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The phase transitions, magnetocaloric effect, and exchange bias in $Mn_{49}Ni_{42-x}Co_xSn_9$ alloys

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ABSTRACT

The structure, phase transitions, magnetocaloric effect, and exchange bias effect in $Mn_{49}Ni_{42-x}Co_xSn_9$ ($x = 0$, 1, 3 and 5) ferromagnetic shape memory alloys have been systematically investigated. X-ray diffraction results measured at room temperature reveal that $Mn_{49}Ni_{42-x}Co_xSn_9$ alloys with $x = 0$, 1 present martensite structure, and $Mn_{49}Ni_{42-x}Co_xSn_9$ alloys with $x = 3$, 5 exhibit mixture phases of both martensite and austenite. The martensitic transformation and exchange bias field (H_{EB}) are very sensitive to the Co content. In addition, large positive magnetic entropy changes were observed in these alloys due to the magnetic-field-induced transition from the paramagnetic martensitic phase to the ferromagnetic austenitic phase, and a large effective refrigeration capacity of 230.8 J/kg was obtained under the magnetic field change of 70 kOe in $Mn_{49}Ni_{37}Co_5Sn_9$ alloy. We realized a continuous tuning of the H_{EB} from 534.7 Oe to 1113.0 Oe after field cooling in presence of 10 kOe.

1. Introduction

The magnetocaloric effect (MCE), defined as the thermal response of magnetic materials to an applied magnetic field, has be widely used to attain very low temperature in magnetic materials by applying a magnetic field isothermally and removing it adiabatically [1,2]. In order to be able to apply the MCE at room temperature, scientists have taken much effort to find new magnetocaloric materials. Since the discovery of giant MCE in Gd-Si-Ge by Pecharsky and Gschneidner in 1997 [3], researchers have dedicated to broaden the magnetic refrigeration temperature region to room temperature so as to replace the conventional vapor-compression-based refrigeration technology. Compared with conventional refrigeration technology, magnetic refrigeration technology has many advantages, such as environment-friendship and high-efficiency. Therefore, it is believed that the magnetic refrigeration technology is very promising for application in the future.

During the last decade, scientists have found several systems with the first order magneto-structural transition possess large MCE, such as Fe-Mn-P-As [4], La-Fe-Si [5], and NiMn(Ga, Sb, In) [6]. Among them, the ternary Ni-Mn-Ga Heusler alloys are well known as ferromagnetic shape memory alloys (FSMAs), which undergo a reverse martensitic transition (MT) from a low-temperature martensitic phase to a high-temperature austenitic phase as temperature increases, and these materials also have magnetic transition near the Curie temperature (T_C). These alloys' MT temperature is sensitive to the composition, and a large magnetic entropy change (ΔS_m) can be achieved in a wide temperature range by tuning the composition. By contrast, the structural and magnetic transformations in Ni-Mn-X (X = In, Sn) can produce both inverse and conventional MCE, respectively, where the inverse MCE is attributed to the first-order transformation from paramagnetic (PM) martensite to the ferromagnetic austenite under an external magnetic field [7]. Therefore, the researchers have paid much attention to explore ΔS_m in the field-induced reverse martensitic transition materials. Ni-Mn based Heusler alloys are found to be promising candidates for magnetic refrigeration applications. In addition to MCE [6,8], Ni-Mn based Heusler alloys also have fascinating multifunction properties, such as magnetic shape memory effect [9,10], elastocaloric effect [11], magnetoresistance [12-14], exchange bias (EB) [15], and direct conversion of heat to electricity [16].

In Ni-Mn based Heusler alloys, the magnetization is mainly resulted from Mn atoms. Some recent studies show that the ΔS_m in Ni-Mn based Heusler alloys can be enhanced to a considerably

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extent by increasing Mn content close to 50 at.% [17,18]. Especially, the enhancement of magnetization difference ΔM between parent phase and martensitic phase is regarded as an effective approach to improve the MCE. It has been reported that Co substitution for Ni site in Ni-Mn-Z (Z = Sb, Ga) or Mn-Ni-X (X = Sn, Ga, In) [19-23] has tremendously enhanced ΔM. This phenomenon can be ascribed to the fact that the magnetic moments between the nearest Mn-Mn atoms with Co doping become ferromagnetic alignment instead of the anti-ferromagnetic alignment between the nearest Mn-Mn atoms without Co doping. Thus, the enhancement of magnetization difference ΔM between parent and martensitic phases is an effective approach to improve MCE.

Based on this motivation as mentioned above, we have prepared Mn-rich $Mn_{49}Ni_{42-x}Co_xSn_9$ (x = 0, 1, 3 and 5) Heusler alloys, and we have investigated the martensitic transition, magnetic properties to improve the MCE. A large ΔS_m and refrigeration capacity (RC) near the MT were obtained. The maxima of both ΔS_m and RC in $Mn_{49}Ni_{37}Co_5Sn_9$ achieve about 39.9 J/kg·K and 436.1 J/kg, respectively, under the magnetic change of 70 kOe. These results reveal the relevant physical mechanism about the improvement of MCE and the prospect of the potential application in magnetic refrigeration in the future. By Co doping, a continuous tuning of the H_{EB} from 534.7 Oe to 1113.0 Oe has been obtained after field cooling in presence of 10 kOe.

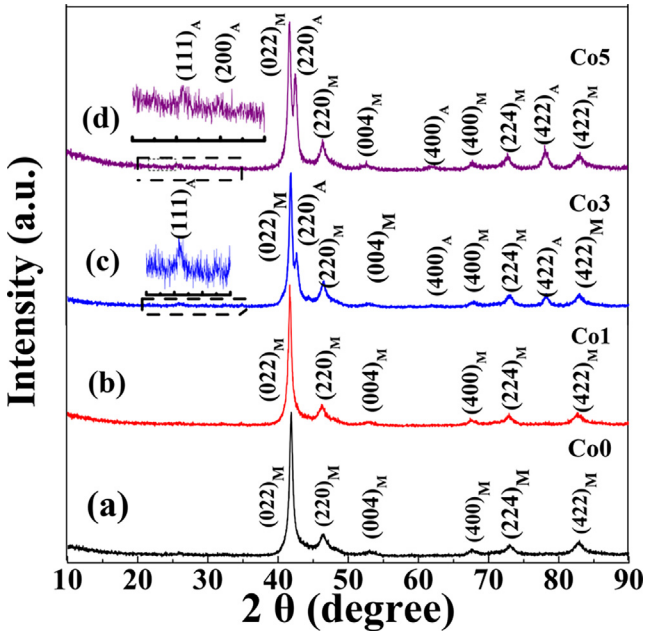

Fig. 1. X-ray diffraction patterns of powder $Mn_{49}Ni_{42-x}Co_xSn_9$ alloys measured at room temperature.

2. Experimental

Polycrystalline $Mn_{49}Ni_{42-x}Co_xSn_9$ (x = 0, 1, 3, 5) Heusler alloys with nominal composition were prepared by arc-melting pure constituent elements Mn (99.95%), Ni (99.98%), Sn (99.999%) and Co (99.8%) under an argon atmosphere in a cooled copper crucible. The weight loss was found to be less than 0.7%. For homogenization, the obtained ingots (~6 g) were re-melted for four times and they were sealed into evacuated quartz tubes, and then annealed at 1173 K for 72 h following quenched in liquid nitrogen. The crystal structures were determined by X-ray diffractometer (XRD, Rigaku 3KWD/MAX2200V) with Cu-Kα radiation at room temperature. In order to characterize the MT, we also performed differential scanning calorimeter (DSC) in heating and cooling modes at a rate of 10 K/min, and in the temperature range of 225–275 K. The magnetization was acquired using a Physical Property Measurement System (PPMS-9, Quantum Design Inc.). Magnetic measurements were taken following zero-field cooled (ZFC), field-cooled cooling (FCC) and field-cooled heating (FCH), respectively.

3. Results and discussion

In order to investigate the effect of Co doping on the structure of the $Mn_{49}Ni_{42}Sn_9$ alloy, the structure of $Mn_{49}Ni_{42-x}Co_xSn_9$ (x = 0, 1, 3 and 5) samples were determined by the XRD method at room temperature, as shown in Fig. 1. Detailed results are collected in Table 1. Both patterns of (a) and (b) in Fig. 1 have a tetragonal $L1_0$ martensitic structure. In comparison of the two patterns, Co doping into $Mn_{49}Ni_{42}Sn_9$ does not change the basic martensitic structure except a small expansion of the two unit cell volumes as listed in Table 1. However, both patterns (c) and (d) for the samples with x = 3, 5, as shown in Fig. 1, present the coexistence of martensitic phase and austenitic phase. Meanwhile, it is obvious that the increase of I_{A220}/I_{M022} with increase of Co content implies the occurrence of MT near room temperature, and the MT shifts to lower temperature with the increase of Co content. Furthermore, the appearance of super-lattice reflection (1 1 1) suggests that the existence of high level of atomic ordering in these alloys [24]. It is no doubt that increase of Co content in $Mn_{49}Ni_{42-x}Co_xSn_9$ alloy can stabilize the austenite phase at room temperature. However, pattern (d) of the sample with increasing Co doping (x = 5) in Fig. 1 presents the coexistence of martensite and austenite, which is not consistent with the result obtained on DSC. This contradiction is resulted from the residual stress as bulk done to powders [25,26].

In order to evaluate the phase transformation temperature, we have conducted DSC on $Mn_{49}Ni_{42-x}Co_xSn_9$ milled powder for cooling and heating cycles, as illustrated in Fig. 2. Large exothermic and endothermic peaks can be observed for the samples with Co content of $x \leq 3$. In general, the cooling cycle shows an exothermic peak, which represents the transition of a high temperature austenitic phase to a low temperature martensite phase; an endothermic peak in the heat cycle reveals reverse MT (martensite to austenite). It can be found that the peaks shift to the lower temperature, thus the disappearance of the large peaks for $Mn_{49}Ni_{37}Co_5Sn_9$ alloys means that the MT temperature is lower than the measured temperature regime (<225 K). T_C denoted as the Curie point of the austenite phase, at which the austenitic state undergoes a ferromagnetic transition according to the fluctuation of the curve during heating procedure, as displayed in Fig. 2. It should be pointed out that the T_C shows non monotonous variation with Co doping due to the fact that the change of the lattice parameters is not monotonous by Co doping in the studied sample [27], as shown in Table 1.

Fig. 3 shows the temperature dependence of magnetization under ZFC, FCC and FCH procedures in a magnetic field of 100 Oe for $Mn_{49}Ni_{42-x}Co_xSn_9$ alloys. It was noticed that the MT appears in all the compounds. For $Mn_{49}Ni_{39}Co_3Sn_9$ alloys, martensitic and reverse martensitic transitions take place in the temperature range of 200–300 K, and the martensitic and austenitic transition start and finish temperatures, denoted as M_s, M_f, A_s, and A_f, are 269 K, 252 K, 274 K, and 283 K, respectively. As a typical characteristic of first order phase transition, a small thermal hysteresis between MT and reverse MT was obtained ($A_f - M_s$ = 14 K and $As - M_f$ = 22 K). In the temperature range of below 185 K, the magnetic phase transition from paramagnetic (PM) martensite to ferromagnetic (FM) martensite was observed around the martensitic Curie temperature $T_{CM} \approx 142$ K. With temperature further decreasing, a