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Stress modulated martensitic transition and magnetocaloric effect in hexagonal Ni_2In-type $MnCoGe_{1-x}In_x$ alloys

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ABSTRACT

Effects of residual strain on martensitic transition and magnetocaloric effect have been studied in hexagonal Ni_2In-type $MnCoGe_{1-x}In_x$ alloys, which were prepared by using conventional arc-melting technique. Our studies indicated that the introduction of residual strain in the thin slices prepared by cold pressing can stabilize the austenite phase, broaden the temperature range of martensitic transition, and decouple the magnetic and structural transition in some extent. As a result, the magnetic entropy change is reduced, but the refrigerating temperature window can be expanded to 54 K or 73 K and the refrigerating capacity is remarkably increased.

1. Introduction

An increasing attention has been attracted to magnetic cooling technique based on magnetocaloric effect (MCE) due to its energy saving and friendly environmental nature. To achieve large MCE, materials with first order magnetic transitions (FOMTs) are usually required, which can induce large entropy change with a great contribution from the lattice. $MnFe_{1-x}P_xAs$ [1], $La(Fe,Si)_{13}$ [2,3], $Gd_5Si_2Ge_2$ [4], and NiMn based heusler alloys [5–8] are the materials with such FOMTs. Among these materials, $MnFe_{1-x}P_xAs$ and $La(Fe,Si)_{13}$ are the ones undergoing magnetoelastic transition, which is accompanied by a considerable lattice distortion and changes in unit-cell volume but the space group remains unchanged. The others, such as $Gd_5Si_2Ge_2$ and $Ni_{50}Mn_{50-x}X_x$, undergo a magnetostructural transition with a change of structure symmetry (space group) across the transition. On the whole, all these kinds of materials exhibit FOMTs with large MCE.

Ternary compounds MM'X with hexagonal Ni_2In-type structure have recently attracted much attention due to the magnetic shape memory effect and possible large magnetocaloric effect related to the magnetostructural coupling. As a member of MM'X family, the stoichiometric MnCoGe alloy crystallizes in the hexagonal Ni_2In-type structure, whose Curie temperature(T_C^A) locates at 265 K, and undergoes a martensitic transition to the orthorhombic TiNiSi-type structure at 420 K upon cooling, whose T_C^M, on the other hand, is 355 K [9,10]. Consequently, MnCoGe alloy undergoes a second order magnetic transition at 355 K for its stoichiometric composition. Except for the study of arc-melted MnCoGe bulk, the magnetocaloric effect (MCE) in melt-spun ribbons of stoichiometric MnCoGe alloys has also been studied. Both the hexagonal and orthorhombic phases were produced in the polycrystalline ribbons and a reversible MCE was detected around their respective second-order transition temperature of 273 K and 355 K [11]. The most interesting feature of MnCoGe based alloy is that introducing chemical pressure, such as interstitial atoms [12], Mn deficiency [13], Co vacancies [14], or the substitution of the main elements by the atoms with different atomic radius and valence electron [15–21], can tune the structural transition to intersect with the magnetic transition of the alloy, thus inducing a magnetostructural coupling. The concurrent magnetic and structural transitions, the so-called magnetostructural transition, T_{mstru}, usually result in a large MCE.

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Physical pressure is another way to modulate the atomic distance of the alloy and as a result modulating the magnetostructural coupling of the alloy. For the materials with coupled nature of magnetic and structural properties, the modulations of the magnetostructural coupling and the magnetic properties via different ways of pressure have been widely studied. For example, the behavior of the NiMnIn and La(FeSi)$_{13}$-based alloys under hydrostatic pressure have been studied. An applied pressure of 2.6 kbar/2.1 kbar can drive the magnetostructural/magnetoelastic transition to a higher/lower temperature by 4.5 K/14 K for Ni–Mn–In/$LaFe_{11.33}Co_{0.47}Si_{1.2}$, while the sharpness of the phase transition retains nearly unchanged within these pressures [22,23]. For the MnCoGe-based alloys, it has been reported that, for the coupled first order system, the hydrostatic pressure drives the coupling temperature T_{mstru} to lower temperature [24,25], whereas for the uncoupled second order ferromagnetic systems, the hydrostatic pressure shifts T_C to higher temperature [26]. Moreover, the modulation of magnetic properties in thin films via introducing the stress from the substrate has been also studied in some systems. For example, depositing $La_{0.7}Ca_{0.3}MnO_3$ films on $BaTiO_3$ substrate, X. Moya and the coworkers realized a sharp change of magnetization around 200 K via modulating the structure of the film by the stress the $BaTiO_3$ exerted on the $La_{0.7}Ca_{0.3}MnO_3$ thin films, consequently, a large extrinsic magnetocaloric effect was induced [27]. By depositing MnAs films epitaxially on GaAs substrate, on the other hand, Mosca et al. modulated the first order transition of the MnAs thin films [28] via the residual strain introduced in the growing process and the stress from the mismatch of lattice. It was found that the magnetocaloric effect remains giant and its spread and maximal position can be tunable through the epitaxy dependent thermal strain in the films.

For the hexagonal Ni_2In-type MnCoGe, our recent investigations revealed that the substitution of Ge by the forth element In which has larger atomic radius but less valence electron number, can make the structural transition temperature to be located between T_C^A and T_C^M for $MnCoGe_{1-x}In_x$, thus inducing a transition from hexagonal paramagnetic state to orthorhombic ferromagnetic state. Here, we name the magnetic ordering temperature caused by structural transition $T_{mstru.}$ For the In contents within 0.5 at. % ≦x≦ 2 at. %, T_{mstru} decreases with increasing In contents from 320 K to 288 K, but the magnetic and structural transitions become decoupled when x > 2 at. %. Our studies indicated that the increasing In contents can stabilize hexagonal phase relative to martensitic phase, thus driving the T_{mstru} to lower temperature.

One knows that most of the MnCoGe-based materials are quite brittle and even naturally cracked into powders for the as-prepared samples. Such a character limits its application noting that a desired shape is usually required for practical refrigerant. We tried to shape the powders into thin slices via cold press. During the process, residual strain is inevitably introduced into the alloy and it may affect the martensitic transition and magnetic properties largely. Here, we report the residual strain modulated magnetostructural transition and magnetocaloric effect in $MnCoGe_{0.995}In_{0.005}$ alloys with T_{mstru} at 320 K, which were clod-pressed under 3 GPa and 5 GPa for 20 min, respectively, followed by the press removing.

2. Experimental

$MnCoGe_{1-x}In_x$ alloys with x = 0.005 were prepared using conventional arc-melting technique under the protection of high pure Ar atmosphere. The ingot was wrapped in Mo foil and sealed in an evacuated quartz tube for annealing at 875 °C for 6 days and cooled down to room temperature in oven. Actually, the as-prepared $MnCoGe_{0.995}In_{0.005}$ sample has naturally cracked into powders after annealing. We put the powders into a cylindrical mold and subsequently cold-pressed the powders into thin slices with diameter of 5 mm and thickness of about 0.5 mm under 3 GPa and 5 GPa for 20 min, respectively. The obtained slices were not made any further annealing. The room-temperature powder x-ray diffraction (XRD) was measured using Cu-Kα radiation to study the crystal structure. Magnetic measurements were performed using a superconducting quantum interference device magnetometer (SQUID-VSM).

3. Results and discussion

Fig. 1 shows the room temperature X-ray diffraction patterns of the as-prepared samples compared to the ones which were further cold-pressed. No obvious changes of lattice parameters were detected. As can be seen, the as-prepared sample crystallizes in mixed orthorhombic and hexagonal structures with the main phase being orthorhombic one, while for the powders which experienced further cold-pressing, more hexagonal structure appears at room temperature noting the increased intensity of the hexagonal phase peak relative to the orthorhombic phase. These results agree well with the broadening of phase transition for the pressed samples, as discussed below.

Fig. 2a displays the magnetization dependence on temperature (M–T curves) measured in zero-field (ZFC) cooling and field-cooling (FC) modes under 0.05 T for the as-prepared $MnCoGe_{0.995}In_{0.005}$ samples and the ones which experienced further cold-pressing. The curves show sharp change of the magnetization accompanied with a thermal hysteresis of 11 K around the temperature of 320 K for the as-prepared samples. The considerable hysteresis denotes the transition as first-order in nature. For the cold-pressed samples, the thermal hysteresis between the ZFC and FC modes retains, but the transition is broadened and becomes less sharp compared to the as-prepared samples. This fact indicates that the pressed samples may undertake a suppressed martensitic transition. We noticed that the powder size before being pressed is larger than 100 μm for the vast majority of samples and the powder has the same magnetic properties as its bulk. Noting that the XRD peaks of the pressed samples show no sign of broadening, this fact indicates that the grain size during the cold-pressing process does not change so much, so the effect of grain size on the observed less sharp of magnetostructural transition may be excluded. The residual strain in the pressed samples may cause extra crystal defect, which may play a role on the

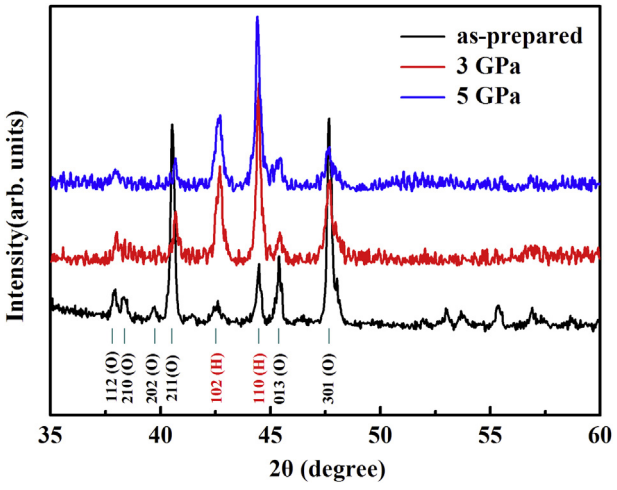

Fig. 1. The XRD pattern of $MnCoGe_{0.995}In_{0.005}$ polycrystalline alloy for the as-prepared samples in comparison to the ones pressed under 3 GP and 5 GPa. The miller indices hkl represents the Ni_2In type hexagonal structure (H) and TiNiSi type orthorhombic structure (O).

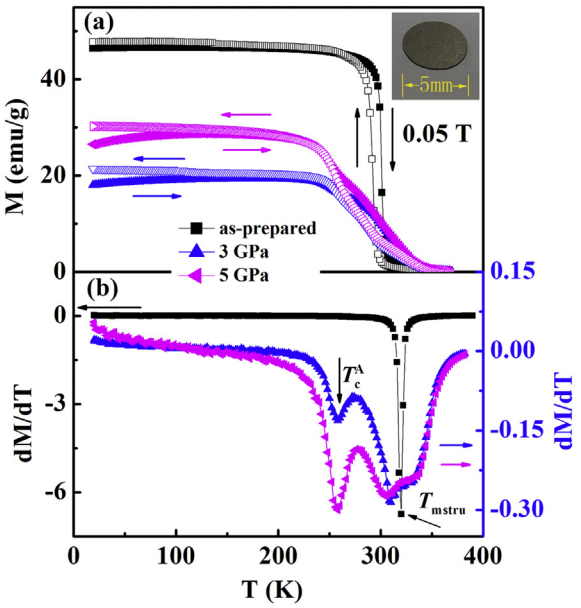

Fig. 2. (a) The temperature dependent magnetization (M–T curves) under 0.05 T in ZFC (solid symbols) and FC (open symbols) modes, and (b) the dM/dT plot in ZFC mode for the as-prepared $MnCoGe_{0.995}In_{0.005}$ samples in comparison to the ones pressed under 3 GPa and 5 GPa pressure, where the arrows indicate the cooling/warming path. The upper inset of Fig. 2(a) displays the photograph of the pressed thin slices with diameter of 5 mm and thickness of 0.5 mm.

evolution of phase transition. However, it is uneasy to detect the exact information of defects from the XRD pattern, noting it shows the average effect of structure.

The magnetic transition temperature can be identified by the minimal value in the dM/dT curves on heating (ZFC mode), as shown in Fig. 2b. For the as-prepared $MnCoGe_{0.995}In_{0.005}$, a single minimum indicates its T_{mstru} locates at 320 K, while for the other two pressed samples under 3 GPa or 5 GPa, two minimums surprisingly appear, indicating these two samples may undergo two transitions. The high temperature transition with pronounced thermal hysteresis locates at a relatively lower temperature, i.e. T_{mstru}~310 K and 306 K for the 3 GPa and 5 GPa samples, respectively, demonstrating that the structural transition still overlaps with the magnetic one though it becomes notably less sharp. More interestingly, an additional transition at lower temperature of 260 K was developed, which is almost the same for the two samples. It can be noticed that the low temperature transition is around the intrinsic Curie temperature T_C^A of hexagonal phase [10]. This fact prompts us to think that the residual strain in the cold-pressed samples may make partial sample decouple. The decoupled sample persists in its hexagonal structure down to low temperature noting that no hints of further martensitic transition below the T_C^A (~260 K) can be identified at temperatures down to 20 K from the M–T curves shown in Fig. 2a and b. This behavior is completely different from the effect of hydrostatic pressure.

For a similar system with composition $Mn_{0.93}Cr_{0.07}CoGe$, the effect of hydrostatic pressure on the magnetostructural transition has been previously studied [24]. It was reported that hydrostatic pressure can push the T_{mstru} to lower temperature with the thermal hysteresis and transition width almost unchanged as the pressure is below 5 kbar. However, when the pressure reaches or exceeds 5 kbar, the transition becomes broadening while the thermal hysteresis retains. For the MM'X family, the austenitic hexagonal phase has a smaller unit cell volume than the martensitic orthorhombic phase. Physical pressures can stabilize the hexagonal phase and drive the martensitic structural transition to a lower temperature through modifying the atomic distance and the strengthening of covalent bonding, similar to the introduced chemical pressure [24,25].

For the present case with residual strain in the pressed samples, the transition width is largely broadened, indicating that the magnetostructural transition spreads over a wide temperature range and the martensitic and hexagonal phase coexists in a much wider temperature span. We suggest that it should be the residual strain that works, which did not release after the press removing. The residual strain plays a similar but different role compared to the hydrostatic pressure. It can make the defects involved redistribute, and can also stabilize the hexagonal phase and drive the magnetostructural transition to lower temperature. The difference from the hydrostatic pressure is that the distribution of the residual strain in the pressed samples should be uneven after removing the press due to the different particle size and different relaxation process of the strains. The unevenly distributed residual strain among the polycrystalline $MnCoGe_{0.995}In_{0.005}$ grains broadens the coexistence range of orthorhombic and hexagonal phases, leading to the differences in the transition temperature among the different micro-areas, thus broadening the transition width. The appeared low temperature transition at 260 K in the pressed samples might correspond to the area or grains that suffer much larger residual strain. The combined effect with the redistributed defects in the grain and grain boundaries enforced by the residual strain should be responsible for the decoupling of magnetostructural transition in partial samples. The decoupled sample retains its hexagonal structure down to low temperature.

Mosca et al. reported strain engineering of magnetocaloric effect in MnAs epilayers [28]. It was found that the introduced strain using film technique can be an effective way to tune the magnetocaloric effect. The pressed $MnCoGe_{0.995}In_{0.005}$ sample under 3 GPa or 5 GPa pressure displays a broadened width of phase transition due to the residual strain. It is expected that tunable magnetocaloric effect and working temperature window can be realized through adjusting the residual strain, similar to the case in MnAs epilayers.

To obtain the MCE of the samples, we comparably measured the isothermal magnetization (M–H) curves of the pressed and as-prepared samples, as shown in Fig. 3a, b, and c. Visible hysteresis can be identified in the M–H curves for the as-prepared sample (Fig. 3a), while the magnetic hysteresis loss approaches to zero for the pressed samples (Fig. 3b and c), though all the three display considerable thermal hysteresis (Fig. 2a). Generally, hysteresis behavior is related to many intrinsic factors [29,30]. For the coupled MnCoGe alloy system, it was reported that both the magnetic field and thermal activation can induce the FOMTs, but the magnetic field is not an effective way to trigger the FOMTs [21,24]. Thermal activation model was usually considered to study dynamic behaviors for the magnetocaloric systems with first-order magnetostructural transition [31], where the energy barrier, which characterizes the hysteresis gap, closely correlates with the electronic band structure, nucleation factors and strain state. For the pressed $MnCoGe_{0.995}In_{0.005}$ in comparison with the as-prepared samples, we believe that the change of local environments and the redistributed defects under residual strain should lead to a change of the energy barrier and the hysteresis gap.

Based on the isothermal M–H curves, we calculated the magnetic entropy change using Maxwell relation, $\Delta S(T,H) = \mu_0 \int_0^H (\partial M/\partial T)_H dH$. The entropy change as a function of temperature for the as-prepared samples in comparison with the pressed ones under 3 GPa and 5 GPa is shown in Fig. 3d, e, and f, respectively. As can be seen, the maximum absolute entropy change, $|\Delta S|$, is 8 J/Kg/K and 4 J/Kg/K, and the full temperature span at half

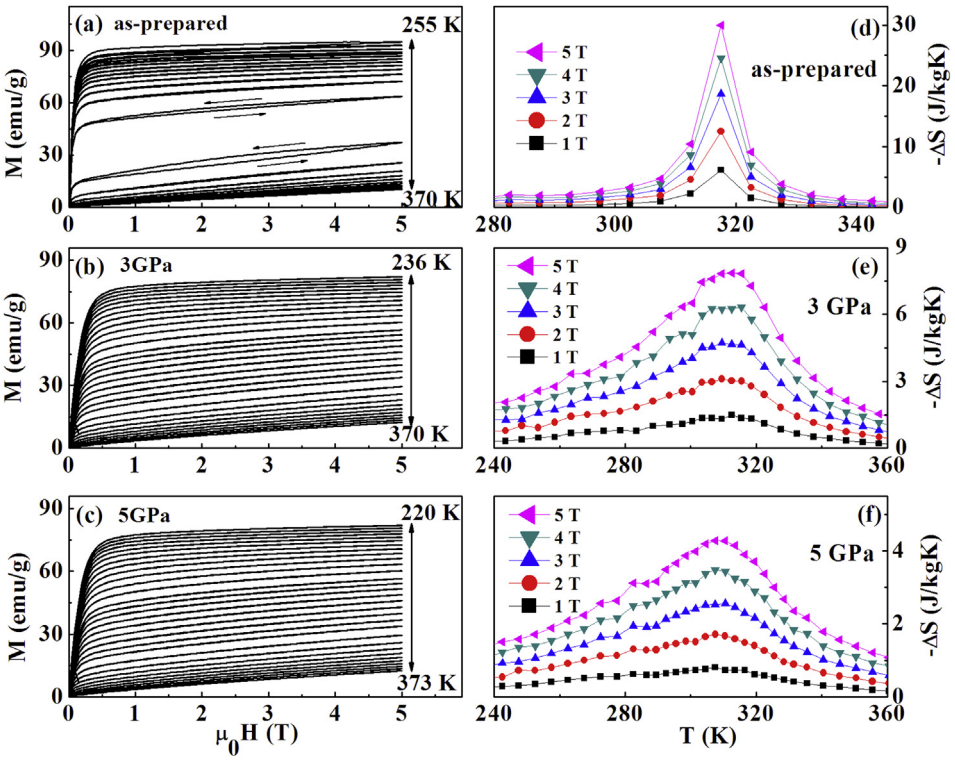

Fig. 3. The isothermal M–H curves of the (a) as-prepared $MnCoGe_{0.995}In_{0.005}$ sample compared to the pressed ones under (b) 3 GPa and (c) 5 GPa pressure. The corresponding magnetic entropy change as a function of temperature under different magnetic fields is shown in (d), (e), (f), respectively.

maximum, ΔT, is 54 K and 73 K under 5 T for the pressed samples at 3 GPa and 5 GPa, respectively, while the as-prepared $MnCoGe_{0.995}Ge_{0.005}$ polycrystalline shows the maximal |ΔS|~30 J/Kg/K and the ΔT~10 K under a magnetic field change of 0–5 T. One can notice that the temperature span ΔT has been noticeably broadened upon the introduction of residual strain though the entropy change ΔS largely reduced. Refrigerant capacity (RC) [32] is a measure of the refrigerating power of a material in practical use. It is defined as $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 in the equation are the temperatures corresponding to the half maximum ΔS. The evaluated RC is 351 J/Kg and 235 J/Kg for the pressed samples at 3 GPa and 5 GPa, respectively, while 198 J/Kg for the as-prepared samples under a magnetic field change of 0–5 T. Due to the significantly broadened ΔS peak, the refrigerant capacity increases a lot for the pressed samples. These results undoubtedly demonstrate that the residual strain, which is similar to the introduced film strain in MnAs epilayers [28], can also influence the martensitic transition and the concurrent magnetostructural coupling, consequently the MCE considerably. The introduced physical pressure plays a similar role compared to chemical pressure. They all stabilize the hexagonal phases and drive the T_{mstru} to lower temperatures, thus the introduced residual strain in the pressed samples can largely modulate the magnetostructural transition of the alloys. In view of the practical application of magnetocaloric material as refrigerant, certain shapes, such as spheres or slices, are usually required to facilitate the exchange of heat. However, the materials with strong magnetostructural coupling are often fragile and hard to be shaped into the desired shapes. The investigation on the evolution of magnetostructural transition and magnetocaloric effect for the pressed slices with residual strain is of particularly important not only for understanding the nature of stress modulated phase transition but also for promoting the potential application of the materials.

4. Conclusion

In summary, our studies have demonstrated that the introduced residual strain in the cold-pressed thin slices under pressure of 3 GPa or 5 GPa can modulate the martensitic transition and the magnetostructural coupling for $MnCoGe_{0.995}In_{0.005}$ alloy. The residual strain, which is of physical nature, can stabilize the hexagonal phase of $MnCoGe_{0.995}In_{0.005}$ alloy and decouple the magnetostructural coupling of the system in some extent. As a result, the temperature window of phase transition becomes broadening while its first order nature is retained. The MCE accompanied with the martensitic transition is also studied. In consistent with the gradual evolution of phase transition, the magnitude of MCE becomes smaller, but the working temperature range extends a lot, as a result, the refrigerant capacity increases for the pressed slices. These results undoubtedly demonstrate that introducing residual strain can be also an effective way to modulate the magnetostructural transition and consequently the performance of MCE.

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