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Abnormal e/a-dependence of T_M and large inverse magnetocaloric effect in $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ alloys

W.J. Feng[a,b,*], L. Zuo[b], Y.B. Li[c], Y.D. Wang[b], M. Gao[a], G.L. Fang[a]

[a] College of Physics Science and Technology, Shenyang Normal University, Shenyang 110034, China
[b] School of Materials and Metallurgy, Northeastern University, Shenyang 110004, China
[c] Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130021, China

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ABSTRACT

The influence of Cu substitution for Ni on magnetic properties and magnetic entropy change has been investigated in the $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ alloys with $x = 0$, 1 and 2. With increasing Cu content from $x = 0$ to 2, a decreasing dependence of the martensitic transformation temperature (T_M) on the number of valence electrons per atom (e/a) is observed, which cannot be explained by the size factor or the number of valence electrons per atom. An inverse magnetocaloric effect was observed in the vicinity of the first order martensitic transition. The maximum value of $-\Delta S_M^{max}$ in the nominal $Ni_{48}Cu_1Mn_{39}Sb_{12}$ alloy is 9.38 J kg^{-1} K^{-1} at 291 K for a magnetic field change from 0 to 5 T, with the refrigerant capacity of 25.9 J kg^{-1}. The large ΔS_M indicate that nominal $Ni_{48}Cu_1Mn_{39}Sb_{12}$ alloy may be a promising candidate for magnetic refrigeration at room temperatures.

1. Introduction

Increasing attention has been attracted by magnetocaloric cooling technology due to the recent discoveries of magnetocaloric materials near room temperature [1–3]. These materials often exhibit a large magnetocaloric effect (MCE), the temperature and entropy changes that result from a change in applied magnetic field. Commonly, the most noticeable MCE occurs at temperatures near magnetic transitions [4]. Several systems undergoing a first-order transition, such as Gd–Si–Ge [1], Fe–Mn–P–As [2], La–Fe–Si [5], and Ni–Mn–Ga [6,7], have demonstrated large MCE.

Among the materials, Ni–Mn–X ferromagnetic shape memory alloys (FSMAs) with X = Ga, Sn, In and Sb are receiving increasing attention [7–9]. As is well known, FSMAs undergo a first-order structural transition from a parent austenitic phase to a martensitic one on cooling, which may cause an abrupt change of magnetization, and a giant MCE. According to Khan et al. [10], a maximum positive magnetic entropy change of 19 J/kg K for a magnetic field change $\Delta B = 0$–5 T was observed at 297 K in $Ni_{50}Mn_{37+x}Sb_{13-x}$ with $x = 1$. Du et al. [11] reported a maximum value of 9.1 J/kg K in $Ni_{50}Mn_{50-x}Sb_x$ with $x = 13$ at 287 K for a magnetic field change of 0–5 T. Ren et al. [12] reported the resistivity increases, while the Curie temperature decreases, with increasing Cu concentration in $Cu_xNi_{1-x}MnSb$ alloys.

On the other hand, it was reported that the number of valence electrons per atom (e/a) can influence the martensitic transformation temperature of Ni–Mn–X. Suppose the number of valence electrons for Ni ($3d^8 4s^2$), Mn ($3d^5 4s^2$), X ($4s^2 4p^m$) atoms as 10, 7 and n, respectively, the calculated e/a is as follows [13,14]:

$$e/a = \frac{10 \times (Ni_{at.\%}) + 7 \times (Mn_{at.\%}) + n \times (X_{at.\%})}{Ni_{at.\%} + Mn_{at.\%} + Y_{at.\%}}$$

The e/a-dependence of T_M was found to increase monotonously in many NiMn-based FSMAs [15]. That is, when the Fermi surface reaches the Brillouin zone boundary, martensitic structural transition occurs due to structural instabilities [16]. Therefore, the change in e/a as well as the Brillouin zone boundary becomes the driving forces for the occurrence of the martensitic structural transformation. Some reported the monotonously increasing e/a-dependence of T_M. However, an opposite/abnormal dependence of T_M on e/a is also observed in $Ni_{2-x}Cu_xMnGa$ [17] and $Ni_{50}Mn_{35-x}Cu_xSn_{15}$ alloys [18].

In our previous work, the nominal $Ni_{49}Mn_{39}Sb_{12}$ alloy displays $\Delta S_M = 6.15$ J kg^{-1} K^{-1} for a magnetic field change of 0–1 T at 279 K [19], and large reversible magnetic entropy change of $\Delta S_M = 5.21$ J kg^{-1} K^{-1} is observed at 347 K [20]. Also, Refs [21,22] reveal that in the Cu-substituted $Ni_{2.15}Mn_{0.85}Ga$ and $Ni_{43}Mn_{46}Sn_{11}$, the higher T_M temperature and large MCE are obtained with increasing Cu content. Therefore, in the present paper, we employed Cu to substitute Ni of $Ni_{49}Mn_{39}Sb_{12}$, aiming to

* Corresponding author at: College of Physics Science and Technology, Shenyang Normal University, 253, Huanghe North Street, Huangg, Shenyang 110034, China. Tel.: +86 024 62652182; fax: +86 024 86575015.
E-mail address: wjfeng@yahoo.com.cn (W.J. Feng).

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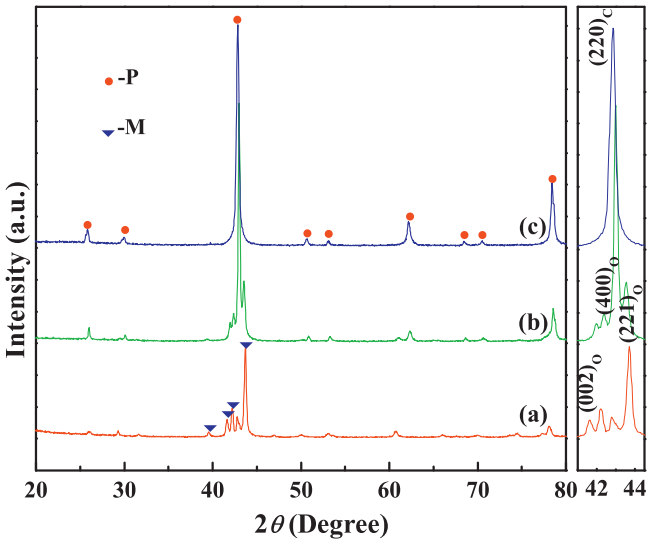

Fig. 1. XRD patterns of the $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ with (a) $x=0$; (b) $x=1$; (c) $x=2$ alloys at room temperature, and the suffices C and O are for cubic and orthorhombic phases, respectively.

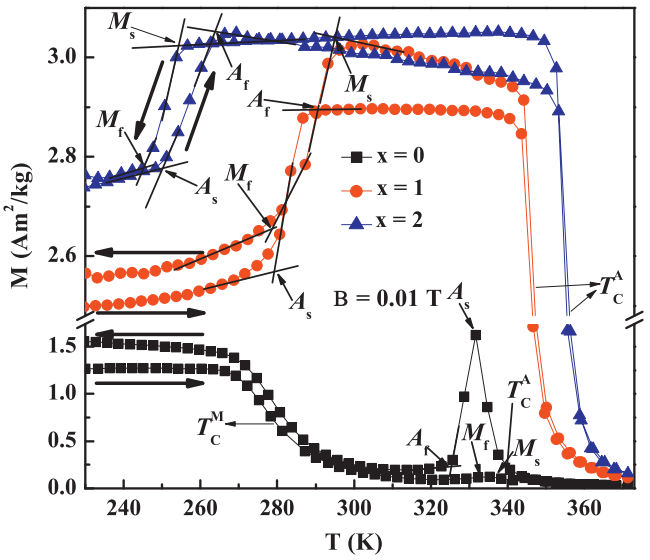

Fig. 2. Magnetization curves as a function of temperature of $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ with $x=0$, 1, 2 alloys on heating and cooling measured in a magnetic field of 0.01 T on heating.

improve the ΔS_M values by the means of the e/a dependence of T_M. Large magnetic entropy change of $\Delta S_M = 9.38\ J\ kg^{-1}\ K^{-1}$ at 291 K for a magnetic field change of 0–5 T, as well as abnormal dependence of T_M on e/a, in $Ni_{48}Cu_1Mn_{39}Sb_{12}$ was observed.

2. Experimental

Polycrystalline $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ ($x=0$, 1, 2) alloys were prepared by arc-melting the appropriate amounts of Ni, Cu, Mn, and Sb with purity of 4 N in argon atmosphere. The ingots were sealed in a silica tube and annealed at 1123 K for 50 h, then quenched in water. X-ray diffraction (XRD) was carried out at room temperature with Cu Kα radiation in a BD2008 diffractrometer. The phase concentration was analysed by using a scanning electron microprobe (SSX550) and energy dispersive X-ray (EDX). The magnetic properties were measured in Lake Shore's 7400 series vibrating sample magnetometer (VSM) in magnetic fields up to 5 T.

3. Results and discussion

Fig. 1 represents the XRD patterns of the $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ alloys with $x=0$, 1, 2 obtained at room temperature. The pattern of $Ni_{47}Cu_2Mn_{39}Sb_{12}$ displays peaks characteristic of the Heusler $L2_1$ structure (parent phase) at room temperature. However, for $Ni_{48}Cu_1Mn_{39}Sb_{12}$, some weak peaks of the martensite phase appear besides those for the $L2_1$ structure, while for $Ni_{49}Mn_{39}Sb_{12}$, the XRD peaks for the martensite phase become obvious, also shown as (a) in Fig. 1. With increase of Cu substitution for Ni, the martensitic transformation temperatures become lower, and even below room temperature. The EDX microanalysis reveal that the average elemental chemical composition of $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ with $x=0$, 1, 2 is determined as $Ni_{49.2}Mn_{39.5}Sb_{11.3}$, $Ni_{48.3}Cu_{1.1}Mn_{39.4}Sb_{11.2}$ and $Ni_{47.2}Cu_{2.0}Mn_{39.6}Sb_{11.2}$, respectively. Sutou et al. [23] suggested that the martensite structure possesses an orthorhombic four-layered structure indicated as 4O(22) in NiMnSb alloy. A martensitic transformation of $L2_1$ structure into an orthorhombic four-layered (4O) structure [23] is present in the Ni–Mn–Sn Heusler system. Recent results of neutron diffraction measurements by Brown et al. suggest that the space group of the 4O structure is *Pmma* [24]. Therefore, we can index $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ alloys with $x=0$ assuming an orthorhombic 4O structure in the region $41^\circ < 2\theta < 44.5^\circ$ (see the right panel of Fig. 1). Our previous results reveal that [19,20], XRD pattern of the nominal $Ni_{49}Mn_{39}Sb_{12}$ alloy displays a $L2_1$-type structure, which is different from our present investigation. However, as mentioned above, the average elemental chemical composition of the present $Ni_{49}Mn_{39}Sb_{12}$ alloy is determined as $Ni_{49.2}Mn_{39.5}Sb_{11.3}$, with less Sb composition than that of previous nominal $Ni_{49}Mn_{39}Sb_{12}$ alloy (or $Ni_{51.6}Mn_{36.7}Sb_{11.7}$). According to Khan et al. [9], less Sb composition in Ni–Mn–Sb alloy means a higher martensitic temperature, which is basically correspondent with our observation.

In the unit cell of the $L2_1$ Heusler alloys structure with a space group of $Fm\bar{3}m$, the austenitic phase is based on a cubic structure with four interpenetrating *Fcc* lattices Ni, Mn, Ni, Sb. By interchange of atoms the structure easily becomes atomic disorder, which can often influence first-order phase transition [23]. That is, the martensitic transition temperature, T_M, is extremely sensitive to the composition in these alloys [24].

Magnetization as a function of temperature of $Ni_{49-x}Cu_xMn_{39}Sb_{12}$ with $x=0$, 1, 2 alloys on heating and cooling measured in a magnetic field of 0.01 T are plotted in Fig. 2. The alloys were initially cooled in the absence of field and data were collected on warming from 220 to some temperature, followed by cooling back to 220 K while recording the data. The characteristic temperatures of structure transition, i.e. A_s, A_f, M_s and M_f, determined from M–T curves, where both the M_f and A_s denote the martensitic transition finishing temperature and reverse martensitic starting transition temperature, respectively. For Cu-free alloy ($x=0$), with the increasing temperature, magnetization remains almost constant until a gradual decreases occurs in the range of 270–300 K. Negligible thermal hysteresis appears. This magnetization transition temperature is defined as the Curie temperature (T_C^M) of martensite phase (about 280 K), which has been reported in many Refs [9,25–27]. With the further increasing temperature, an antiferromagnetic-type transition was observed in both heating and cooling magnetization curves in the range of 320–350 K. According to Khan et al. [9,10], this transition should be ascribed to martensitic transformation, with a transition temperature of T_M (the temperature corresponding to the maximum on the curves of the dM_{ZFC}/dT–T), followed by a decrease of magnetization at the Curie temperature of the austentite (T_C^A). It should be noted that temperature hysteresis occurs between heating and cooling pro-