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Magnetic and martensitic transformations of NiMnX(X=In, Sn, Sb) ferromagnetic shape memory alloys

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Martensitic and magnetic transformations of the Heusler Ni₅₀Mn_{50-y}X_y (X=In, Sn and Sb) alloys were investigated by differential scanning calorimetry measurement and the vibrating sample magnetometry technique. In all these alloy systems, the austenite phase with the ferromagnetic state was transformed into the martensite phase, which means that these Heusler alloys have potential as Ga-free ferromagnetic shape memory alloys (FSMAs). Furthermore, multiple martensitic transformations, such as two- or three-step martensitic transformations, occur in all these alloy systems. It was confirmed by transmission electron microscopy observation that the crystal structure of the martensite phase is an orthorhombic four-layered structure which has not been reported in other FSMAs. Therefore, the present Ga-free FSMAs have the great possibility of the appearance of a large magnetic-field-induced strain. © 2004 American Institute of Physics.

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Ferromagnetic shape memory alloys (FSMAs) which can be controlled by magnetic field have attracted considerable attention as a type of magnetic actuator materials. Among the various FSMAs, the NiMnGa alloy system, which shows a large magnetic field-induced strain (MFIS) over 5%, has been extensively studied.¹⁻⁶ However, there are some problems in the application of those FSMAs, e.g., high cost due to the expensive constituent element Ga, as well as a low martensitic starting transformation temperature (M_s) and a Curie temperature (T_c) below 100°C which are insufficient for FSMA actuators. Therefore, the development of Ga-free FSMAs with high M_s and T_c temperatures is required.

Recently, the present authors have found that some NiMnAl alloys with the ferromagnetic state transform into the martensite phase with a long period stacking order structure such as 8M, 10M, and 14M.⁷⁻⁹ Furthermore, Fujita *et al.* have reported that an MFIS of 0.17% can be obtained at -20°C in the NiMnAl single crystal with the martensite state.¹⁰ However, a large MFIS has not been obtained and the M_s temperature of the NiMnAl alloy in ferromagnetic state is below room temperature. Other NiMn-based Heusler alloys, such as NiMnIn, NiMnSn and NiMnSb alloys, have been studied by some researchers from the viewpoint of magnetism.¹¹⁻¹⁵ In the present study, NiMn-based FSMAs and the martensitic and magnetic transformations in Ga-free NiMnIn, NiMnSn and NiMnSb Heusler alloys were investigated.

The alloys Ni₅₀Mn_{50-y}In_y, Ni₅₀Mn_{50-y}Sn_y and Ni₅₀Mn_{50-y}Sb_y (y=10~16.5) were prepared by induction

melting under an argon atmosphere. The obtained ingots were cut into small pieces by a diamond saw and homogenized at 1000°C for 1 day in a vacuum and then quenched in water. The martensitic and magnetic transformation temperatures were measured by differential scanning calorimetry (DSC) and vibrating sample magnetometry (VSM), where cooling and heating rates of DSC and VSM measurements were 10 and 3°C/min, respectively. The crystal structure of the martensite phase was observed by transmission electron microscopy (TEM) and the lattice constant of the martensite structure was determined from the x-ray diffraction (XRD) pattern.

Figure 1 shows the DSC cooling and heating curves for the Ni₅₀Mn₃₇Sb₁₃ alloy. Exothermic and endothermic peaks appear at around 50–60°C during both cooling and heating, respectively, which correspond to the Curie temperature (T_c). This T_c temperature is in good agreement with that measured by the VSM technique as shown in Fig. 2(c). Furthermore, large exothermic and endothermic peaks which correspond to martensitic and reverse transformations, respectively, appear at around 5–30°C, where the martensitic transforma-

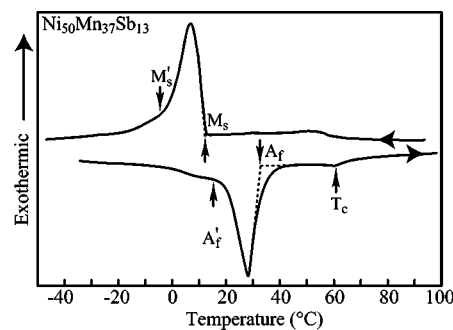


FIG. 1. DSC curve of Ni₅₀Mn₃₇Sb₁₃ alloy.

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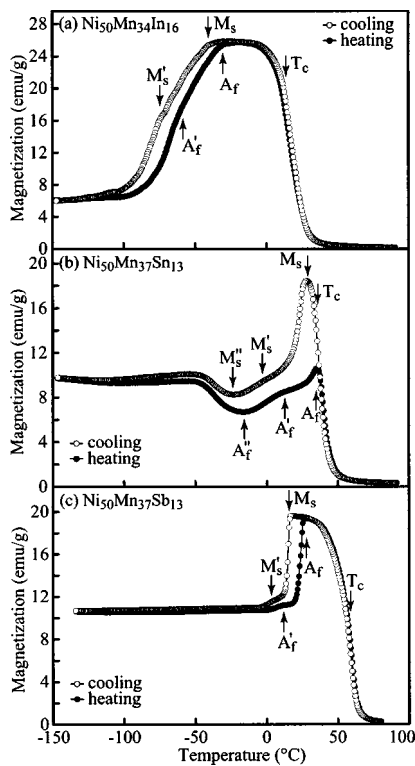


FIG. 2. Thermomagnetization curves of the (a) $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$, (b) $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ and (c) $\text{Ni}_{50}\text{Mn}_{37}\text{Sb}_{13}$ alloys measured by VSM.

tion starting (M_s) and finishing (A_f) temperatures are defined as the temperatures at which the extrapolation lines of those peaks and the base line cross as shown in Fig. 1. In addition, after the martensitic transformation and before the reverse transformation, there are additional small peaks in the DSC curve which would indicate the martensite to martensite transformation. They are designated as M'_s and A'_f temperatures, as shown in Fig. 1.

Figure 2 shows the thermomagnetization curves on cooling and heating obtained by the VSM technique for (a) $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$, (b) $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ and (c) $\text{Ni}_{50}\text{Mn}_{37}\text{Sb}_{13}$ alloys at a magnetic field strength of $H=500$ Oe. The thermomagnetization curves first drastically increase due to the magnetic transformation from the paramagnetic to the ferromagnetic state in the cooling stage from around 80°C . The T_c temperature is defined as the temperature at which the slope of magnetization versus temperature curve is the largest, as shown in Figs. 2(a)–2(c). Subsequently, the magnetization abruptly decreases due to the martensitic transformation and intricately changes with further cooling. These phenomena are in good agreement with those obtained by the DSC which suggest the existence of the martensite-to-martensite transformation as indicated by M'_s (and M''_s) in all the alloy systems. Especially, it is supposed that a three-step martensitic transformation occurs in the $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ alloys, because the trace of each reverse transformation is observed in thermomagnetization curves on heating as indicated by A'_f and A''_f in Fig. 2(b). Such multiple martensitic transformations consisting of two or three steps have been observed in the NiMnGa FSMAs.¹⁶ In the present study, it was also confirmed by x-ray analysis at various temperatures below M_s that the x-ray peak profile changes with decreasing temperature, which means that the martensite structure changes with transformation temperatures. However, since several martensite structures coexist in the martensite phase in the present

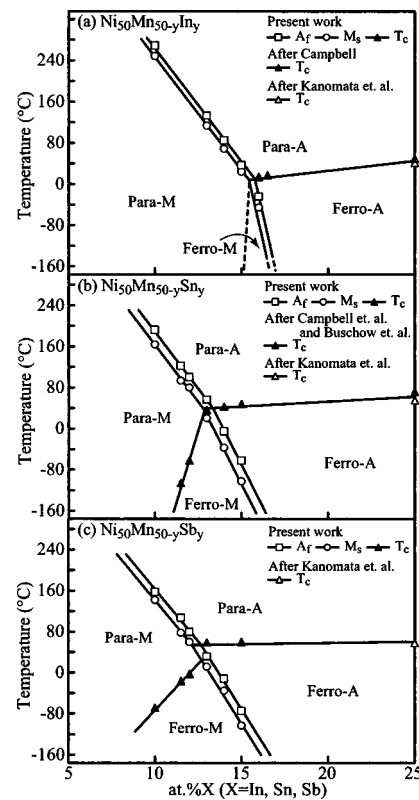


FIG. 3. Martensitic and magnetic transition temperatures of the (a) $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$, (b) $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sn}_y$ and (c) $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sb}_y$ alloys, where the Curie temperature of the stoichiometric alloys previously reported (see Refs. 11–15) are also shown, where Para and Ferro mean paramagnetic and ferromagnetic, respectively, and A and M indicate the austenite and martensite phases, respectively.

alloys, further investigation is required to clarify the transformation sequence.

Figure 3 shows vertical section diagrams with the M_s and A_f temperatures obtained by the DSC measurement and with the T_c obtained by VSM technique in (a) $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$, (b) $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sn}_y$ and (c) $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sb}_y$ alloys, where the data on T_c of $\text{Ni}_{50}\text{Mn}_{25}\text{In}_{25}$,^{11–15} $\text{Ni}_{50}\text{Mn}_{25}\text{Sn}_{25}$ ^{12,14,15} and $\text{Ni}_{50}\text{Mn}_{25}\text{Sb}_{25}$ ¹⁵ stoichiometric Heusler alloys are also plotted. Similar results were obtained in the transformation versus composition curves of the $\text{Ni}_{50}\text{Mn}_{50-y}\text{X}_y$ ($X=\text{In, Sn and Sb}$) alloy systems. The M_s and A_f temperatures decrease with increasing In, Sn and Sb contents and the slopes in the M_s and A_f temperatures as a function of X content in the ferromagnetic state are larger than those in the paramagnetic state. This is because the T_0 temperature ($= (M_s + A_f)/2$) at which the parent and martensite phases are in equilibrium are varied by the magnetic contribution to Gibbs energy. Especially in the NiMnIn system, the martensitic transformation temperatures in the ferromagnetic state drastically decrease with increasing In content. It is noted that the compositional dependence of the Curie temperatures T_c of the austenite phase is small, while the T_c of the martensite phase strongly depends on the alloy compositions and drastically decreases with decreasing In, Sn or Sb content in all the systems. In particular, in the NiMnIn alloy system, the compositional dependence of the T_c temperature of the martensite phase is the largest of those in the three alloy systems and the T_c of martensite phase in the $\text{Ni}_{50}\text{Mn}_{25}\text{In}_{15}$ alloy is estimated to be below -200°C . Furthermore, it can be seen from Figs. 3(b) and 3(c) that the martensite phase with the ferromagnetic

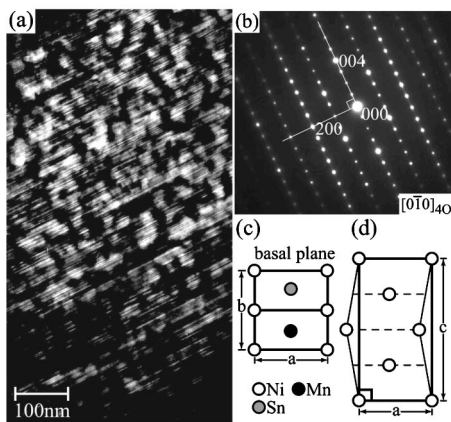


FIG. 4. TEM bright-field image showing a typical microstructure and (b) the corresponding SADP at room temperature taken from the martensite phase which occurs from the austenite phase directly in the $\text{Ni}_{50}\text{Mn}^{37.5}\text{Sn}_{12.5}$ alloy. (c) and (d) Basal plane and the stacking sequence of the orthorhombic four-layered structure indicated as 4O which is suggested by the SADP, respectively.

state can be obtained at room temperature in the NiMnSn and NiMnSb alloy systems. The M_s temperature in the ferromagnetic state obtained for the $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sn}_y$ and $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sb}_y$ alloy systems is around 30°C , which is higher than that obtained for the $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$ and $\text{Ni}_{50}\text{Mn}_{50-y}\text{Al}_y$ ⁸ alloys, whose highest M_s temperature in the ferromagnetic state is around 0°C .

In this study, the crystal structures of the martensite phase of NiMnX which directly transforms from the austenite phase were investigated by TEM observation and XRD examination at room temperature. Figures 4(a) and 4(b) show a TEM bright-field image and the corresponding selected area diffraction pattern (SADP) at room temperature taken from the martensite phase of the $\text{Ni}_{50}\text{Mn}^{37.5}\text{Sn}_{12.5}$ alloy. Figure 4(a) shows a typical morphology of the modulated layer structure with high density of twins or stacking faults, and Fig. 4(b) showing the $x/4\{220\}L_2$ extra spots suggests that this martensite phase has a four-layered structure. Such a four-layered martensite has not been reported in other FSMA. Although two kinds of stacking sequence, i.e., $(3\bar{1})$ and $(2\bar{2})$, are possible as the basic period of this four-layered order stacking structure, the stacking sequence $(2\bar{2})$ shown in Figs. 4(c) and 4(d) is more possible, because the a and the c axes of this martensite structure make a right angle as shown in SADP. Consequently, it is suggested that the observed martensite structure possesses an orthorhombic four-layered structure indicated as 4O $(2\bar{2})$. The lattice constants of the $L_2(a_0)$ and the 4O (a , b and c) structures determined by x-ray analysis in the $\text{Ni}_{50}\text{Mn}^{37}\text{Sn}_{13}$ were $a_0 = 0.5973$ nm, and $a = 0.4313$, $b = 0.2870$ and $c = 0.8401$ nm, respectively, and those in the $\text{Ni}_{50}\text{Mn}^{37}\text{Sb}_{13}$ were $a_0 = 0.5971$ nm, and $a = 0.4305$, $b = 0.2885$ and $c = 0.8407$ nm, respectively. In addition to this 4O structure, it was confirmed by TEM observation that other modulated structures, such as the monoclinic 6M and 10M reported in other FSMA,^{4,9,16,17} partially coexist in all the NiMnX alloys. Although the 4O structure was also detected in the martensite phases in the $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ alloy, the lattice constant could not be determined by XRD analysis because of coexistence with a large number of other structures. The lattice constant of the L_2 phase in the $\text{Ni}_{50}\text{Mn}^{35}\text{In}_{15}$ alloy was a_0

$= 0.6017$ nm. Since the modulated structures are an important factor for obtaining a large MFIS, in the present Ga-free NiMnX ($X = \text{In}, \text{Sn}$ and Sb) alloys as well as in the NiMnGa FSMA,^{4,16} a large MFIS is expected to be obtained.

In conclusion, it was found that the Heusler $\text{Ni}_{50}\text{Mn}_{50-y}\text{X}_y$ ($X = \text{In}, \text{Sn}$ and Sb) alloys in the ferromagnetic state thermally transform into the martensite phase with a modulated structure. It was confirmed that the martensite phase directly transformed from the austenite phase has an orthorhombic four-layered structure described as 4O $(2\bar{2})$ which has not been reported in other FSMA. In the NiMnGa FSMA, the twinning stress in the martensite phase tends to decrease in the order of 2M (nonmodulated tetragonal) $> 14\text{M}$ (seven-layered orthorhombic) $> 10\text{M}$ (five-layered tetragonal),¹⁸ which is corresponding to the decrease of the β angle of the martensite structure from the larger value to around 90° ,⁹ if the martensite structures are defined as monoclinic-type structure defined by Otsuka *et al.*¹⁹ Since the β angle of the present four-layered structure is 90° , the twinning stress is expected to be low, which means that the mobility of twin should be high. Therefore, the appearance of a large MFIS can be expected for the NiMnX alloys with 4O structure.

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