Effects of Si substitution on phase transformation and exchange bias in Ni-Mn-In ribbons

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Abstract The effects of partial Si substitution for In on phase transformation and exchange bias (EB) behaviour in as-spun and annealed Ni\textsubscript{48}Mn\textsubscript{39}In\textsubscript{13-x}Si\textsubscript{x} (x = 0-4) ribbons have been investigated. It was observed that an increase in Si concentration strongly affects the magnetic state of the martensitic phase and the EB properties of the ribbons. Both martensitic transition temperature ($T_M$) and the Curie temperature ($T_C$) of the austenitic phase decrease with increasing Si concentration for $x \leq 3$, while the ribbon for $x = 4$ possess the modulated martensitic monoclinic structure at room temperature, but its magnetization is unlike (considerably smaller than) those of other ribbons. Both the exchange bias field ($H_E$) and the coercivity ($H_C$) are strongly dependent on Si content. The values of $H_E$ and $H_C$ vary from 216 Oe and 314 Oe to 434 Oe and 1682 Oe, respectively, for the as-spun ribbons at 10 K after cooling in a field of 20 kOe, as $x$ is increased from 0 to 4, while they change from 258 Oe and 192 Oe to 456 Oe and 1488 Oe for the annealed ones. The EB phenomena are attributed to the exchange interactions that occurred in AFM-FM interfaces in Si-substituted Ni-Mn-In ribbons.

1. Introduction

The exchange bias (EB) phenomenon is usually described as a shift from the origin of the magnetic hysteresis loop of a material with ferromagnetic/antiferromagnetic (FM/AFM) interfaces, in which the Curie temperature ($T_C$) of FM phase is higher than the Néel temperature ($T_N$) of AFM phase, after it is cooled from above $T_N$ to low temperatures in the presence of a magnetic field. Since it was discovered in Co particles surrounded by a layer of AFM CoO[1], extensive research has been conducted on thin films, bulk inhomogeneous materials and magnetic nanoparticles, because of its potential application in many aspects, including spin-valve and tunneling devices[2], permanent magnets[2,3], magnetic recording media and other devices[2]. In recent years, Ni-Mn-X (X = In, Sn, Sb) FM Heusler alloys have attracted considerable interest[4]. These alloys undergo martensitic transformation from FM austenite to low magnetic state martensite. This characteristic makes them exhibit several interesting physical properties, such as the shape memory effect [5], magnetocaloric effect [6], magnetoresistance[7], and the EB behaviour[8]. Recently, Pathak et al. reported that the effects of the substitution of In by Si, Ge and Al on phase transition temperature, magnetic entropy changes, electrical and exchange bias properties of the FM Ni\textsubscript{50}Mn\textsubscript{35}In\textsubscript{15} Heusler alloys [9-12]. In previous work, we reported the magnetocaloric effects properties associated with both the first- and
the second-order phase transitions and EB behaviour of $\text{Ni}_{48}\text{Mn}_{39}\text{In}_{13}$ ribbons [13]. In this work, we report phase transformation and EB behaviour in the as-spun and annealed Si-doped Ni-Mn-In ribbons.

2. Experiment

The ingots with the nominal compositions of $\text{Ni}_{48}\text{Mn}_{39}\text{In}_{13-\text{x}}\text{Si}_\text{x}$ ($\text{x} = 0-4$) were prepared by arc melting pure elements under argon atmosphere in a water-cooled Cu crucible. The ingots were remelted several times and subsequently melt-spun using a single-roll melt-spinner at a wheel linear speed of 30m/s. Some of the as-spun ribbons were annealed at 1173 K for 20 min. and finally quenched in ice water. The structural analyses of the ribbons were carried out at room temperature with conventional powder X-ray diffraction (XRD) techniques using Cu-$\text{K}_\alpha$ radiation. Magnetization measurements were performed in the temperature interval of 10–350 K, using a superconducting quantum interference device magnetometer (SQUID, Quantum Design Inc.) in fields up to 20 kOe. The magnetic field was applied along the ribbon axis. Zero-field-cooled (ZFC) and field cooled (FC) thermomagnetic curves were recorded at 200 Oe with a temperature heating or cooling rate of 5 K/min.

![Figure 1. XRD patterns of the as-spun Ni$_{48}$Mn$_{39}$In$_{13-\text{x}}$Si$_\text{x}$ ($\text{x} = 0-4$) ribbons at room temperature](image1)

![Figure 2. Temperature dependence of ZFC and FC magnetization curves $M(T)$ for the annealed Ni$_{48}$Mn$_{39}$In$_{13-\text{x}}$Si$_\text{x}$ ($\text{x} = 0, 2, 3, 4$) ribbons, measured in a field of 200 Oe](image2)

3. Results and discussion

Figure 1 gives XRD patterns of the as-spun Ni$_{48}$Mn$_{39}$In$_{13-\text{x}}$Si$_\text{x}$ ($\text{x} = 0-4$) ribbons at room temperature. The lattice constants obtained from XRD data are summarized in Table 1. It can be seen that the ribbons for $\text{x} \leq 3$ crystallize in a partially ordered B2 phase instead of a highly ordered L2$_1$ phase, due to the near absence of superstructure peaks (111) and (311)[13]. In this case, the lattice constant is half that of the L2$_1$ phase, while the Ni$_{48}$Mn$_{39}$In$_{13}$Si$_4$ ribbon is in the martensitic phase with a ten-layered modulated (10M) structure. The unit cells are monoclinic with $\beta = 88.96^\circ$ and 89.08° for as-spun and annealed ribbons, respectively. Due to the smaller atomic radius of Si than that of In, increasing Si concentration decreases lattice constants. After annealing, the lattice constants little change in the error bar range for the same Si concentration (As seen in table 1). However, the grain size increases upon annealing, according to the results of SEM observation (not shown here).

The temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of the annealed Ni$_{48}$Mn$_{39}$In$_{13-\text{x}}$Si$_\text{x}$ ($\text{x} = 0, 2, 3, 4$) ribbons, measured in a field of 200 Oe, is shown in
The magnetization curves $M(T)$ for the as-spun and annealed ribbons revealed that all the ribbons show a splitting of ZFC and FC magnetizations at low temperatures, indicating irreversible behaviour.

Table 1. Lattice parameters of Ni$_{48}$Mn$_{39}$In$_{13-x}$Si$_x$ (x = 0-4) ribbons

| Crystal structure | As-spun Lattice parameter (Å) | Annealed Lattice parameter (Å) |
|-------------------|-------------------------------|-------------------------------|
|                   | a    | b    | c    | a    | b    | c    |
| 0                 | B2   | 3.000(1) | 2.999(5) |
| 1                 | B2   | 2.994(5) | 2.992(7) |
| 2                 | B2   | 2.989(2) | 2.987(3) |
| 3                 | B2   | 2.982(5) | 2.981(4) |
| 4                 | 10M  | 4.411(3) | 5.900(6) | 21.258(3) | 4.410(5) | 5.899(5) | 21.257(1) |

From figure 2, it can be seen that as the temperature increase, a FM transition occurs above the splitting point. This temperature is defined as $T_C^M$, which represents the Curie temperature of the FM martensitic phase. An increase in Si concentration results in a decrease in both the martensitic structural transition temperature ($T_M$) and the Curie temperature ($T_C$) of austenitic phase for $x \leq 3$, which is consistent with those of reference[9], whereas for $x = 4$, the ribbon is in martensitic state in the vicinity of room temperature, as seen in the figure 1(e). In Ni-Mn-In alloys, actually, the structural transition of martensitic phase is mainly controlled by In content[14] and the Si substitution for In only extends composition range of austenitic phase, resulting in decrease of $T_M$ and $T_C$. As the Si content further increases (namely, the In content decreases), it makes the structure of the sample transforms martensitically above room temperature. For the ribbon with lower In concentration, long-range FM ordering weakens, so its magnetization is unlike (considerably smaller than) those of other ribbons due to the introduction of large amounts of AF phase at this concentration [14].

Figures 3(a) and 3(b) shows magnetic hysteresis loops of the as-spun and annealed Ni$_{48}$Mn$_{39}$In$_{13-x}$Si$_x$ (x = 0-4) ribbons at 10 K after FC at 20 kOe from 300 K. The measurements were actually carried out from -20 to 20 kOe. For clear visualization of the variation of the loop shift, only the hysteresis loop from -3 to 3 kOe is shown in the figure. The corresponding EB field $H_E$ and coercivity $H_C$ as a function of Si contents are shown in figures 3(c) and 3(d) for the Ni$_{48}$Mn$_{39}$In$_{13-x}$Si$_x$ ribbons. The values of $H_E$ and $H_C$ are calculated using $H_E = -(H_I + H_H)/2$ and $H_C = |H_I - H_H|/2$, where $H_I$ and $H_H$ are negative and positive fields at which the magnetization equals to zero. As it is evident from the figures, the hysteresis loop at 10 K is shifted significantly to the negative field axis at the region of measured temperature, which indicates that the exchange bias indeed exists in these ribbons. The values of $H_E$ and $H_C$ vary from 216 Oe and 314 Oe to 434 Oe and 1682 Oe for the as-spun ribbons, respectively, as $x$ is increased from 0 to 4, while they change from 258 Oe and 192 Oe to 456 Oe and 1488 Oe for the annealed ones. Moreover, the EB properties are different in the as-spun and annealed ribbons. $H_E$ was found to increase, while the coercivity $H_C$ decreases, after annealing. It has been well-known that the origin of exchange bias in the compounds can be attributed to different interaction mechanisms.

One important mechanism is that the coupling of the ferromagnet to the antiferromagnet at the interface causes a unidirectional anisotropy [1-3], which may interpret our results. In fact, neutron diffraction technique study showed that antiferromagnetic order exists in Ni–Mn–Sn alloys [15].

In addition, as Mn is substituted for Sn, excess Mn atoms occupy Sn sites in Ni-Mn-Sn system. In such spatial configurations, Mn atoms can have Mn atoms as nearest neighbours along the [110] directions. The Mn-Mn spacing, in this case, is smaller than that of in the stoichiometric compound; therefore, the Mn in the Sn sites interacts antiferromagnetically with the Mn in the Mn sites inducing AF exchange interaction, leading to local noncollinear spin structures, which can pin the FM moments in different configurations at low temperature [16]. Similarly, for Ni$_{48}$Mn$_{39}$In$_{13-x}$Si$_x$ ribbons, the EB
Figure 3. The magnetic hysteresis loops measured at 10 K after FC at 20 kOe of the Ni_{48}Mn_{39}In_{13-x}Si_{x} (x = 0-4) ribbons, (a) as-spun, (b) annealed, (c)-(d) the corresponding \( H_{E} \) and \( H_{C} \) as a function of Si contents

Figure 4. Variation of the \( H_{E} \) and \( H_{C} \) as a function of temperature from 10 K to 100 K for the as-spun and annealed Ni_{48}Mn_{39}In_{10-x}Si_{2} ribbons

phenomena can be qualitatively understood in terms of the coupling between FM and AFM spins at their interfaces in the martensitic state. The reasons are as follows: firstly, in off-stoichiometric Ni-Mn-In alloys, the rapid solidification can increase site disorder and excess Mn atoms in the In sites interact antiferromagnetically with Mn atoms in the Mn sites. Si atoms with smaller atomic radius substitute for In atoms, leading to the decrease of lattice constants and also the Mn-Mn distance between Mn atoms occupying in these Mn and In sites. This may effectively enhance the AFM interaction between the Mn atoms in the system, leading to the increment of \( H_{E} \) and \( H_{C} \) with the increase in Si contents. Secondly, the existence of internal stress in the as-spun ribbons with small grain sizes results in smaller \( H_{E} \) and larger \( H_{C} \). However, after annealing, the relaxation of internal stress results in the decrease in the Mn-Mn distance for the same Si content. This strengthens the exchange coupling at the AFM/FM interfaces, giving rise to the increment of \( H_{E} \) and the decrease of \( H_{C} \) because of the growth of grains after annealing [13]. Thirdly, as the Si content further increases, namely, the In content decreases, the sample transforms from partially ordered B2 structure of the austenitic phase for \( x = 3 \) to 10M modulated monoclinic structure of martensitic phase for \( x = 4 \). Furthermore, taking the effect of martensitic transformation into account, the different martensitic structure may be formed with further increasing the Si content at a low temperature, resulting in different fractions of AFM and FM phases in the phase separated martensitic state. At lower In concentration, the relative large amounts of AFM phase is introduced at this concentration, which can strongly pin the FM moments in different configurations at low temperature, so an more large extra field is required to overcome the microscopic torque from different spin configurations, resulting in the \( H_{E} \) and \( H_{C} \) values increase enormously. The EB behavior for ribbons agrees in general well with for bulk Ni-Mn-In-Si alloys previously reported by A. K. Pathak et al. [11], the shifts of the hysteresis loops increase with increasing Si concentration. The value of \( H_{E} \) of the ribbon relatively larger than that of bulk compounds is presumably resulted from the forming of different volume fraction of martensitic phases at low temperature due to different preparation processes with their different cooling speed.

For exploring the temperature dependence of EB, as an example, figure 4 shows variation of the \( H_{E} \) and \( H_{C} \) as a function of temperature from 10 K to 100 K for the as-spun and annealed Ni_{48}Mn_{39}In_{11}Si_{2} ribbons. The values of \( H_{E} \) almost linearly decrease with increasing temperature and
becomes zero above 80 K. On the other hand, \( H_C \) initially increases with temperature and then decreases after reaching a maximum. Such temperature dependencies of \( H_E \) and \( H_C \) are typical for EB systems.

4. Conclusions

The effects of the partial substitution of In by Si on the magnetic phase transition and EB behavior in Ni\(_{48}\)Mn\(_{39}\)In\(_{13-x}\)Si\(_x\) (\( x = 0\)-4) ribbons have been investigated. The substitution of a small amount of Si in In sites affects phase constitutions. The transition temperatures \( T_m \) and \( T_c \) decrease with an increase in Si concentration. Shift in the hysteresis loops of the ribbons occurs, when the samples were cooled down to 10 K in an applied magnetic field of 20 kOe. The values of \( H_E \) and \( H_C \) vary from 216 Oe and 314 Oe to 434 Oe and 1682 Oe for the as-spun ribbons, respectively, as \( x \) is increased from 0 to 4, while they change from 258 Oe and 192 Oe to 456 Oe and 1488 Oe for the annealed ones. The EB phenomena observed in the Ni\(_{48}\)Mn\(_{39}\)In\(_{13-x}\)Si\(_x\) (\( x = 0\)-4) ribbons are attributed to the occurrence of AFM and FM interactions at low temperature of martensitic state. The behaviour is an addition to multifunctional properties of the Ni\(_{48}\)Mn\(_{39}\)In\(_{13-x}\)Si\(_x\) Heusler alloy ribbons.

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