaloric effect

Text

Magnetic refrigeration based on magnetocaloric effect (MCE) has been regarded as a promising alternative to the conventional vapor-cycle refrigeration as it is eco-friendly and energy-efficient.[1-3] Recently, the hexagonal Mn-Co-Ge alloys have attracted extensive attention due to the giant magnetocaloric effect. For the stoichiometric MnCoGe alloy, it undergoes a martensitic transformation (MT) at transition temperature $T_t \sim 420$ K from the hexagonal Ni_2In -type parent phase (space group $P6_3/mmc$, No. 194) to the orthorhombic TiNiSi -type martensite (space group $Pnma$, No. 62) on cooling. The orthorhombic martensite orders ferromagnetically at $T_C^M \sim 355$ K.[4] In order to achieve the coupling of structural transformation and magnetic transition, i.e. first-order magnetic transition (FOMT) from paramagnetic parent phase to ferromagnetic martensite, many successful attempts have been made by various methods, such as applying external fields, introducing interstitial atoms[5] or vacancies[6, 7] and doping other alloy elements,[8-10] which leads to the giant magnetocaloric effect. For instance, the FOMT has been achieved by substitution of Fe for Mn or Co atoms in the Mn-Co-Ge alloys.[11, 12] The large difference in magnetization between the parent phase and martensite indicates that the Mn-Co-Ge alloys should exhibit the magnetic field-induced forward martensitic transformation, which is analogous to that found in NiMnGa.[13] However, the temperature shift driven by magnetic field in NiMnGa is very small due to the difficulty in synchronizing T_t and T_C^M . The studied Mn-Co-Ge alloy system is also different from NiMnX[14] or NiCoMnX ($X=\text{In, Sn, Sb}$)[15-18] alloys, in which a reverse martensitic transformation from the martensite to the parent phase is triggered by the external magnetic field as the parent phase exhibits higher magnetization. In this study, the $\text{MnCo}_{0.78}\text{Fe}_{0.22}\text{Ge}$ alloy was focused, which exhibits FOMT based on our previous results.[11] Thermal and magnetic properties were presented. Moreover, in-situ high-energy X-ray diffraction experiments were conducted for revealing the structure change across the transformation and exploring the possibility of magnetic-field induced transition.

The ingot with the nominal composition $\text{MnCo}_{0.78}\text{Fe}_{0.22}\text{Ge}$ was prepared by arc-melting of pure metals for 4 times. During this process, the weight loss due to Mn's evaporation is less than 0.3% of the total weight of the ingot. The ingot was followed by annealing at 1148 K for 72 hrs in sealed quartz tube with protection of argon to obtain a good homogeneity. Then the ingot was grinded into powders with annealing at 573 K for 1 hr to remove the stress for the subsequent measurements. The martensitic transformation temperatures were measured by differential scanning calorimetry (DSC) at rates of 10 K/min during heating and cooling. The magnetic properties were measured at heating and cooling rates of 5 K/min, using physical properties measurement system (PPMS). In-situ high-energy X-ray diffraction experiments were conducted at 11-ID-C beamline, Advanced Photon Source, Argonne National Laboratory. The cryomagnet, equipped with temperature control system, was used to provide the applied magnetic field up to 7 T between 310 K and 10 K. The 2-dimensional (2-D) detector was used to collect the Debye rings of the powder sample. Using the software FIT2D, the 2-D Debye rings were integrated along the azimuth angle into 1-D intensity versus 2θ diffraction curves. The lattice parameters were determined by Le Bail Refinement using EXPGUI software package.[19]

Fig. 1. The thermo-magnetization curves (left Y-axis) under applied field of 0.05 T and 5 T between 200 K and 400 K and the heat flow versus temperature curves (in blue line, right Y-axis) during heating and cooling.

Fig. 1 shows the thermo-magnetization curves under 0.05 T and 5 T, respectively, and the heat flow versus temperature curves during cooling and heating. It is shown that the studied alloy undergoes a first-order transformation from the paramagnetic parent phase into the ferromagnetic martensite as seen from the obvious difference in magnetizations for low-temperature (LT) phase and high-temperature (HT) phase and the large hysteresis between cooling and heating processes. The phase transformation temperatures, M_s (262 K), M_f (240 K), A_s (255 K) and A_f (273 K), representing the start and finish temperature of forward and reverse martensitic transformation, can be determined by the heat flow versus temperature curves. Also, M_s is shifted to higher temperature under the applied magnetic field of 5 T, compared to that under the applied field of 0.05 T. Thus, it can be supposed that magnetic field-induced martensitic transformation will occur in this alloy.

Fig. 2. (a) Isothermal magnetization curves between 227 K and 263 K and (b) the magnetic entropy change versus temperature calculated.

Fig. 2(a) displays the isothermal magnetization curves between 227 K and 263 K around the magnetostructural transformation. For clarity, only the process of increasing magnetic field is shown except the data for 245 K and 248 K. The measurements for each temperature were conducted after the sample was cooled from 400 K, the complete paramagnetic state of austenite. This so-called loop process avoids the impact of the residue martensite induced by the external field due to the incomplete recovery at the previous measurement when doing the consecutive measurements for various temperatures.[20] Based on the Maxwell equation, the temperature dependence of magnetic entropy was obtained, which is shown Fig. 2(b). At 254 K, large magnetocaloric effect upto $-10.97 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ under $\mu_0 H = 5 \text{ T}$ was gained, which is

comparable to the well-known giant magneocaloric materials, such as $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$, [1] $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ [21] and $\text{MnFeP}_{0.45}\text{As}_{0.55}$. [2]

Fig. 3. (a) The diffraction patterns between 300 K and 200 K during cooling and (b) the calculated temperature-dependent lattices parameters and unit-cell volume.

In order to study the origin of the giant MCE, in-situ synchrotron high-energy X-ray diffraction experiments were conducted. Initially, the thermally induced martensitic transformation was studied as the sample was cooled down and heated up between 300 K and 200 K with data collected in every 5 K interval. The diffraction patterns during cooling are illustrated in Fig. 3(a), which reveals the temperature-dependent phase changes. For clarity, only a small section with $2.69^\circ \leq 2\theta \leq 3.13^\circ$, containing some typical strong diffraction peaks with the Miller indices, in the whole diffraction spectrum ($0-8.27^\circ$) is displayed. On cooling, it undergoes the forward martensitic transformation from the hexagonal parent phase into orthorhombic martensite. At $\sim 260 \text{ K}$, the typical (211) peak of martensite appears distinguishable, which corresponds to M_s temperature

determined from DSC. Interestingly, the transformation from parent phase to martensite goes continuously in a slow and incomplete way over a wide temperature ranging from 260 K to 200 K, i.e., the residue parent phase exists even cooling down to 200 K, which indicates the incomplete nature of the martensitic transformation. Furthermore, the lattice parameters at various temperatures are determined by Le Bail refinement, which is shown in Fig. 3(b). For instance, $a=b=4.1032$ and $c=5.3062$ Å for the hexagonal parent phase and $a=5.9370$, $b=3.8332$ and $c=7.0946$ Å for the orthorhombic martensitic phase at 250 K with the coexistence of parent phase and martensite. Considering the orientation relationship $a_o=c_h$, $b_o=a_h$, $c_o=\sqrt{3} a_h$ and $V_o=2V_h$,^[22] a large lattice strain, $(a_o-c_h)/c_h=11.89\%$, in the a_o direction can be obtained. In addition, an unusually huge volume expansion, $(V_o-2V_h)/(2V_h)$, of 4.35% in unit-cell is observed, which is beneficial to large magnetocaloric effect as the structural entropy change is proportional to the volume change around the phase transition.[23] Therefore, if the magnetic-field-induced transformation really occurs in this alloy, the colossal outputs of strain as well as entropy change, associating with the transformation, are expected. Moreover, it can be deduced uniaxial compression stress on the c_h direction or hydrostatic pressure will hinder the occurrence of the martensitic transformation and subsequently shift the transformation temperature, which can be used to tune the transformation temperature.

Fig. 4. Contour map of the diffraction patterns at various temperatures during cooling under magnetic field of 0 T and 6T, respectively, as well as during heating.

Furthermore, Fig. 4 shows the contour map of the diffraction patterns at various temperatures during cooling under 0 T and 6 T as well as during heating, respectively. The color gradient represents the change of the normalized intensity for the diffraction peaks. Obviously, the M_s point is ~ 270 K with $\mu_0 H = 6$ T, which is shifted by 10 K compared to that under 0 T. It is consistent with the shift of M_s obtained by thermo-magnetization curve under the applied magnetic field of 5 T. According to Clausius - Clapeyron relation $\Delta T = (\Delta M / \Delta S) \times \Delta B$, ΔS is $39 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ determined by the DSC curve and ΔM is about 80 emu/g. So the calculated value for ΔT should be ~ 12 K, which agrees well with the measured one of 10 K.

Fig. 5. The diffraction patterns under applied field up to 6 T at 300 K (a), 250 K (b), and 200 K (c).

Further the effect of the isothermal application of the external magnetic field on phase transformation was studied to verify the existence of magnetic-field-induced transformation. Holding the sample at the fixed temperatures of 300 , 250 and 200 K, the magnetic field was applied up to 6 T and removed gradually with recording data in every 0.5 T interval. Considering Clausius-Clapeyron relation, the condition for magnetic field-induced martensitic transformation can be estimated with:

$$\mu_0 H \geq [(T - M_s) / (\Delta M_s / \Delta B)] \quad (1)$$

where T is the absolute experiment temperature.[24] This approximately gives a required magnetic field of ~20 T at 300 K ($>M_s$) and 0 T at 250 K and 200 K ($<M_s$). As shown in Fig. 5(a), at 300 K, the patterns do not change by applying magnetic field up to 6 T, which means the temperature is so far away from M_s (255 K) that the applied field of 6 T cannot drive the transformation from parent phase into martensite. At 200 K shown in Fig. 5(b), no obvious changes for the diffraction peaks can be detected under the field of 6 T, indicating that it is difficult for the residual parent phase to transform into martensite by applying magnetic field. However, the typical peaks of parent phase can still be detected, which indicates the incomplete martensitic transformation. At 250 K shown in Fig. 5(c), two phases initially coexist at zero field. As it is below M_s temperature, the transformation is easy to be triggered. With increasing applied field, the relative intensity of typical peaks, (211) and (013), of martensite is enhanced, which provides unambiguous evidence on the occurrence of phase transformation from parent phase into martensite.

Fig. 6. The magnetic field dependence of weight fraction of parent phase during increasing and decreasing the external field at 250 K.

The weight fraction of parent phase versus magnetic field was semi-quantitatively obtained, shown in Fig. 6. The Reference Intensity Ratio (RIR) method was used. As the RIR value for this composition is absent, the values of similar alloys were adopted (MnCoGe, space group *Pnma*, No. 194, 3.66; FeCoGe, space group *Pnma*, No. 62, 5.52). It can be seen that the transformation started once subjected to the applied field and was processed consecutively with increase the field, which corresponds to the features of the thermoelastic martensitic transformation. Since the large lattice strain and huge volume change in unit-cell associate with the martensitic transformation, the occurrence of magnetic field-induced transformation will bring in a considerable output of strain, i.e. magnetic field-induced strain (MFIS), as well as entropy change. Although the MnCoGe-based alloy is quite brittle and naturally collapses into powders, it can be mixed with ductile polymer to prepare composite.[25] In this case, the large strain output and volume change can be utilized for practical application. Therefore, the Fe-doped MnCoGe alloys may be categorized as magnetic shape memory alloys. As the complete reversibility requires the experiment temperature is above the A_f point (273 K), the intensity of the

martensite peaks does not recovery after removing the applied field, which means that the field-induced martensite will not transform back into parent phase.

In summary, large magnetocaloric effect ($\Delta S_M = -10.97 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) was obtained in hexagonal $\text{MnCo}_{0.78}\text{Fe}_{0.22}\text{Ge}$ alloys, which undergoes a first-order phase transformation from paramagnetic hexagonal parent phase into ferromagnetic orthorhombic martensite during cooling. In-situ synchrotron high-energy X-ray diffraction experiments were conducted to study the crystal structure and magnetic-field induced structural evolution of the hexagonal $\text{MnCo}_{0.78}\text{Fe}_{0.22}\text{Ge}$ alloys. The magnetic field-induced martensitic transformation was directly observed at 250 K, which is associated with a large lattice strain of 11.89% and a huge volume expansion of 4.35%, leading to the giant MCE. Thus, the Fe-doped MnCoGe alloys may be categorized as both magnetic shape memory alloys and magnetic refrigeration materials.

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