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Martensitic and magnetic transformation behaviours in Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ polycrystalline alloys

Zhigang Wu$^1$, Zuhong Liu$^2$, Hong Yang$^1$, Yinong Liu$^1$ and Guangheng Wu$^3$

$^1$ School of Mechanical and Chemical Engineering, The University of Western Australia, Crawley, WA 6009, Australia
$^2$ Department of Physics, University of Science and Technology Beijing, Beijing 100083, People’s Republic of China
$^3$ Beijing National Laboratory for Condense Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing 100080, People’s Republic of China

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Abstract
This study investigated the effect of Co substitution for Ni in Mn$_{50}$Ni$_{42}$Sn$_8$ alloy with the aim of increasing the magnetic driving force for inducing its martensitic transformation. The martensitic transformation temperatures, enthalpy and entropy changes were found to decrease progressively with increasing Co content, while the transformation hysteresis increased. Co substitution for Ni also significantly increased the magnetization of the austenite, but with negligible effect on that of the martensite. A large magnetization difference of 109 emu g$^{-1}$ was achieved across the transformation in a Mn$_{50}$Ni$_{34}$Sn$_8$Co$_8$ alloy. The large magnetization difference between the two phases provides enhanced thermodynamic driving force for the transformation. Consequently, the martensitic transformation was induced by the application of a magnetic field in Mn$_{50}$Ni$_{36}$Sn$_8$Co$_6$ and Mn$_{50}$Ni$_{34}$Sn$_8$Co$_8$ alloys. The effect of Co substitution for Ni on the magnetic interaction among the constituents for the austenite and martensite was clarified in this study, which provides a guide for alloy design for magnetoactuation applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Magnetomartensitic transformations in certain alloys have attracted extensive research interest in the past 15 years, since the discovery of giant magnetic-field-induced strains (MFIS) of 5–10% in near stoichiometric Ni–Mn–Ga alloys in 1996 [1–3]. The large MFIS is associated with the rearrangement of martensite variants, driven by the magnetocrystalline anisotropy of these variants. The magnetic driving force for this type of actuation, which is derived from the magnetic anisotropy of the martensite variant, is generally small, of the order of 300–400 J m$^{-3}$ [4]. Given that the shape change is typically 6%, this yields a magnetically generated stress of 5–6 MPa. Such stress is barely enough to overcome the mechanical resistance for martensite variant detwining [2, 4]. The low force output has been proven to be a main limitation for the application of these materials for mechanical actuation. An intrinsic solution to this problem is to increase the magnetic driving power for the martensitic transformation. To increase power density, a new group of off-stoichiometric Heusler Ni–Mn–Z (Z = In, Sn, Sb) alloys have been developed. These alloys present concurrent martensitic and magnetic transformation, in which one phase (the martensite) has much lower magnetization compared with the other (the austenite) [5]. In Ni$_{50}$Mn$_{34}$In$_{16}$ alloy, the magnetization difference between the two transforming phases is around 70 emu g$^{-1}$, which gives rise to large magnetic power of 700 J m$^{-3}$ at 1 T field. This large magnetization difference provides the necessary thermodynamic diving force, thus the opportunity for obtaining a magnetic-field-induced reverse martensitic transformation.
In recent years, much effort has been put into increasing the magnetic driving force for martensitic transformation in Ni–Mn–Z (Z = In, Sn, Sb) alloys. This driving force is the Zeeman energy $E_{\text{Zeeman}} = \mu_0 \Delta M \cdot H$, where $\mu_0$ is the permeability of a vacuum, $\Delta M$ is the saturation magnetization difference between the austenite and martensite and $H$ corresponds to the strength of the applied field. Co substitution for Ni has been found effective for increasing $\Delta M$ between the phases in Ni–Mn–Z (Z = In, Sn, Sb) alloys, leading to successful field-induced phase transformation in these alloys [6–10]. In these alloys, it is known that the net magnetic moment mainly comes from the contribution of Mn [11], and the magnetic moment distribution of Mn is very sensitive to interatomic distance. The magnetic interaction between the Mn atoms can change from ferromagnetic to antiferromagnetic alignment when the distance becomes below a critical value, which is $\sim 0.3$ nm [12]. With the objective of increasing $\Delta M$ for the magnetic-field-induced transformation, understanding of the magnetic moment contribution of Mn in off-stoichiometric is essential.

In our previous study on Mn$_{50}$Ni$_{40-x}$In$_x$Co$_x$ alloys, we proposed an atomic configuration model in which the mechanism of magnetic exchange interaction between Mn–Mn and Mn–Co was explained. For better understanding of the properties of structural and magnetic transitions in other Mn-rich Mn–Ni-based alloys, it is necessary to extend the studies to a new series of Mn$_{50}$Ni$_{42-x}$Sn$_x$Co$_x$ alloys, with a focus on the effect of Co substitution for Ni on the martensitic transformation and magnetic properties.

2. Experimental procedures

Polycrystalline Mn$_{50}$Ni$_{42-x}$Sn$_x$Co$_x$ ($x = 0, 2, 4, 6$ and $8$) alloy ingots were prepared by means of arc melting in argon atmosphere using high purity (99.99%) elemental metals. The samples are referred to as Co0, Co2, Co4, Co6 and Co8, respectively. The button shaped ingots were heat treated at 1173 K for $24$ h in vacuum followed by quenching into water for homogenization. Transformation behaviour of the alloys was studied by means of differential scanning calorimetry (DSC) using a TA Q10 DSC instrument with a cooling/heating rate of $10$ K min$^{-1}$. Phase identification and crystal structures were determined by means of x-ray powder diffraction using Cu-K$\alpha$ radiation. Microstructures of the samples were studied with optical microscopy and the compositions were determined by means of x-ray energy dispersive spectrometry (EDS). The magnetic properties were studied using a superconducting quantum interference device magnetometer (SQUID).

3. Results and discussion

3.1. Crystal structure

Figure 1 shows XRD spectra of Mn$_{50}$Ni$_{42-x}$Sn$_x$Co$_x$ alloys at room temperature. It is seen that from Co0 through to Co6, the alloys show nearly identical diffraction patterns of the martensite with a non-modulated body centred tetragonal structure. The lattice parameters of the martensite are determined to be $a = b = 0.545$ nm, and $c = 0.697$ nm. Alloy Co8 shows a single phase structure with bcc fundamental lattice reflections of (2 2 0), (4 0 0) and (4 2 2) and superlattice reflections of (1 1 1), (2 0 0) and (3 1 1). The superlattice structure can be determined by comparing the relative intensities of (1 1 1) and (2 0 0) [13]. It is evident that $I_{111}/I_{200} > 1$, implying that the superlattice is of the Hg$_2$CuTi-type, shown in the inset of figure 1(e). This observation is consistent with the observation in Mn$_2$NiZ (Z = In, Sn and Sb) alloys [14, 15] and Mn$_{50}$Ni$_{37}$In$_{10}$Co$_3$
Figure 2. Optical micrographs for (a) alloy Co6 and (b) alloy Co8.

Table 1. Composition and $e/a$ ratio of the Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ alloys.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Mn (at%)</th>
<th>Co (at%)</th>
<th>Ni (at%)</th>
<th>Sn (at%)</th>
<th>$e/a$</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>49.1</td>
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<td>42.3</td>
<td>8.6</td>
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<tr>
<td>2</td>
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<td>8.8</td>
<td>7.987</td>
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<tr>
<td>4</td>
<td>48.6</td>
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<td>38.4</td>
<td>8.9</td>
<td>7.967</td>
</tr>
<tr>
<td>6</td>
<td>48.6</td>
<td>6.1</td>
<td>36.6</td>
<td>8.7</td>
<td>7.959</td>
</tr>
<tr>
<td>8</td>
<td>49.1</td>
<td>8.0</td>
<td>34.2</td>
<td>8.7</td>
<td>7.925</td>
</tr>
</tbody>
</table>

Table 2. Transformation temperatures and hysteresis of the Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ alloys.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_M$ (K)</th>
<th>$T_A$ (K)</th>
<th>$T_o$ (K)</th>
<th>$\Delta H$ (J/g)</th>
<th>$\Delta S$ (J/K)</th>
</tr>
</thead>
<tbody>
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<td>330</td>
<td>340</td>
<td>1.0</td>
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</tr>
<tr>
<td>2</td>
<td>340</td>
<td>320</td>
<td>330</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>330</td>
<td>310</td>
<td>320</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
<td>320</td>
<td>300</td>
<td>310</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>310</td>
<td>290</td>
<td>300</td>
<td>0.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

3.2. Microstructure and alloy composition

Figure 2 shows optical micrographs of the microstructures of Co6 and Co8 alloys after homogenization treatment. Both alloys have a single phase throughout the matrix. Alloy Co6 presents evident martensite plates, indicating the martensite state at room temperature. Co8 shows a few martensite plates in the austenite matrix, which may be due to the occurrence of partially stress-induced martensitic transformation. Cracks are visible along the columned grain boundaries for both alloys, indicating the brittleness of these materials.

The composition of these alloys was determined by quantitative EDS analysis. The results are summarized in table 1. For all the alloys, the Mn contents are approximately 49 at%, indicating that the volatilization loss of Mn is $\sim$1 at% during the arc-melting process. The continuous reduction of Ni is compensated well by the addition of Co. The Sn content remained nearly unchanged, at between 8.6 and 8.9 at%. The valence electron concentration per atom ($e/a$ ratio) was calculated using the compositions obtained from the EDS analysis with the sum of s, p and d electrons for Mn (7), Ni (10), Co (9) and Sn (4). It is seen that the $e/a$ ratio decreased from 8.011 to 7.925 with increasing Co substitution for Ni from 0 to 8 at%, obviously due to the smaller number of valence electrons of Co (9) relative to that of Ni (10).

3.3. Martensitic transformation

Figure 3 shows DSC curves of the Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ alloys. It is seen that the martensitic transformation behaviour evolves progressively with increasing Co addition. Both the transformation temperatures and the enthalpy change decreased. The transformation temperatures ($T_M$: the forward transformation peak temperature, $T_A$: the reverse transformation peak temperature and $T_o = \frac{1}{2}(T_M + T_A)$), transformation hysteresis ($\Delta T = T_A - T_M$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) of the alloys are summarized in table 2. The $\Delta H$ values were determined directly from the DSC measurements, and $\Delta S$ is estimated based on $\Delta S = \Delta H / T_o$.

Figure 4 shows the effect of $e/a$ ratio on phase transformation temperatures ($T_M$, $T_A$ and $T_o$) and hysteresis ($\Delta T$) of the alloys. It is seen that $T_M$ and $T_A$ increased with increasing $e/a$ ratio (decreasing Co content). This is consistent with the general trend of positive dependence of martensitic transformation temperatures on $e/a$ ratio observed in Ni–Mn–Z ($Z = Ga, In, Sn and Sb$) alloys [17]. It appears
that there are two linear dependences of the transformation temperatures on \( e/a \) ratio. At below \( e/a = 7.967 \), corresponding to 4 at% of Co, the linear coefficient is 18 K per 0.01 \( e/a \) unit for \( T_a \). At above \( e/a = 7.967 \), the coefficient is 3.5 K per 0.01 \( e/a \) unit. Similarly, \( \Delta T \) also shows two distinct dependences on \( e/a \) ratio. It increases with more Co content at below 7.967 and remains independent of \( e/a \) ratio at above.

Figure 5 shows the effects of Co addition on the transformation enthalpy and entropy changes of the alloys, shown as functions of transformation temperature \( T_a \) in (a) and of \( e/a \) ratio in (b). It is seen that both the enthalpy and entropy changes increased continuously with increasing \( T_a \) and with \( e/a \) ratio, caused by Co addition. The influence of \( e/a \) ratio on the entropy change of martensitic transformation has been reported for Ni\(_{50+x}\)Mn\(_{25-x}\)Ga \([18, 19]\), Ni\(_{50}\)Mn\(_{50−x}\)In \([20]\), and Ni\(_{50}\)Mn\(_{50−x}\)Sn \([21]\) alloys. In these alloy systems, \( \Delta S \) increases with increasing transformation temperatures and \( e/a \) ratio, which is in good agreement with the findings in this study. The change of \( \Delta S \) is mainly attributed to the change of the magnetic component of the total \( \Delta S \) caused by increasing the Co addition. With increasing Co content, the magnetic entropy change increases in the alloys. This argument is supported by the evidence that the magnetization of the austenite increases while that of the martensite remains unchanged with increasing Co content in the alloys, as shown in figure 7. For the forward transformation, \( \Delta S^{A\rightarrow M} \), the (positive) increase of magnetic entropy change reduces the (negative) lattice entropy change, thus resulting in the decrease of the total (negative) \( \Delta S \) for these alloys.

3.4. Thermomagnetization

Figure 6 shows the magnetization of the alloys during a heating–cooling cycle between 200 and 395 K in a field of 50 Oe (figure 6(a)) and 70 kOe in (figure 6(b)). The sample was first cooled down to 200 K in a zero magnetic field prior to the measurement. A magnetic field was applied at 200 K and then the sample was heated at a rate of 10 K min\(^{-1}\) up to 395 K and cooled back again to 200 K in the same field.

At a low field of 50 Oe, as shown in figure 6(a), alloys Co4, Co6 and Co8 undergo a structural transformation between a ferromagnetic austenite and a ferrimagnetic martensite with obvious transformation hysteresis between the heating and cooling curves. For Co4, the magnetization drop of the austenite upon heating to \( \sim 380 \) K is due to the Curie transition of the austenite, denoted as \( T_{C}^{A} = 380 \) K. The Curie transition was not observed in Co6 and Co8 within the testing temperature range, suggesting higher Curie transition temperatures at above 400 K for these two alloys. In the inset of figure 6(a), alloys Co2 and Co4 present similar martensitic transformation, but with much smaller magnitude of magnetizations of the austenite compared with those of Co4, Co6 and Co8. The Curie temperatures of the austenite of Co6 and Co2 alloys seem close to 400 K, which are higher than that of Co4. Normally, with more Co substitution for Ni, the Curie temperature is expected.

### Table 2. Thermal and thermodynamic parameters of the martensitic transformation of the Mn\(_{50}\)Ni\(_{42−x}\)Sn\(_{8}\)Co\(_{x}\) alloys.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( T_M ) (K)</th>
<th>( T_A ) (K)</th>
<th>( T_a ) (K)</th>
<th>( \Delta T ) (K)</th>
<th>( \Delta H ) (J g(^{-1}))</th>
<th>( \Delta S ) (J K(^{-1}) kg(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>377</td>
<td>391</td>
<td>384</td>
<td>16.23</td>
<td>42.27</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>369</td>
<td>383</td>
<td>376</td>
<td>15.84</td>
<td>42.13</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>362</td>
<td>375</td>
<td>369</td>
<td>14.30</td>
<td>38.75</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>330</td>
<td>348</td>
<td>339</td>
<td>11.21</td>
<td>33.07</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>278</td>
<td>304</td>
<td>291</td>
<td>4.69</td>
<td>16.12</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 4](image-url) Effect of Co addition on phase transformation temperatures and hysteresis expressed as functions of \( e/a \) ratio.

![Figure 5](image-url) Effect of Co addition on enthalpy and entropy changes of the Mn\(_{50}\)Ni\(_{42−x}\)Sn\(_{8}\)Co\(_{x}\) alloys, (a) as function of transformation \( T_a = (T_M + T_A)/2 \), and (b) as function of \( e/a \) ratio.
to increase, due to the stronger exchange interaction between Co–Mn than that between Ni–Mn [22]. The anomaly of $T_C^A$ in these alloys is not clear at this stage.

It is evident that the martensitic transformation temperature decreased with increasing Co content in these alloys, consistent with the observation from DSC measurement (figure 3). The Curie temperatures of these alloys are obviously higher than those in Ni$_5$Mn$_{1+x}$Sn$_{1-x}$ [21, 23, 24] alloys, which are around 320 K. It has been reported that $T_C$ is 588 K in Mn$_2$NiGa alloy [25], suggesting the generally higher $T_C$ in Mn-rich Mn$_2$NiZ alloys relative to Ni-rich Ni$_2$MnZ alloys. It is also worth noting that the transformation hysteresis is around 40 K for Co$_8$, which is much higher than the value determined from DSC measurement (26 K). The large hysteresis usually means higher frictional resistance to the propagation of the transformation interfaces. This may lead to large difficulty for two-way magnetic-field-induced martensitic transformation in Co$_8$ alloy.

Figure 6(b) shows the thermomagnetization behaviour of the five alloys between 200 and 395 K at a field of 70 kOe. The martensitic transformation temperatures were lowered under the influence of the higher magnetic field. For alloy Co$_8$, the transformation temperatures are $T_M = 255$ K and $T_F = 285$ K at 70 kOe, which are approximately 30 K lower than those at 50 Oe.

Figure 7 shows magnetization of the austenite at the martensitic transformation starting temperature $M_s$ ($M_M^s$), magnetization of the martensite at the martensitic transformation finishing temperature $M_f$ ($M_M^f$), magnetization difference across the transformation ($\Delta M = M_M^s - M_M^f$) at 70 kOe as functions of Co content in the alloys. It is seen that $M_M^s$ increased rapidly from 13 emu g$^{-1}$ in Co$_0$ to 117 emu g$^{-1}$ in Co$_8$, while $M_M^f$ remained almost constant ($\sim$ 5 emu g$^{-1}$), thus resulting in an increasing $\Delta M$ across the martensitic transformation with increasing Co content. The maximum $\Delta M$ is 109 emu g$^{-1}$ in alloy Co$_8$.

3.5. Magnetic coupling

Figure 8 shows the atomic configuration in the unit cell of Mn$_{50}$Ni$_{42-x}$Sn$_x$Co$_x$ alloys. Illustration (a) represents the unit cell of the austenite with Mn–Mn–Ni–Sn stacking order (Hg$_2$CuTi-type structure) and illustration (b) represents the unit cell of the martensite with Mn–Mn–Ni–Sn tetragonal structure.

For Mn$_2$YZ (Y: 3d elements; Z: III–V A group elements) compounds, it has been observed that Y elements with more valence electrons prefer to occupy A and C sites, whereas Y elements with fewer valence electrons have preference for B site occupancy [26]. For the Mn$_{50}$Ni$_{42-x}$Sn$_x$Co$_x$ alloys, Co substitutes Ni at C site, and the excess Ni atoms prefer to occupy A sites, displacing Mn(A) to Mn(D) site, as illustrated in figure 8(a). Based on this rule, the atomic occupation for Mn$_{50}$Ni$_{42-x}$Sn$_x$Co$_x$ alloys can be written as [Mn(A)Ni(A)]$_{25}$Mn(B)$_{25}$[Co(C)Ni(C)]$_{25}$[Sn(D)Mn(D)]$_{25}$.

In the austenite (figure 8(a)), the Mn(A) and Mn (B) are the nearest neighbours with a distance of 0.26 nm ($\sqrt{3}a/4$ in between. The nearest distance between Mn(B) and Mn(D) atoms is 0.301 nm (a/2). It has been found that the magnetic interaction between Mn atoms changes from ferromagnetic to antiferromagnetic alignment when
the Mn–Mn distance reduces to below a critical value of approximately 0.30 nm [12]. Therefore, Mn(A)–Mn(B) is expected to form antiferromagnetic alignment, whereas Mn(B)–Mn(D) forms ferromagnetic alignment in the austenite. After the replacement of Mn(A) by Ni(A), there will be a significant increase in the net magnetic moment for the austenite, which is due to the reduction of the antiferromagnetic Mn(A)–Mn(B) coupling and the formation of the ferromagnetic Mn(B)–Mn(D) coupling. Co substitution for Ni at C site also provides magnetic moment contribution to some extent due to its larger magnetic moment ($\sim$1 $\mu_B$) relative to that of Ni ($\sim$0.3 $\mu_B$). The significant increase in $M_{MA}$ can also be attributed to the enlarged temperature window for the ferromagnetic austenite to develop, caused by Co addition. The $M_{MA}$ is measured at $M_s$ (upon cooling), as seen on the $M$–$T$ curves (figure 6(b)) of these alloys. It is also seen in figure 3 that the transformation temperatures decreased significantly with increasing Co content. This means that the $M_{MA}$ values were actually taken at different temperatures for these alloys. Therefore, the increase in $M_{MA}$ with increasing Co content is largely due to the widening of the temperature window of the ferromagnetic austenite, in addition to the effect of Co alloying as aforementioned.

Upon the martensitic transformation, the crystallographic transformation changes the crystal lattice in the unit cell, consequently altering the exchange coupling of the magnetic atoms. Upon transforming form the cubic austenite (figure 8(a)) to the tetragonal martensite (figure 8(b)), a- and b-axes shrink by 9.5% and c-axis elongates by 15.7%. Through the transformation, the nearest distance between Mn(B) and Mn(D) decreases from 0.301 nm (a/2, parent phase) to 0.273 nm (a/2, martensite phase) which is below the critical distance for ferromagnetic coupling. This leads to the moments of Mn(B) and Mn(D) changing from in parallel alignment in the austenite to antiparrallel alignment in the martensite. The distance between Mn(A) and Mn(B) changed from 0.261 nm ($\sqrt{3}a/4$) in the austenite to 0.273 nm in the martensite, which causes no change to the magnetic alignment between Mn(B) and Mn(D). Exchange interaction between Mn(A) and Mn(B) is still antiparallel alignment. Therefore, the magnetic coupling of the martensite is expected to be ferrimagnetic.

3.6. Magnetic-field-induced martensitic transformation

The magnetic driving force for a magnetic-field-induced martensitic phase transformation arises from the Zeeman Energy $E_{Zeeman} = \mu_0 \Delta M \cdot H$. The $\Delta M$ for the present Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ alloys has been significantly increased by substituting Co for Ni. To verify this increased $\Delta M$ in regards to benefiting the field-induced martensitic transformation, alloys Co6 and Co8 were magnetized isothermally at different temperatures, as shown in figure 9.

Figure 9(a) shows the magnetization behaviour of alloy Co6. At 5 K, the martensite shows low magnetization of 11 emu g$^{-1}$ (at 70 kOe). At 390 K, the austenite shows a typical soft ferromagnetic behaviour, with a saturation magnetization of 68 emu g$^{-1}$. At 335 K, the martensite shows a very low saturation magnetization ($\sim$2 emu g$^{-1}$) at below 20 kOe. Upon increasing the magnetic field to above 50 kOe, the magnetization increased rapidly, signifying the phase transformation from the martensite to the austenite. The maximum magnetization reached is 30 emu g$^{-1}$ at 70 kOe. This magnetization is much lower than the saturation magnetization of the austenite ($\sim$70 emu g$^{-1}$). This is obviously due to the fact that the transformation is incomplete at 335 K. At 340 K (8 K below $T_A$), the martensite starts
Figure 9. Isothermal magnetization behaviours of (a) alloy Co6 and (b) alloy Co8 at different temperatures.

to transform to the austenite at 30 kOe and saturates at 72 emu g$^{-1}$ at 7 T, indicating the completion of the reverse transformation. Upon removal of the external magnetic field, the magnetization decreases slowly at above 30 kOe, and then quickly drops to 20 emu g$^{-1}$, indicating the occurrence of the forward martensitic transformation.

Figure 9(b) shows the magnetization behaviour of alloy Co8. The magnetization behaviours of the martensite at 5 K and the austenite at 390 K are similar to those of Co6. At 280 K, the martensite starts to transform to austenite at the field of 30 kOe upon magnetizing. The magnetization maximized at 75 emu g$^{-1}$ at 70 kOe, indicating the incomplete magnetic-field-induced transformation. At 290 K (14 K below $T_A$), the martensite starts to transform to the austenite at 10 kOe and saturates at $\sim$100 emu g$^{-1}$ at 70 kOe, indicating the completion of the reverse transformation. Upon removal of the external magnetic field, the austenite remained saturated and did not transform back to the martensite. This is due to the large transformation hysteresis in Co8. The testing temperature of 290 K is well above the forward transformation temperature ($T_M = 278$ K), thus resulting in the retained austenite after demagnetization. It is worth noting that the complete field-induced transformation can be achieved at lower temperature below $T_A$ in Co8 (14 K below $T_A$) than that in Co6 (8 K below $T_A$), which is due to the larger $\Delta M$ across the transformation of Co8 relative to that of Co6. This indicates that the magnetic driving force is increased with increasing the Co content in Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ alloys in a certain field, thus easier for obtaining a field-induced transformation.

4. Conclusions

In this study, the effects of Co substitution for Ni on the martensitic transformation and magnetic behaviour of Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ alloys were investigated. The experimental evidence and the discussions lead to the following conclusions:

(1) The Mn$_{50}$Ni$_{42-x}$Sn$_8$Co$_x$ alloys exhibit a martensitic transformation from an Hg$_2$CuTi-type austenite to a non-modulated tetragonal martensite. The martensitic transformation temperatures were found to decrease significantly with increasing Co substitution for Ni, due to the decreasing $e/a$ ratio in the alloys. The enthalpy and entropy changes of the transformation are both found to decrease with increasing Co addition.

(2) The magnetization of the austenite is significantly increased from 13 emu g$^{-1}$ in the Co0 alloy to 117 emu g$^{-1}$ in the Co8 alloy, whereas that of the martensite remains unchanged at $\sim$5 emu g$^{-1}$. Consequently, magnetization difference between the austenite and the martensite increases significantly with increasing Co substitution for Ni. The largest $\Delta M$ for the martensitic transformation obtained is 109 emu g$^{-1}$ in alloy Co8.

(3) The increased magnetization of the austenite is attributed to two reasons: (i) higher magnetic moment contribution of Co relative to Ni and (ii) widening of the temperature window for ferromagnetic austenite to magnetize.

(4) The low magnetization of the martensite is due to the significantly shortened distance between Mn(B) and Mn(D), which leads to the antiparallel alignment of the magnetic moments of neighbouring Mn atoms in the tetragonal martensitic structure.

(5) The magnetic-field-induced martensitic transformation from ferromagnetic martensite to ferromagnetic austenite was successfully induced in alloys Co6 and Co8 under a field within the range 30–70 kOe.

Acknowledgments

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