Martensitic and magnetic transformation in Mn$_{50}$Ni$_{50-x}$Sn$_x$ ferromagnetic shape memory alloys

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A martensitic transformation (MT) from a body-centered-cubic austenitic phase to a tetragonal martensitic phase has been found in Mn$_{50}$Ni$_{50-x}$Sn$_x$ ($0 \leq x \leq 11$) alloys. The martensitic transformation temperature can be decreased by about 71.6 K by increasing the Sn concentration by 1 at. %. For $9 \leq x \leq 11$, Mn$_{50}$Ni$_{50-2x}$Sn$_x$ ferromagnetic shape memory alloys are obtained. Due to the large magnetization difference ($\Delta M = 60$ emu/g) and small thermal hysteresis ($\Delta T = 6$ K) in the Mn$_{50}$Ni$_{40}$Sn$_{10}$ alloy, a two-way magnetic-field-induced martensitic transformation is observed with $dT/dH = 2$ K/T. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4758180]

I. INTRODUCTION

As valuable multifunctional materials, ferromagnetic shape memory alloys (FSMAs) have been investigated for several years. Following the discovery of magnetic-field-induced strain in the Ni$_2$MnGa alloy,$^1$ extensive research has been carried out with the focus on discovering new FSMAs. To date, Ni$_2$MnAl,$^2$ CoNiGa,$^3,4$ CoNiAl,$^5$ Ni$_2$FeGa,$^6$ Ni$_2$MnX ($X =$ In, Sn, Sb),$^7$ and Mn$_2$NiGa$^8$ have been successively developed. Among them, FSMAs with a high Mn content and low content of the main group element have been studied the most.$^2,7$ Numerous studies have demonstrated that high Mn content is crucial for realizing many properties such as magnetoresistance,$^9$ magnetocaloric effect,$^{10}$ and exchange bias.$^{11}$ The Mn$_2$NiGa alloy with the highest Mn content, indeed exhibits superior properties, such as an excellent two-way shape memory effect with a strain of 1.7%, a high Curie temperature ($T_C = 588$ K),$^8$ a magnetic field induced martensitic transformation (MFIMT)$^{12}$ and interesting transport properties.$^{13}$ However, Mn$_2$NiGa is the only Mn$_2$Ni-based FSMA found to date. Therefore, more Mn$_2$Ni-based FSMAs need to be developed. Recently, Paul and Ghosh$^{14}$ predicted the existence of martensitic transformation (MT) behavior in Mn$_2$NiSn on the basis of first-principles calculations. This suggests that Mn$_2$NiSn could be the next Mn$_2$Ni-based FSMA, but so far, there have been no experimental studies of Mn$_2$NiSn. In this work, we report studies of a series of FSMAs with composition Mn$_{50}$Ni$_{50-x}$Sn$_x$ ($9 \leq x \leq 11$). A two-way MFIMT has been observed in the Mn$_{50}$Ni$_{40}$Sn$_{10}$ alloy.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Mn$_{50}$Ni$_{50-x}$Sn$_x$ ($x = 0, 2, 4, 6, 8, 9, 10, 10.5, 11$) alloys were prepared by arc melting, annealed at 1073 K for 72 h, and then quenched in liquid nitrogen. The martensitic transformation temperature ($T_M$) was measured by differential thermal analysis (DTA). The crystal structure was determined from x-ray diffraction (XRD) patterns. Magnetism measurements were performed on a physical property measurement system (Quantum Design).

In order to reveal more clearly the effect of doping Sn into the Mn$_{50}$Ni$_{50}$ alloy, the electron localization functions (ELF) of Mn$_{50}$Ni$_{50-x}$Sn$_x$ alloys were calculated using the self-consistent full-potential linearized-augmented-plane-wave (FP-LAPW) method based on the generalized gradient approximation within the density functional theory.$^{15,16}$

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns measured at room temperature for the Mn$_{50}$Ni$_{50}$Sn$_{11}$ and Mn$_{50}$Ni$_{42}$Sn$_{8}$ alloys. Their martensitic transformation temperatures are below and above the room temperature, respectively. For Mn$_{50}$Ni$_{39}$Sn$_{11}$, the (220), (004), and (224) peaks can be indexed well to a body-centered-cubic structure with a lattice parameter of $a = 6.021$ Å. The super-lattice diffraction peaks such as (111) and (113) can also be found, which suggests a high level of atomic order. With relatively low Sn content, the Mn$_{50}$Ni$_{42}$Sn$_{8}$ sample possesses a tetragonal structure with lattice parameters $a = b = 5.462$ Å and $c = 6.923$ Å.

Fig. 2 shows, in the main part of the diagram, the temperature dependence of the AC susceptibility for the Mn$_{50}$Ni$_{50-x}$Sn$_x$ ($x = 9, 10, 11$) alloys. The inset shows DTA curves for the Mn$_{50}$Ni$_{50-x}$Sn$_x$ ($x = 0, 2, 4, 6, 8$) alloys on cooling and heating. It can be seen from the DTA curves that for the equiatomic NiMn alloy ($x = 0$), $T_M$ is 961 K. After doping 8 at. % Sn into the NiMn alloy, the $T_M$ of Mn$_{50}$Ni$_{42}$Sn$_{8}$ falls to only 388 K. Thus, $T_M$ can be effectively controlled by adjusting the Sn content doped into the NiMn alloy. In order to study the magnetism of these alloys, the $\chi$-$T$ curves were measured. As each sample was cooled, the susceptibility underwent a sudden jump at about 285 K, corresponding to the Curie temperature of austenite ($T_C^A$). Further decreasing...
the temperature caused a sharp drop in the curve, corresponding to the MT. The same phenomena were observed on heating, except for a shift in the temperature of the reverse transformation. Note that the TM of these alloys has been lowered below TC. Thus, the FSMAs Mn50Ni50/C0xSnx (9/C20x/C2011) are obtained. It is also interesting to observe that each curve exhibits a cusp at lower temperature, which has been discussed in detail in our previous work.17

Fig. 3 shows the phase diagrams for Mn50Ni50/C0xSnx (x = 0, 2, 4, 6, 8, 9, 10, 10.5, 11) as functions of the Sn content. The data were obtained from the DTA and susceptibility measurements. It is clear that TM decreases rapidly with increasing Sn content. On average, the rate of change is 71.6 K/at. % Sn content. This suggests that doping with Sn can effectively stabilize the austenitic phase. Accordingly, the stability of the two phases (austenite and martensite) can be controlled by the Sn content in Mn50Ni50/C0xSnx alloys. In addition, it may be noticed that the absolute value of the slope for TM vs Sn content increases when the Mn50Ni50/C0xSnx alloys become ferromagnetic. This indicates that magnetism can also help to stabilize the austenitic phase. However, the mechanism is still unclear and requires further examination that falls beyond the scope of the present work. The inset of Fig. 3 shows the dependence of the thermal hysteresis (ΔT) on the Sn content for Mn50Ni50/C0xSnx alloys. It is obvious that ΔT decreases linearly with increasing Sn content and that ΔT = 6 K when x = 10, which is smaller than that of other Ni3Mn-based FSMAs.18–20 Accordingly, energy consumption in the MT process for Mn50Ni50/C0xSnx alloys will be greatly reduced compared to Ni3Mn-based FSMAs.

Most researchers consider that TM has a close relationship to the valence electron concentration (e/a): TM decreases with decreasing e/a.21,22 In order to investigate the relationship of TM and e/a in this kind of alloy, the dependences of TM on e/a for Ni50Mn50/C0xSnx (x = 0–16) and Mn50Ni50/C0xSnx (x = 0–11) alloys are shown in Fig. 4. The data for Ni50Mn50/C0xSnx were obtained from Ni2Mn-based Heusler alloys studied by Krenke et al.22 For the Ni3MnSn system, e/a
decreases when Sn is substituted for Mn in the parent NiMn alloy. It is evident that decreasing e/a can indeed reduce the T_M of this system.22 Similarly, for the Mn_5SiSn system, substituting Sn for Ni in NiMn alloy can also lower the e/a of the system. We can observe that the T_M vs e/a of Mn_5Ni_10Sn_10 follows the same rule as for Ni_5Mn_50Sn_10. Therefore, the underlying mechanism for the observation that doping with Sn can stabilize the austenitic phase is the modification of e/a. In addition, it can be seen that the absolute value of the slope decreases when Sn replaces Mn in NiMn alloy. This suggests that the bond energy between Sn and Ni sites whereas it attains local maximum values (about 2.24 × 10^-5) near the Sn atoms. Thus, the T_M of Mn_50Ni_40Sn_10 is less sensitive to the Sn content than for Ni_50Mn_50Sn_10.

The ELF is a method for analyzing the electronic structure, chemical bonding and in turn the stability of compounds.23,24 In order to study the effect of doping with Sn on the large change in martensitic transformation temperature in the Mn_50Ni_50Sn_10 alloys, the ELF for Mn_50Ni_50 and Mn_50Ni_25Sn_25 alloys have been calculated as shown in Fig. 5. For Mn_50Ni_50, the value of the ELF is small at the Mn and Ni sites whereas it attains local maximum values (about 1.344 × 10^-2) between the two sites as shown in Fig. 5(a). For Mn_50Ni_25Sn_25, the ELF is negligible at the Mn and Ni sites but has large values (about 2.241 × 10^-5) near the Sn atoms. This suggests that the bond energy between Sn and Mn or Ni is larger than that between Mn and Ni, which determines the stability of the austenitic phase in Mn_50Ni_50Sn_10 and may be one of the reasons for the characteristic magnetic features observed in these compounds.

Fig. 6 shows the M-T curves for the Mn_50Ni_40Sn_10 alloy in the presence of 0.05 T and 13 T fields. The T_M decreases from 178 K to 152 K as the field increases from 0.05 T to 13 T, indicating a ratio dT/dH of about 2 K/T. The isothermal magnetization curves of the Mn_50Ni_40Sn_10 alloy at different temperatures were also measured as shown in the inset of Fig. 6. The curves at 130 K and 240 K show that the sample is in the martensitic phase and austenitic phase, respectively. On the other hand, the curves measured between 170 K and 178 K show two-way metamagnetic behavior. Thus, a reversible MFIMT is confirmed in Mn_50Ni_40Sn_10 alloy.

IV. CONCLUSION

The martensitic transformation temperature of Mn_50Ni_10Sn_x (0 ≤ x ≤ 11) alloys can be effectively controlled by adjusting the Sn content. When 9 ≤ x ≤ 11, the ferromagnetic shape memory effect is realized. The underlying mechanism is the modification of the electron localization functions and in turn the bond energy by substitution of Sn for Ni. Compared to Ni_50Mn_50Sn_10, the heat hysteresis (∆T) of Mn_50Ni_10Sn_x is smaller and the T_M is less sensitive to the Sn content. These properties make the Mn_50Ni_50Sn_x alloys good candidates for applications. Furthermore, due to the large magnetization difference between the two phases (60emu/g) and small ∆T (6 K), a two-way magnetic field induced martensitic transformation can be observed in the Mn_50Ni_40Sn_10 alloy with dT/dH = 2 K/T.

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