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Martensitic transformation and magnetocaloric properties of Sn doping Mn–Ni–Ga alloys

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ABSTRACT

The effects of Sn addition on phase transformation behavior and magnetocaloric properties of $Mn_{50}Ni_{25}Ga_{25-x}Sn_x$ (x=0, 0.1, 0.5, 1 and 2 at%) alloys were investigated in this work. The results show that the addition of Sn reduces the structural transformation temperatures. It is found that the second phase exists in the austenite matrix of the as-casted alloys at room temperature. After being annealed at 1073 K for 48 h, the precipitates totally soluted into the matrix. Magnetization measurements indicate that the saturation magnetizations of the alloys increase significantly with increase in Sn contents. In addition, the $\Delta M/\Delta S$ obviously increases with increase in the Sn contents, implying the higher efficiency shift of the martensitic transformation temperature under the magnetic field.

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) have attracted considerable attention as potential microactuator materials because they show a large recovery strain up to 10% and a high responding frequency (kHz) [1–4]. These characteristics are attributed to the magnetic-field-induced strain, related to the field-induced martensite variants re-arrangement or magnetic-field-induced crystallographically reversible martensitic transformation [5–11]. Several FSMAs, including Ni–Mn–Ga [12], Ni–Fe–Ga [13], Co–Ni [14,15], Fe–Pt [16,17] and Fe–Pd [17] systems, have been reported so far. From the viewpoint of practical applications, magnetic-field-induced martensitic transformation is more attractive than the re-arrangement of martensite variants for magnetically driven actuators because a large output stress is expected. However, the shift of martensitic transformation start temperature (M_s) in Ni–Mn–Ga alloys is reported to be only about 1 K under a field of 2 T [18–20], which means that an extremely large magnetic field is required to induce martensitic transformation. In most other FSMAs, the situation is similar to that in the Ni–Mn–Ga alloys. Thus, the magnetic-field-induced shape memory effect resulting from the magnetic-field-induced martensitic transition is difficult to obtain in conventional FSMAs.

As an outstanding magnetic actuator material, extensive studies have been focused on off-stoichiometric Ni_2MnGa. When increasing manganese to over 40 at%, a new type of ferromagnetic Heusler alloy Mn_2NiGa was discovered [21–24], and the alloy shows a high Curie temperature (T_c) and M_s temperature, a large lattice distortion up to 21.5% and a large magnetization difference upon transformation, indicating Mn–Ni–Ga as a promising material with magnetic-field-induced martensitic transformation.

It is well known that a magnetic field generates a magnetization force in materials, which may be used as the driving force for martensitic transformation [25,26], that is a change in martensitic transformation temperatures due to a variation in external magnetic field. The martensitic temperature shift, ΔT, induced by a magnetic field change ΔH is approximately given by the Clausius–Clapeyron relation in the magnetic phase diagram as follows: $\Delta T/\Delta H=(\Delta M/\Delta S)$, where ΔM and ΔS are the difference in magnetization and entropy between the parent phase and the martensite phase, respectively. From the above equation, it is reasonable to believe that the new alloy system with a high value of $\Delta M/\Delta S$ opens up the possibility of the recoverable strain resulting from the magnetic-field-induced martensitic transformation.

It is reported that transformation behaviors and magnetization properties of magnetic shape memory alloys are significantly related to the valence electron concentration e/a, and can be tuned by two main methods. One is altering the ingredients of the alloys and the other method is atomic substitution by other elements. For example, by increasing the Ni content of the Ni_2MnGa alloy, the entropy changes in the range from -3.5 to -20.4 J/kg K in polycrystalline alloys while in the single crystals the change observed has been as high as -86 J/kg K [27]. The transition can also be tuned by atomic substitution at the Mn site or the Ga site [28]. In particular, 25 at% Cu at the Mn site results in a ΔS of -60 J/kg K in the temperature range of 308–334 K [29,30].

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Substitution of Co for Ni in $Mn_{48}Co_xNi_{32-x}Ga_{20}$ alloys achieves a higher ΔM, and induced the magnetic-field-induced reverse martensitic transformation under 8 T field [31]. In this work, we select the Sn element as the substation for Ga as far as we know for the first time, and we hope that this study may introduce a new type of magnetic shape memory alloy with high $\Delta M/\Delta S$ value.

2. Experimental

A series of polycrystalline $Mn_{50}Ni_{25}Ga_{25-x}Sn_x$ (x=0, 0.1, 0.5, 1 and 2 at%) alloys were prepared by non-consumable arc-melting a mixture of stoichiometric amounts of pure constituent elements (>99.99 wt%) in a vacuum atmosphere. The obtained button ingot was turned over and remelted four times to achieve composition homogenization. After that, the ingot was annealed at 1073 K for 48 h in a quartz tube with a vacuum of 10^{-4} Torr and then quenched into ice-water to obtain the high chemical order.

For the study of martensitic transformation behavior and the entropy change during phase transformation, the differential scanning calorimetry (DSC) measurements were performed at a heating and cooling rate of 20 K/min using a PE diamond instrument in the temperature range of 100–500 K. The microstructure and compositions of the experimental alloys were examined by using a scanning electron microscope (SEM) equipped with a microanalysis system.

X-ray diffraction measurements were carried out in a Rigaku D/max-rB with Cu-$K\alpha$ radiation at room temperature for phase identification. The magnetization measurements were carried out using a Model-6000 type Physical Properties Measurement System (PPMS) in an applied field up to 5 T at room temperature and at 373 K.

3. Results and discussion

Typical secondary-electron images of the as-casted and annealed $Mn_{50}Ni_{25}Ga_{23}Sn_1$ alloy are shown in Fig. 1. Fig. 1(a) is taken from the as-casted specimen and is characterized by two different regions, i.e., the white matrix and the rod-like dark particles with an average size of about 1–3 μm. A careful study by EDS microanalysis was carried out to estimate the chemical composition of the precipitates and the matrix, and the result for precipitates is shown in Fig. 1(b). The results of EDS analysis indicate that the matrix has the composition of $Mn_{49.66}Ni_{24.86}Ga_{24.62}Sn_{0.86}$, while the precipitates are richer in Mn and poor in Ni, Ga and Sn (~75.77, 2.56, 21.1 and 0.57 at%, respectively), which correspond well to a solid composition, revealed by the phase diagram as a Mn_3Ga-type phase. According to Mn–Ni, Mn–Ga and Ni–Ga binary phase diagrams, the Mn-rich precipitates caused by non-equilibrium effect are likely to be an intermetallic compound Mn_3Ga with an $L1_2$ BCC structure. Fig. 1(c) is taken from the specimen annealed at 1073 K for 48 h. The alloy shows the homogeneous distribution of the chemical compositions and the segregation of minor or secondary phase cannot be observed, indicating that a 1073 K annealing temperature is necessary to produce a single phase for Mn–Ni–Ga–Sn alloys.

The XRD patterns collected at room temperature for as-casted and annealed $Mn_{50}Ni_{25}Ga_{25-x}Sn_x$ (x=0, 0.1, 0.5, 1 and 2 at%) samples are displayed in Fig. 2. It is noted from Fig. 2(a) that parent phase peaks as previously reported [21] can be detected in each sample due to the low martensitic transformation temperature. In addition, some extra reflections from body-centered cubic precipitates with a lattice parameter of 0.3926 nm can also be observed in the as-casted specimen, which are in accordance with the results of EDS analysis and the further detailed crystal characteristics of these precipitates are currently being determined by TEM and SAED. We also note that the patterns for these precipitates disappear when the specimen is annealed at 1073 K for 48 h, confirming that the precipitates have totally soluted into the matrix. Meanwhile, an order-dependent superlattice reflection at 2θ=26.1° can also be detected in both the as-casted and annealed samples, indicating a highly ordered structure, consistent with that of a solution-treated sample reported in Ref. [22]. For the patterns obtained from the samples annealed at 1023 K for 48 h, the main

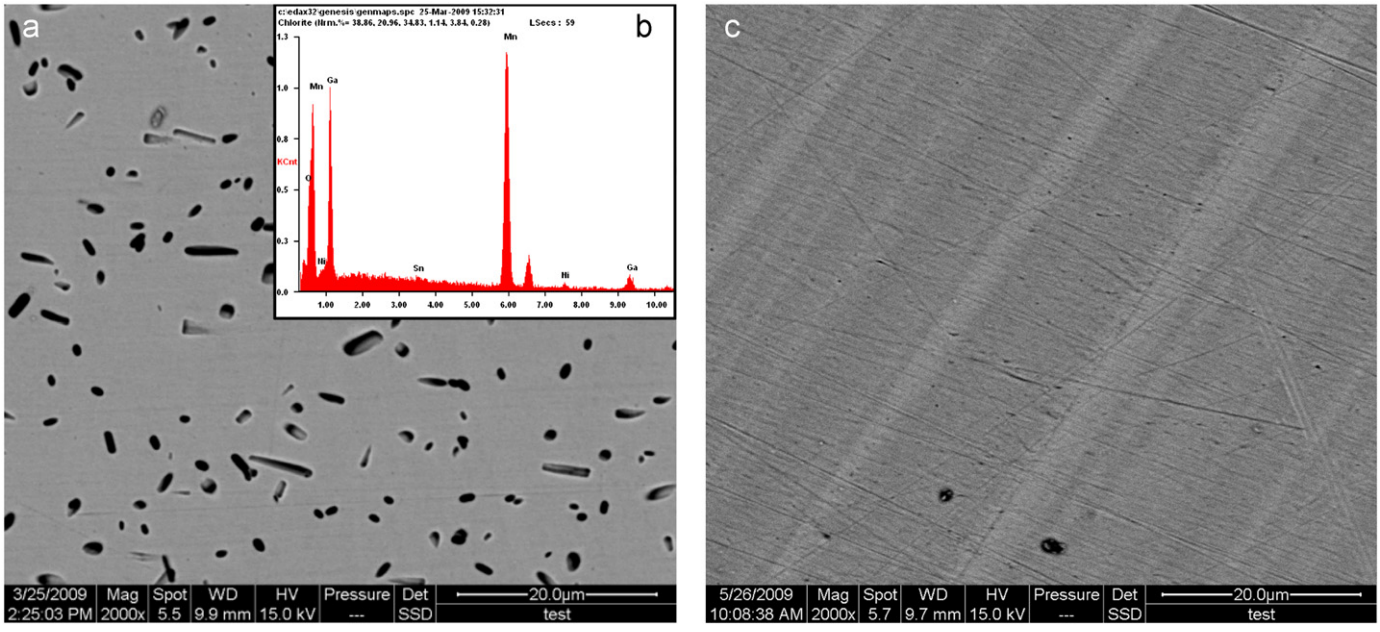

Fig. 1. Typical SEM images and EDS spectrum for the $Mn_{50}Ni_{25}Ga_{24}Sn_1$ alloy: (a) as-casted specimen, (b) EDS spectrum of the as-casted specimen and (c) annealed specimen.