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Metamagnetic phase transformation and magnetocaloric effect in quinary $Ni_{45}Co_5Mn_{40}In_xSn_{10-x}$ heusler alloy

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ABSTRACT

The structure, martensitic transformation, and magnetocaloric properties of quinary $Ni_{45}Co_5Mn_{40}In_x$-Sn_{10-x} Heusler alloys have been investigated. The substitution of In for Sn was found to decrease in c/a parameter which enhances the martensite structure symmetry toward cubic phase and stabilize the martensitic phase. The martensitic transformation temperature was found to increase almost linearly, while Curie temperature of the austenitic phase decreases with increasing the In contents in the alloys. The doping of In keeps the low magnetization of martensitic phase and high magnetization of austenite phase, maintaining the strong metamagnetic behavior and magnetocaloric effect. The alloys exhibit large magnetic entropy change in the structure phase transition, meanwhile, the hysteresis loss is reduced by 74% with increasing the content of In to 8%, suggesting an effective way to reduce thermal hysteresis.

1. Introduction

Much effort has been made to develop the Mn-rich metamagnetic shape memory alloys since the discovery of the magnetic-field-assisted shape memory effect in metamagnetic Mn_2NiZ Heusler alloys [1–7]. For the Mn-rich Mn_2NiZ (Z = Ga, In, Sn, Sb) system, the alloys hold the promise for higher saturation magnetization owing to its higher Mn content, and have been found to exhibit concurrent magnetic and martensitic transformations [4–9]. In these alloys, martensitic transformation occurs between a ferromagnetic austenite and a low-magnetization martensite, which may be paramagnetic, antiferromagnetic or ferromagnetic [10–12]. The large difference in magnetization (ΔM) between these two phases provides strong magnetic driving force for such matemagnetic transformation to be induced by a magnetic field. In contrast, martensitic transformation in other designated ferromagnetic shape memory alloys (FSMAs) have been found to be driven by temperature or stress, instead of magnetic field. This is because the Zeeman energy $\mu_0\Delta M \cdot H$ makes minor contributions to the Gibbs free energy change (ΔG) of the transformation in those alloys due to the small value of ΔM between the two phases [13]. Moreover, the magnetic field-induced transformation usually result in significant changes in electrical resistivity and magnetic entropies, which often lead to some other useful effects and properties, such as giant magnetoresistance effect [10,14] and giant magnetocaloric effect [15,16], showing great potential for technological applications.

Co doping has been reported to obtain prominent effect on increasing ΔM in many Mn-rich MnNiZ (Z = In, Sn, Sb, Ga) alloys [17–20], due to the introduction of Co atoms as a ferromagnetic activator to promote the ferromagnetic alignment of the moments of the nearest neighboring Mn atoms through modifying atomic occupations. For example, the austenite of $Mn_{50}Ni_{37}In_{10}Co_3$ alloy shows a high magnetization of ~110 emu/g at 5 T, compared to 75 emu/g for $Mn_{50}Ni_{40}In_{10}$ [8,9]. Particularly, the alloy $Ni_{45}Co_5$-$Mn_{40}Sn_{10}$ is shown to be singular relative to nearby alloys in magnetic properties [20,21]. The austenite of $Ni_{45}Co_5Mn_{40}Sn_{10}$ has remarkably high magnetization (150 emu/g), low magnetic anisotropy, and almost minimum thermal hysteresis under high applied magnetic field and furthermore at relatively small applied field. In addition, it has been proved that the martensitic transformation behavior of $Ni_{50}Mn_{50-x}Z_x$ (Z = In, Sn, Sb) alloys are sensitive to alloy composition. For instance, the martensitic transformation temperatures of $Ni_{50}Mn_{50-x}Z_x$ are strongly dependent on the alloy composition, generally decreasing with increasing In, Sn, and Sb contents [22]. Wachtel et al. reported that NiMnSn Heusler alloys show the martensitic transformation if the Sn contents are less than 16.5% [23]. Therefore, in this study, we introduced In atoms in $Ni_{45}Co_5$-$Mn_{40}Sn_{10}$ alloy to prepare a quinary alloy system and investigated the effect of In doping on crystal structure, martensitic transformation and magnetocaloric properties. It has found that In-doping enhances the symmetry of martensite structure, increases the martensitic transition temperature, and reduces the Curie temperature of austenite phase, while maintains the strong metamagnetic behavior and magnetocaloric properties, including the large magnetic-entropy changes and low hysteresis loss.

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2. Experimental method

The samples with nominal composition of $Ni_{45}Co_5Mn_{40}In_xSn_{10-x}$ (x = 2, 4, 5, 6, and 8) ingots were prepared by arc-melting technique in argon atmosphere from high purity (99.99%) elemental metals. The ingots were melted four times and turned over in between to guarantee good alloying. The obtained ingots were subsequently homogenized by annealing in evacuated quartz tubes at 1173 K for 24 h, and then quenched in ice water.

The structure of the alloys was characterized by means of X-ray powder diffraction (XRD) using a Rigaku Dmax/2500 instrument with Cu Kα X-ray radiation, and the samples for powder XRD measurements were made by fine grinding. The Rietveld refinements were performed on the XRD patterns to obtain the detailed information about the crystallographic structure of samples by means of General Structure Analysis System (GSAS) package [24]. The magnetic properties and phase transformation were studied using a vibrating-sample magnetometer system (Versalab, Quantum Design Co.). The magnetic entropy changes of samples, ΔS_m, as a function of temperature is calculated by using the Maxwell relation:

$$\Delta S_m(T,H) = S_m(T,H) - S_m(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1)$$

For a first-order system, the magnetic entropy change curve usually exhibits a extremely high spike, which has been proved a spurious signal [25–27]. To accurately derive the magnetic entropy changes (ΔS_m) at magnetostructural transitions, the contribution of high spike to the total magnetic entropy change is deducted. The plateau of magnetic entropy change curves is adopted as the effective ΔS_m.

3. Results and discussion

Fig. 1 shows XRD patterns of powder samples of the prepared alloys measured at room temperature. The alloys show a single phase with body-centered tetragonal martensitic structure and belong to space group of I4/mmm. The lattice parameters of prepared $Ni_{45}Co_5Mn_{40}In_xSn_{10-x}$ alloys are carefully determined by the Rietveld refinement. Fig. 2 shows the refinement results of $Ni_{45}Co_5Mn_{40}In_2Sn_8$ powder sample. As noted by R_p and R_{wp} factors, the fitted pattern is in well agreement with the experiment data. The effect of In content on the lattice parameters is shown in the inset of Fig. 2. Although the structure of samples remains unchanged at room temperature, the lattice parameters vary regularly by increasing the In content. It is found that there is a small expansion in the a-direction and a larger shrink in the c-direction with increasing In content, a (=b) elongates by 0.13% and c shrinks by 0.60% for x = 8. The parameter c/a ratio of tetragonal structure decreases regularly from 1.7713 to 1.7585 with increasing In content from x = 2 to x = 8, indicating a higher structure symmetry in $Ni_{45}Co_5Mn_{40}In_xSn_{10-x}$ alloys. In the meantime, the unit cell volume decreases monotonously with In substitution for Sn, from 105.27 to 104.90 Å^3.

Fig. 3 shows the magnetization behavior of the five samples during thermal cycling with a heating/cooling rate of 5 K/min in magnetic fields of different strengths. The martensitic and austenitic transformation starting and finishing temperature are defined as M_s, M_f, and A_s, A_f respectively, which are determined at a low field of 0.02 T and summarized in Table 1. Under a magnetic field of 0.02 T, as shown in Fig. 3a, the sample $Ni_{45}Co_5Mn_{40}In_2Sn_8$ shows a sharp increase in magnetization upon cooling to 452 K, indicating the Curie transition of the austenite phase, which is similar to that of $Ni_{45}Co_5Mn_{40}Sn_{10}$ alloy [20,21]. The transformation from the high magnetization austenite to low magnetization martensite occurred at 352 K on cooling, as indicated by M_s. Upon heating, the sample shows a almost completely reversible behavior, with the reverse martensitic transformation starting at 354 K and finishing at 362 K on heating, leaving a thermal hysteresis of 10 K above the

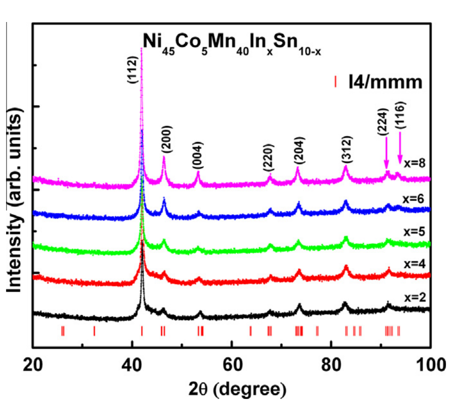

Fig. 1. X-ray powder diffraction patterns of $Ni_{45}Co_5Mn_{40}In_xSn_{10-x}$ alloys.

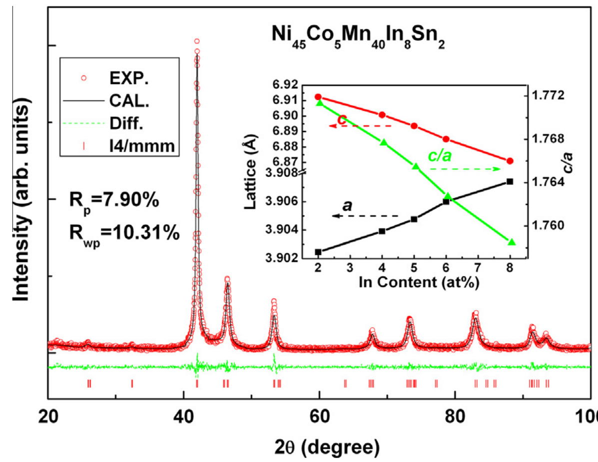

Fig. 2. Rietveld refinement of X-ray diffraction pattern for $Ni_{45}Co_5Mn_{40}In_8Sn_2$ sample. The open circles show the observed counts and the solid line is the calculated profile. The difference between the observed and calculated patterns is shown as a continuous line at the bottom of the two profiles. The vertical bars indicate the positions of reflections on JCPDS. Inset shows the dependence of lattice parameter and ratio c/a of martensitic structure on In content.

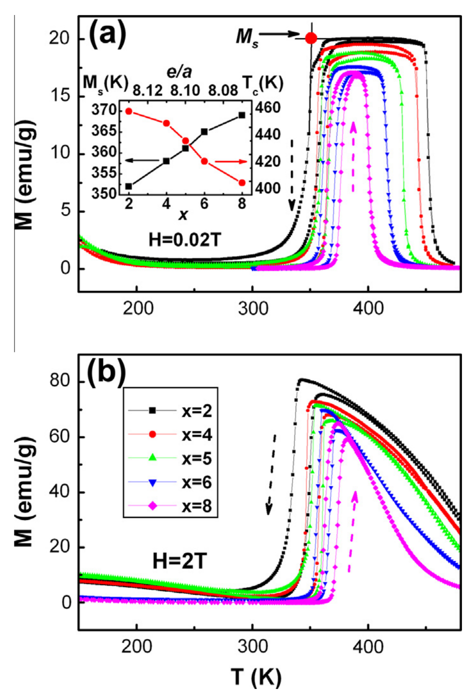

Fig. 3. Thermomagnetization curves measured under the magnetic field of (a) 0.02 T, and (b) 2 T for $Ni_{45}Co_5Mn_{40}In_xSn_{10-x}$ alloys. The dash arrows indicate heating and cooling path. Inset of Fig. 3a shows the dependence of martensitic transformation temperature M_s and Curie temperature T_c of austenite phase on In content and valence electron concentration.