Effects of pre-deformation on the martensitic transformation and magnetocaloric property in Ni–Mn–Co–Sn ribbons*

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(Received 9 April 2010; revised manuscript received 6 May 2010)

This paper investigates the martensitic transformation and magnetocaloric effect in pre-deformed Ni–Mn–Co–Sn ribbons. The experimental results show that the reverse martensitic transformation temperature $T_{\rm M}$ increases with the increasing pre-pressure, suggesting that pre-deformation is another effective way to adjust $T_{\rm M}$ in ferromagnetic shape memory alloys. Large magnetic entropy changes and refrigerant capacities are obtained in these ribbons as well. It also discusses the origin of the enhanced martensitic transformation temperature and magnetocaloric property in pre-deformed Ni–Mn–Co–Sn ribbons.

Keywords: pre-deformation, martensitic transformation, magnetocaloric property
PACC: 7550, 7530S

1. Introduction

The off-stoichiometric Ni–Mn–X (X=Sn, In, and Sb) Heusler alloys and the related intermetallic compounds upon partial substitution of Co for Ni/Mn, as the multifunctional ferromagnetic shape memory alloys (FSMAs), have attracted more and more attention in recent years.[1−19] Among these alloys, a martensitic transformation (MT) from the ferromagnetic parent phase to an antiferromagnetic/paramagnetic martensite phase has been observed in some particular composition ranges. Besides the bulk samples, the melt-spun ribbons of these alloys have also been investigated in the past several years, since the rapidly quenching by melt spinning is an effective method to synthesize highly textured polycrystalline FSMAs.[9−12] The MT in the FSMAs is often accompanied by a sharp change of the magnetization and electrical resistivity, which can be induced by temperature, stress, or magnetic field. As a consequence, many functional properties such as magnetic shape memory,[3] magnetic superelasticity,[4] magnetocaloric effects,[2,5−16] and magnetoresistance,[17,18] have been observed around the MT temperature $T_{\rm M}$. Therefore, tuning $T_{\rm M}$ of FSMAs is of great importance for extending their working temperature regions. Considering the strong dependence of $T_{\rm M}$ on the valence electron concentration per atom e/a and Mn–Mn distances, up to now, the mostly used methods to tune $T_{\rm M}$ in Ni–Mn based FSMAs are as follows: (i) adjusting the elemental chemical composition;[1,5] (ii) partial substitution for X with the same main group isoelectronic elements;[14] (iii) doping the interstitial atoms;[15] (iv) applying hydrostatic pressure;[16,19] (v) changing the annealing condition.[11,12]

It is well known that the pre-deformation can increase $T_{\rm M}$ in some shape memory alloys (such as TiNi, TiNiNb etc.), which has been verified by differential scanning calorimetry, electrical resistance and thermal dilatation measurements.[20−23] Accordingly, it can be assumed that the pre-deformation would affect the MT behaviour of Ni–Mn based FSMAs as well. In this paper, we prepared some pre-deformed Ni–Mn–Co–Sn ribbons and carried out magnetic measurement to investigate the effects of pre-deformation on MT behaviour and magnetocaloric effect in these ribbons.

*Project supported by the National Basic Research Program of China (Grant No. 2005CB623605), the National Natural Science Foundation of China (Grant Nos. 50701022 and 50831006) and the Program for New Century Excellent Talents of China (Grant No. NCET-08-0278).
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2. Experiment

Ni–Mn–Co–Sn ribbons were prepared by melt-spinning the as-cast alloys with the nominal composition $Ni_{43}Mn_{41}Co_5Sn_{11}$ in a quartz crucible and ejected onto a rotating copper wheel with a surface velocity of 10 m·s^{-1}. The melt-spun ribbons were initially dipped into liquid nitrogen for several minutes to obtain a martensitic state. Then the pre-pressure was applied on the ribbons with the direction perpendicular to the surface by an Instron 4466 testing machine with a 10 kN load cell. The pressure was retained for five minutes, during which the temperature was heated to 350 K, ensuring that the reverse MT occurs and the specimen is in the austenitic state finally. Here the pre-deformed ribbons compressed under 1.05 and 1.95 GPa are denoted as ribbons A and B, respectively. The magnetization measurements were carried out by using a vibration sample magnetometer (7300, Lakeshore) under a magnetic field up to 10 kOe (1 Oe=79.5775 A/m). The applied magnetic field was parallel to the ribbon's surface.

3. Results and discussion

Figure 1 presents the temperature dependence of magnetization $M(T)$ for these ribbons at 100 Oe on heating. All these ribbons show similar thermomagnetic behaviour. With increasing temperature, a reverse MT with a sharp jump of magnetization occurs from the weak-magnetic martensitic phase to the ferromagnetic parent phase. Further increasing the temperature causes the reduction of the magnetization, corresponding to a ferromagnetic–paramagnetic transition at the Curie temperature of austenite T_C^A. However, it is obvious that the reverse transformation temperature interval increases with the increasing pre-pressure. As we know, the pre-deformation would give rise to an inhomogeneity of the polycrystalline matrix, and then, the transformation would occur at different temperatures in different locations, leading to the broad transformation temperature interval.[22]

As shown in Fig. 1, T_M, which is defined as the temperature corresponding to the maximum of dM/dT, increases with the increasing pre-pressure, this fact suggests that the relative stability between the parent phase and martensitic phase can be affected by the pre-deformation.[20−23] The pre-deformation-induced stabilization effect of the martensite has been investigated in a number of shape memory alloys, including TiNi, TiNiNb and CuAlNi etc.[20−23] Some hypotheses have been proposed to explain this stabilization effect. Piao *et al.* suggested that the stress-induced plastic deformation would relax the internal elastic strain energy stored in the multi-variant martensite, due to the constraint of the grain boundaries, which was responsible for the stabilization effect of the martensite.[21] On the other hand, Lin *et al.* attributed this effect to the structural defects, such as dislocations and vacancies generated during pre-deformation.[20] They pointed out that these defects would increase the frictional resistance and hinder the movement of the austenite/martensite phase boundary for the reverse MT.[20] The aforementioned reasons should be useful to account for the enhanced T_M of pre-deformed Ni–Mn–Co–Sn ribbons. On the other hand, due to the lower volume of the martensitic phase in contrast to the cubic phase,[19] the pre-pressure should favour the martensitic phase from the thermodynamic point of view and support the martensite to a higher temperature, which is also responsible for the increase of T_M. However, there is no significant enhancement of T_C^A, as can be seen from Fig. 1, this fact indicates that the pre-deformation has little effect on the second-order magnetic phase transition of the high temperature parent phase.[16]

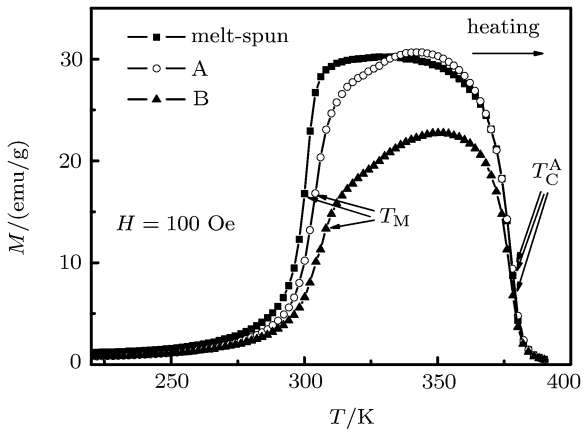


Fig. 1. Temperature dependence of the magnetization for the melt-spun, ribbons A and B in the field of 100 Oe on heating.

As we know, in Ni–Mn–X FSMAs, the external magnetic field would rearrange the martensite structural variants and result in the decrease of $T_{\rm M}$, preferring the austenite state.[3,16] In order to better understand the effect of magnetic field and pre-deformation on the MT, the $M(T)$ curves for these ribbons were measured in the fields of 100 Oe and 10 kOe, respectively, as shown in Fig. 2(a). It is obvious that the values of $T_{\rm M}$ decrease with the increase of applying field. As listed in Table 1, with the applied field changing from 100 Oe to 10 kOe, the change of $T_{\rm M}$ ($\Delta T_{\rm M}$) increases with the increase of pre-pressure, this fact indicats a competition between the magnetic field and the pre-deformation. It is worth noting that the values of $T_{\rm M}$ keep almost unchanged after several thermal and/or magnetic cycling, which is in contrast to the previous results of TiNi based shape memory alloys.[22,23] In addition, we measured the $M(T)$ curves for ribbons A after 60 days, in which the value of $T_{\rm M}$ is the same as the earlier results, as shown in Fig. 2(b).

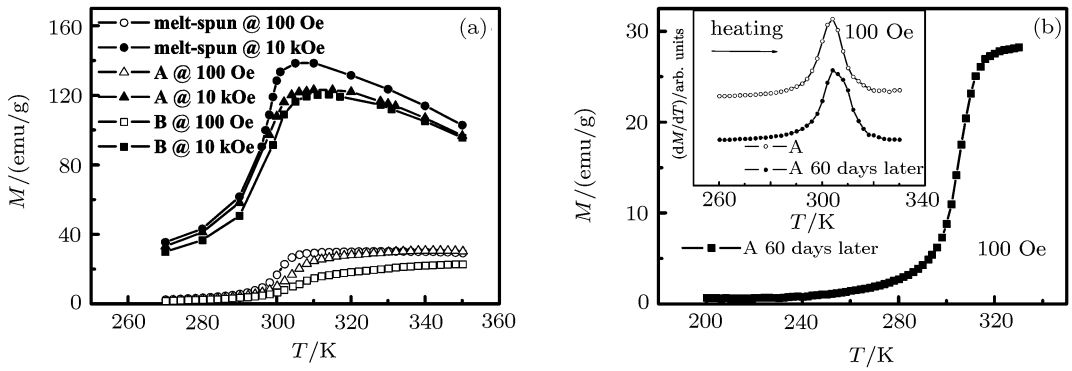


Fig. 2. Variation of the magnetization for (a) the melt-spun, ribbons A and B in the magnetic fields of 100 Oe and 10 kOe, respectively, and for (b) ribbons A after 60 days in the field of 100 Oe versus temperature on heating. Inset of (b) presents temperature dependence of dM/dT for ribbons A measured at different time.

Table 1. Values of the reverse MT temperature ($T_{\rm M}$), the change of $T_{\rm M}$ between the magnetic field of 100 Oe and 10 kOe ($\Delta T_{\rm M}$), the Curie temperature of austenite ($T_{\rm C}^{\rm A}$), magnetic entropy change ($\Delta S_{\rm M}$), and refrigerant capacities (RC) for Ni–Mn–Co–Sn ribbons (melt-spun, A, and B).

ribbons	$T_{\rm M}$/K at 100 Oe	$T_{\rm M}$/K at 10 kOe	$\Delta T_{\rm M}$/K	$T_{\rm C}^{\rm A}$/K	$\Delta S_{\rm M}$/(J/(kg·K)) at 10 kOe	RC/(J/kg) at 10 kOe
melt-spun	300	299	1	378	9.8	48
A	304	300	4	378	5.8	56
B	308	302	6	378	5.4	58

Isothermal magnetization curves M–H for these ribbons were measured around $T_{\rm M}$ in a magnetic field up to 10 kOe on heating. As presented in Fig. 3(a), an obvious metamagnetic behaviour associated with a field-induced reverse MT from a low magnetization martensite to a high magnetization austenite can be observed in melt-spun ribbons. As for ribbons A and B, however, it becomes more and more difficult to observe the metamagnetic behaviour in the field up to 10 kOe. As mentioned above, the pre-deformation would induce the enhancement of the antiferromagnetic exchange interaction in the martensite state, and then increase the metamagnetic critic field, which is responsible for the gradual disappearance of the metamagnetic behaviour in the magnetic field of 10 kOe for ribbons A and B.[16]

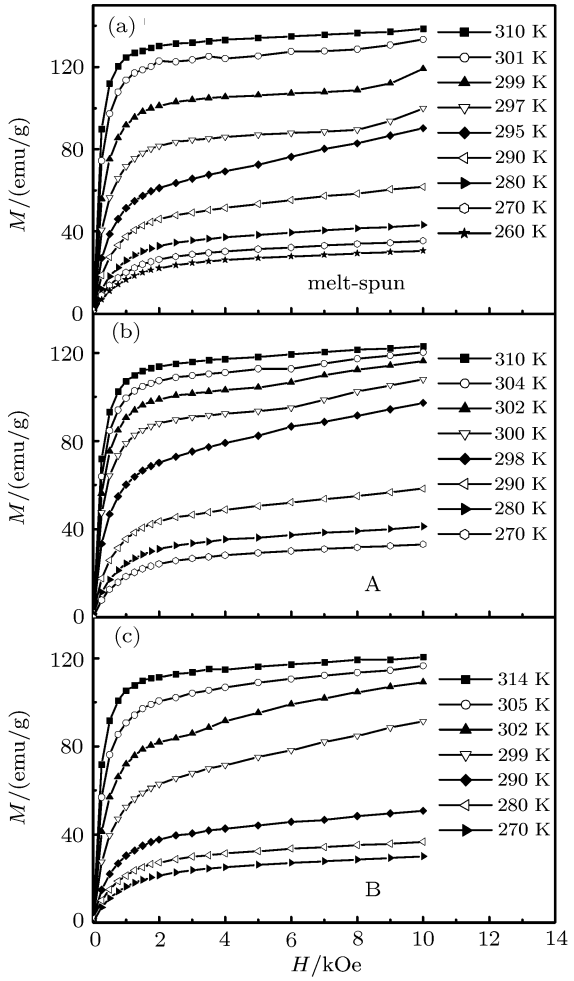


Fig. 3. Magnetization isotherms for the melt-spun, ribbons A and B around $T_{\rm M}$ in the field up to 10 kOe on heating.

Figure 4 shows the magnetic entropy change ($\Delta S_{\rm M}$) for these ribbons as a function of temperature in the field up to 10 kOe. Large values of $\Delta S_{\rm M}$ are obtained in these ribbons around room temperature at relatively low magnetic field, which is of importance for the practical application. As shown in Fig. 4, the maximum value of $\Delta S_{\rm M}$ for melt-spun ribbons is larger than that of ribbons A and B, but the peak spans of $\Delta S_{\rm M}$ for the pre-deformed ribbons are broader. Accordingly, we calculated the values of the refrigerant capacities (RC), here RC is defined as the integration over the full width at half maximum in the $\Delta S_{\rm M}$ (T) curves. As is listed in Table 1, RC values of ribbons A and B are larger than that of the melt-spun ones, which would be ascribed to the broad transformation temperature interval in pre-deformed ribbons.

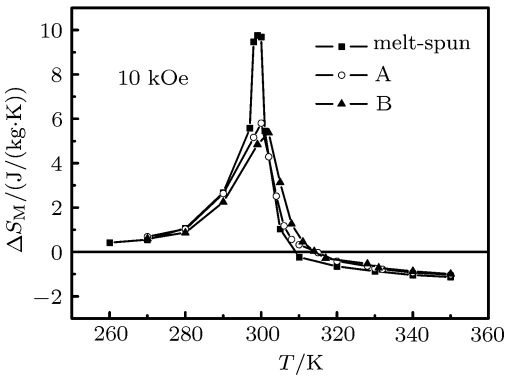


Fig. 4. Temperature dependence of $\Delta S_{\rm M}$ for the melt-spun, ribbons A and B in the magnetic field of 10 kOe.

4. Conclusions

In conclusion, the effects of pre-deformation on the MT and magnetocaloric property have been investigated in the Ni–Mn–Co–Sn ribbons. It is found that $T_{\rm M}$ increases distinctly with increasing pre-pressure due to the stabilization effect of the martensite, this fact indicates that the transformation temperatures in the Ni–Mn based FSMAs can be effectively adjusted by pre-deformation. Large $\Delta S_{\rm M}$ and RC are obtained in these ribbons around room temperature in the relatively low magnetic field.

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