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Optimization of Ni–Co–Mn–Sn Heusler alloy composition for near room temperature magnetic cooling

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ABSTRACT

Ni–Co–Mn–Sn based Heusler alloys are promising magnetocaloric materials. The effect of both Co and Mn substitution in these alloys was studied. The magnetocaloric properties, thermopower, electrical resistivity, structural and magnetic phase transitions of Ni–Co–Mn–Sn alloys were determined. Interestingly, tuning Co and Mn composition resulted in high maximum entropy change (ΔS_{max}) of ~32 J/kg K near room temperature in $Ni_{48}Co_2Mn_{38}Sn_{12}$ alloys. Alloying additions of cobalt increased magnetization and decreased the martensitic transition temperature (M_s). The Curie temperature of the austenite (T_c^A) and martensite (T_c^M) phases increased with increasing Co content. However, this decrease of M_s and increase of T_c^M resulted in decrease of the change in magnetization during the martensitic transition. Hence, Mn content was tuned to increase ΔS_M and to tune M_s to a value relevant to room temperature applications. Thus, through tuning both Co and Mn composition, a high ΔS_M was obtained near room temperature, making these alloys attractive magnetocaloric materials for room temperature applications.

1. Introduction

Magnetic cooling, which is based on the Magnetocaloric Effect (MCE), has attracted intense research and development interest as an alternative cooling technology for near room temperature cooling applications. It has several advantages, including high energy efficiency, absence of chlorofluorocarbons, low vibration and minimum noise. Since the discovery of the "Giant" MCE in $Gd_5(Si_xGe_{1-x})_4$ [1,2] compounds, other materials with a first order magnetostructural transition, such as $La(Fe_{1-x}Si_x)_{13}$ [3], $MnFeP_{0.45}As_{0.55}$ [4] and Heusler alloys [5] have been reported.

In Ni–Mn–X based Heusler alloys, strong interactions between the crystal structure and the magnetic properties results in large inverse MCE. Upon cooling from high temperatures, Ni–Mn–X Heusler alloys may undergo multiple transitions: (i) a magnetic transition from the paramagnetic to the ferromagnetic austenitic phase at the Curie temperature of austenite (T_c^A); (ii) a martensitic transition from the ferromagnetic austenitic phase to the weakly magnetic (paramagnetic or antiferromagnetic) martensite phase at the martensitic transition temperature (M_s); (iii) a magnetic transition from a weakly magnetic state to a ferromagnetic state at the Curie temperature (T_c^M) of the martensitic phase [6–14].

In such Ni–Mn–Sn Heusler alloys, M_s is quite sensitive to alloy composition. M_s can change by more than 30 K with only ~1% change in Mn or Sn content. To use such Ni–Mn–Sn Heusler alloys in magnetic cooling systems for near room temperature applications, a high magnetic entropy change (ΔS_M), wide working temperature range, as well as tunable M_s are required. Hence, tuning M_s to near room temperature while retaining high ΔS_M is a necessity. Therefore, in this work, we examined the role of alloy composition, specifically Co and Mn, on M_s and ΔS_M. We replaced Ni by Co; this substitution can increase the magnetization of the alloy [15–18] since Co has higher magnetic moment (~1.0 μ_B) than Ni (~0.31 μ_B).

In contrast to studies on the magnetocaloric effect in Heusler alloys, electrical and thermal transport have scarcely been investigated. Resistivity and thermopower in $Ni_{2+x}Mn_{1-x}Ga$ series were investigated by Pirolkar et al. ($x = 0.19$) [19] and Kuo et al. ($x = 0$ to 0.24) [20]. Sharma et al. [21] investigated resistivity and magnetoresistance in a $Ni_{49}CuMn_{34}In_{16}$ alloy.

In this work, we studied the crystal structure transition and entropy change of Ni–Co–Mn–Sn alloys. Co substitution for Ni increased the magnetization value of the alloys, while decreasing M_s. T_c^M and T_c^A of the martensite and austenite phases also increased with increasing Co content. Since M_s decreased by Co addition, we adjusted the Mn content to tune the transition temperature to a range suitable for room temperature applications. We find that

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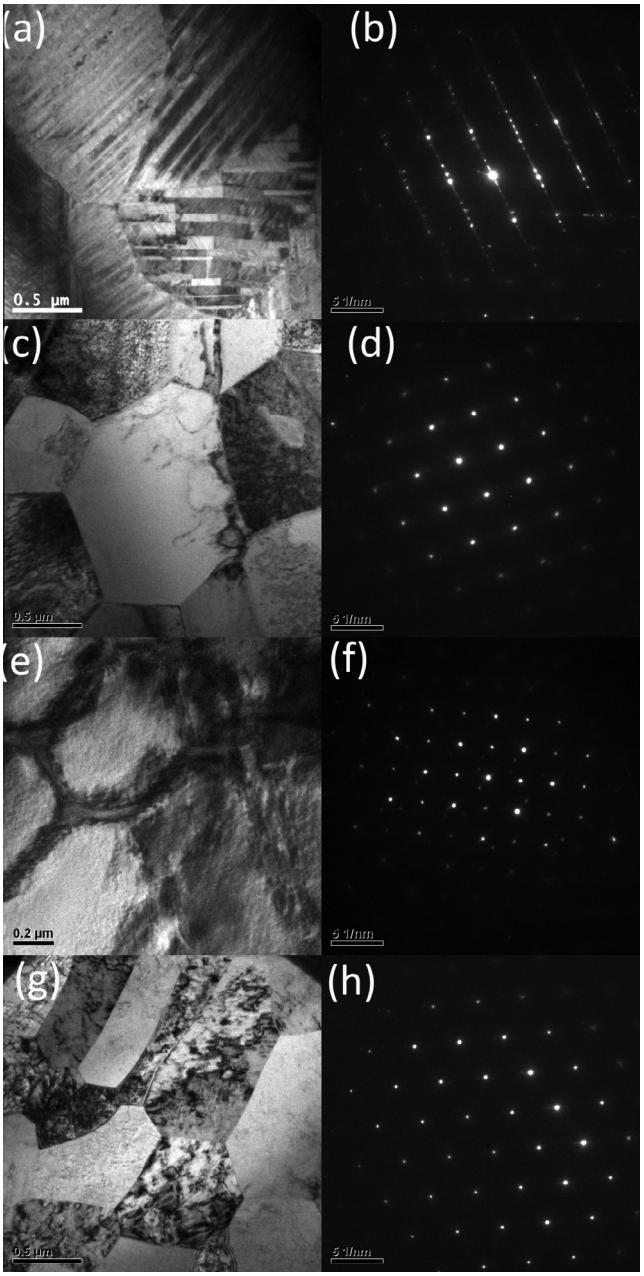

Fig. 1. TEM analysis (a) BF micrograph of the austenite phase in $Ni_{50}Mn_{37}Sn_{13}$. (b) 7 M orthorhombic martensite of $Ni_{50}Mn_{37}Sn_{13}$. Microstructure of platelike martensite. (c) BF micrograph of the austenite phase in $Ni_{48.5}Co_{1.5}Mn_{37}Sn_{13}$. (d) (011) Zone of $Ni_{48.5}Co_{1.5}Mn_{37}Sn_{13}$. (e) BF micrograph of the austenite phase in $Ni_{47.5}Co_{2.5}Mn_{37}Sn_{13}$. (f) (001) Zone of $Ni_{47.5}Co_{2.5}Mn_{37}Sn_{13}$. (g) BF micrograph of the austenite phase in $Ni_{48}Co_2Mn_{38}Sn_{12}$. (h) (011) Zone of $Ni_{48}Co_2Mn_{38}Sn_{12}$.

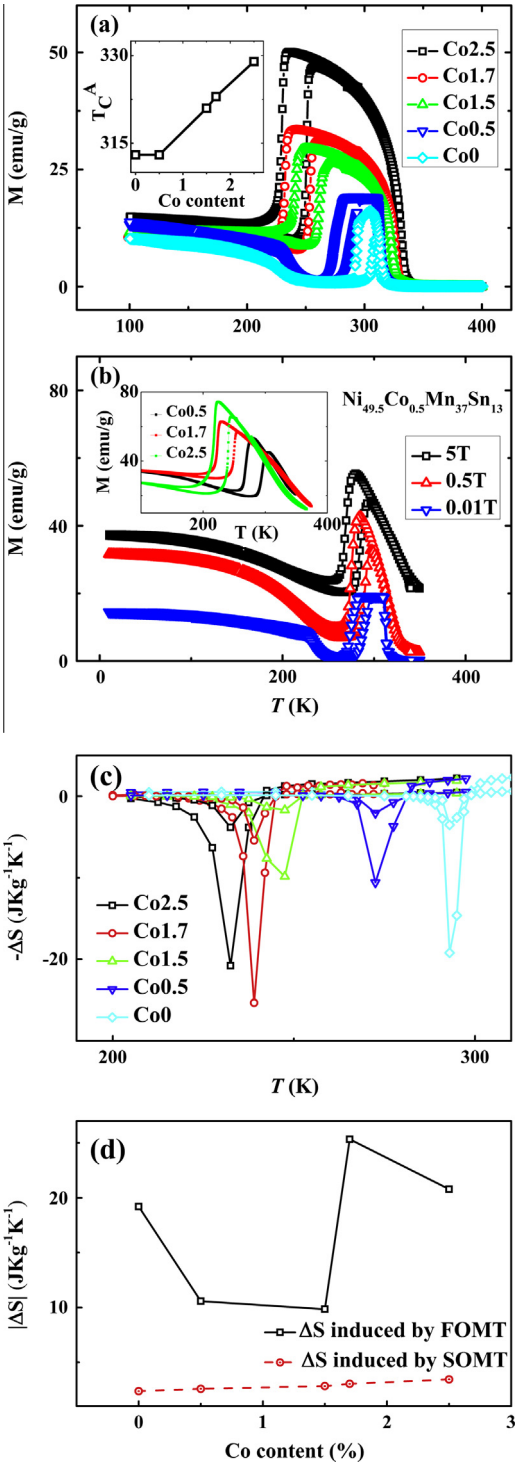

Fig. 2. (a) FCC and FCW $M(T)$ curves in 100 Oe magnetic field of $Ni_{47.5}Co_{2.5}Mn_{37}Sn_{13}$, $Ni_{48.3}Co_{1.7}Mn_{37}Sn_{13}$, $Ni_{48.5}Co_{1.5}Mn_{37}Sn_{13}$, $Ni_{49.5}Co_{0.5}Mn_{37}Sn_{13}$, $Ni_{50}Mn_{37}Sn_{13}$ and inset figure shows the T_c^A with different Co content. (b) FCW, FCC $M(T)$ curves of $Ni_{49.5}Co_{0.5}Mn_{37}Sn_{13}$ in 100 Oe, 5000 Oe and 50 kOe and inset figure shows the M_s, T_c^A and T_c^M with different Co content. (c) ΔS of Co0, Co0.5, Co1.5, Co1.7 and Co2.5 samples in 1 T and 5 T applied magnetic field. (d) ΔS of samples with different Co content induced by martensitic transition and magnetic transition of austenite.

the optimum alloy composition is $Ni_{48}Co_2Mn_{38}Sn_{12}$. Resistivity and thermopower measurements were also correlated to these magnetic and structural measurements.

2. Experimental

Polycrystalline $Ni_{50}Mn_{37}Sn_{13}$, $Ni_{49.5}Co_{0.5}Mn_{37}Sn_{13}$, $Ni_{48.5}Co_{1.5}Mn_{37}Sn_{13}$, $Ni_{48.3}Co_{1.7}Mn_{37}Sn_{13}$, $Ni_{47.5}Co_{2.5}Mn_{37}Sn_{13}$ and $Ni_{48}Co_2Mn_{38}Sn_{12}$ alloys were prepared by arc melting followed by melt spinning at 60 rpm wheel speed in an inert atmosphere to produce melt spun ribbons. The samples are referred to as Co0, Co0.5, Co1.5, Co1.7, Co2.5 and Mn38Co2. Melt spinning offers advantages such as compositional homogeneity. Textured polycrystalline material with small grain size can be produced by this method, which can facilitate martensite nucleation [22].

The field dependence of the magnetization curves were measured by a commercial superconducting cryostat PPMS (Physical Property Measuring System, Quantum Design) equipped with a vibrating sample magnetometer. The magnetization values were recorded at different temperatures under a maximum magnetic field of 50 kOe. The isothermal magnetic entropy change (ΔS_M) was calculated from the isothermal magnetization curves [23].