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Metamagnetic shape memory effect in a Heusler-type $Ni_{43}Co_7Mn_{39}Sn_{11}$ polycrystalline alloy

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Shape memory and magnetic properties of a $Ni_{43}Co_7Mn_{39}Sn_{11}$ Heusler polycrystalline alloy were investigated by differential scanning calorimetry, the sample extraction method, and the three-terminal capacitance method. A unique martensitic transformation from the ferromagnetic parent phase to the antiferromagneticlike martensite phase was detected and magnetic-field-induced "reverse" transition was confirmed in a high magnetic field. In addition, a large magnetic-field-induced shape recovery strain of about 1.0% was observed to accompany reverse martensitic transformation, and the metamagnetic shape memory effect, which was firstly reported in a $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ Heusler single crystal, was confirmed in a polycrystalline specimen.
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Since a magnetic-field-induced strain was reported for NiMnGa,[1,2] many other ferromagnetic shape-memory alloys, such as FePd,[3] FePt,[4] NiCoGa,[5,6] NiCoAl,[7] and NiFeGa,[8] have also been reported. The origin of the extremely large magnetic-field-induced strain (MFIS) can be explained by the rearrangement of martensite variants due to an external magnetic field, whose driving force is related to the large magnetocrystalline anisotropic energy of the martensite phase.[1,9] According to this mechanism, because the driving force is limited by the anisotropy energy even if a large external magnetic field is applied, the generated stress induced by the external magnetic field is restricted to only several megapascals.[10]

Very recently, Sutou *et al.* have found a new series of ferromagnetic shape memory alloy systems, Ni–Mn–*X* (*X*: In, Sn, and Sb), with an unusual behavior of the magnetic properties, where the magnetization of the martensite phase is considerably smaller than that of the parent phase.[11] Especially, the Ni–Mn–In based alloys have been found to show a drastic change of magnetization due to martensitic transformation, and the transformation from the ferromagnetic parent to antiferromagnetic (or paramagnetic) martensite phase has been detected in the $Ni_{46}Mn_{41}In_{13}$ and $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ Heusler alloys.[12,13] The martensitic transformation temperatures of these alloys are decreased about to 30–50 K by the magnetic field up to $H=7$ T, and magnetic-field-induced reverse transformation (MFIRT), namely, metamagnetic phase transition, has been confirmed. Furthermore, in a $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ Heusler single crystalline specimen it was reported that an almost perfect shape memory effect of about 3% strain associated with this phase transition is induced by a magnetic field, such effect being termed the metamagnetic shape memory effect (MMSME).[12] This alloy system opens up the possibility of utilizing the magnetic-induced shape memory effect.

On the other hand, although the transformation from the ferromagnetic parent to antiferromagneticlike martensite has not been found in the Ni–Mn–Sn alloys, some details on the magnetic properties and crystal structures of the Ni–Mn–Sn alloys have been recently reported.[14–16] In the present study, the magnetic and martensitic transformation behaviors of $Ni_{43}Co_7Mn_{39}Sn_{11}$ Heusler polycrystalline alloy, which was selected as a sample with a relatively high T_C and large ΔM,[17] were investigated, and the MFIRT from an antiferromagneticlike martensite phase to a ferromagnetic parent phase and the MMSME due to the MFIRT were confirmed.

Two types of $Ni_{43}Co_7Mn_{39}Sn_{11}$ (at. %) alloy were prepared by induction and arc-melting under an argon atmosphere and were homogenized at 1173 K for 24 h and 720 h in a vacuum. The ingots were cut into small pieces with a diamond saw. The Curie temperature and the latent heat during the martensitic transformation of the NiCoMnSn alloy were determined by differential scanning calorimetry (DSC) at heating and cooling rates of 10 K min^{-1} using arc-melted polycrystalline specimens with a cubic shape of about $3\times2\times2.5$ mm^3, which showed a columnarlike grain structure with an average grain width of about 300 μm. The magnetic properties were examined by the sample extraction method at heating and cooling rates of 3 K min^{-1} using induction-melted polycrystalline specimens (average grain size $\approx$500 μm) with a size of about $0.4\times0.4\times3$ mm^3, which contains two to three grains. The crystal structures of the parent and martensite phases were identified by transmission electron microscopic (TEM) observation and x-ray diffraction (XRD) using powder specimens. The shape recovery induced by the magnetic field was measured by a three-terminal capacitance method using an arc-melted polycrystalline specimen with a shape of about $2\times1.5\times2.5$ mm^3.

Figure 1 shows the DSC curve for the NiCoMnSn alloy. It is seen that large exothermic and endothermic peaks due to

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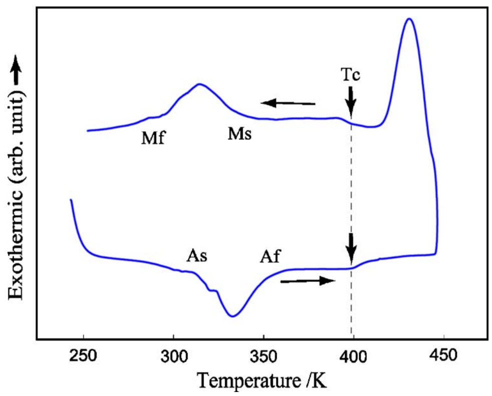

FIG. 1. (Color online) DSC heating and cooling curves showing the martensitic and magnetic transformations in the $Ni_{43}Co_7Mn_{39}Sn_{11}$ alloy. The magnetic transformation temperature T_C was determined to be about 400 K.

the martensitic and reverse transformations are detected in the temperature range from 300 to 350 K, where a large exothermic peak at about 430 K was an artificial one due to the change from heating to cooling. Besides these peaks, small peaks corresponding to the paramagnetic/ferromagnetic transition are shown at about 400 K. Since the Curie temperature T_C of the Ni–Mn–Sn ternary shape memory alloys is about 320 K,[11,14] the addition of 7 at. % Co causes an increase of about 80 K for the T_C.

Figure 2(a) shows the thermomagnetization curves for the NiCoMnSn alloy at magnetic field strengths of $H=0.05$ and 4 T. In the case of 0.05 T, it can be seen that the magnetization of the parent phase is lost by martensitic transformation and that that of the martensite phase becomes almost zero. On the other hand, that at 4 T shows a similar behavior to that at 0.05 T, but the magnetization of the martensite phase slightly increases and all the martensitic transformation temperatures (M_s and M_f: transformation starting and finishing temperatures, and A_s and A_f: reverse transformation starting and finishing temperatures) decrease about 13–15 K, where the transformation temperatures are defined as demonstrated in the 0.05 T curves of Fig. 2(a). Here, the thermomagnetization curve for cooling does not coincide with that for heating in the parent phase region. This seems to be brought about by an artificial effect on the specimen setting. All the data on the martensitic transformation temperatures, which were obtained from the measurement performed in the magnetic field of 0.01, 2, 4, and 7 T, are plotted in Fig. 2(b). The obtained data show very small thermal hysteresis (A_f-M_s and A_s-M_f) and transformation intervals (M_s-M_f and A_f-A_s) less than 10 K. These results are clearly different from those determined by the DSC curve shown in Fig. 1. This discrepancy may have resulted from a difference in the specimen size, i.e., a large polycrystalline specimen consisting of some columnar grains of about 300 μm in diameter was used for the DSC, while a small specimen containing two to three grains was prepared for the sample extraction method. In general, it is known that the thermal hysteresis and transformation intervals of a specimen with a large grain size relative to the size of specimen are smaller than those with a small relative grain size.[18,19] In any case, it can be seen in Fig. 2(b) that the martensitic transformation temperatures decrease with increasing magnetic field and that the magnetic field of 7 T induces the decreases in the transformation temperature of about 28 K for the M_s and of about 23 K for the A_f. The temperature decrease ΔT induced by magnetic field change ΔH is approximately given by the Clausius-Clapeyron relation in the magnetic phase diagram,

$$\Delta T \approx \left(\frac{\Delta M}{\Delta S}\right)\Delta H, \quad (1)$$

where ΔM and ΔS are the differences in magnetization and entropy between the parent and martensite phases, respectively. The ΔS of the $Ni_{43}Co_7Mn_{39}Sn_{11}$ alloy is calculated from the enthalpy data obtained by the DSC as $\Delta S=22.2$ J/K kg. The theoretical value of ΔT calculated from Eq. (1) using $\Delta H=7$ T and $\Delta M \approx 80$ J/T kg (=emu/g) shown in Fig. 1 was given as $\Delta T_{cal}=25$ K, where the agreement between the experimental and theoretical values is quite satisfactory. It is not clear at present whether the magnetism of the martensite phase is antiferromagnetic or paramagnetic; it is considered to be antiferromagneticlike in this letter. In the powder XRD and TEM examinations it was confirmed that the parent and martensite phases have the $L2_1$ Heusler-type ordered structure where $a=0.5965$ nm and there is a mixture of 10M and 6M modulated structures, which is similar to observations in Ni–Mn–Al alloys.[20,21]

Figure 3 shows the magnetization curves at several temperatures. While the curves at 320 and 200 K exhibit ferromagnetic and ferrimagneticlike M-H behaviors, respectively, the curves at 280–300 K show a metamagnetic transition with a hysteresis of about $\Delta H_h=1.5$ T, which is due to MFIRT from the antiferromagneticlike martensite to ferromagnetic parent phase. These results are in accordance with the thermomagnetization behavior shown in Fig. 2(a). These characteristic magnetic features are very similar to those in the NiCoMnIn metamagnetic shape memory alloys,[12] and the MMSME can also be expected to be obtained in the NiCoMnSn alloys.

Figure 4 shows the strain versus magnetic field curves demonstrating the recovery strain induced by the magnetic

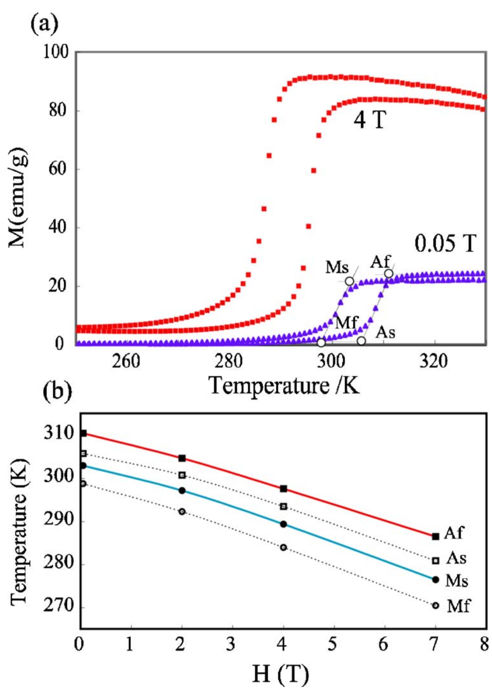

FIG. 2. (Color online) (a) Thermomagnetization curves of the $Ni_{43}Co_7Mn_{39}Sn_{11}$ alloy under magnetic fields of 0.05 and 4 T, and (b) the martensitic transformation temperatures determined from the thermomagnetization curves. All the martensitic transformation temperatures decrease with increasing magnetic field.

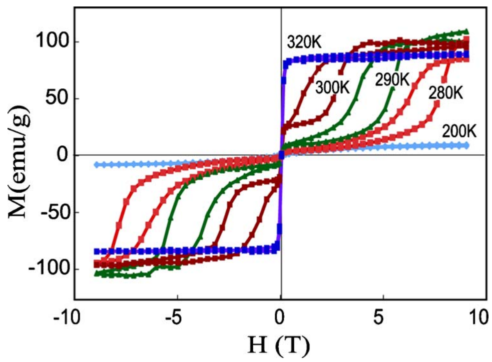

FIG. 3. (Color online) Magnetization vs magnetic field curves for the $Ni_{43}Co_7Mn_{39}Sn_{11}$ alloy between 200 and 320 K. The curves at 280, 290, and 300 K show metamagnetic transition behavior.

field at 310 K in a NiCoMnSn polycrystalline specimen, where a compressive prestrain of about 1.3% was applied and a magnetic field was applied in parallel to the compressive axis of the specimen. Initially, the examination was performed at 300 K where the magnetic-field-induced strain can be expected from the magnetic properties shown in Figs. 2 and 3. Very little recovery strain, however, was detected even in a high magnetic field. The same specimen after the test at 300 K was heated up to 310 K, and the MFIS was measured. It is seen in Fig. 4 that the recovery strain starts to increase at about 2 T, and gradually increases to 7 T with an increasing magnetic field, where a step appearing at about 2.2 T is unknown. The recovery strain at 310 K was about 1.0% corresponding to 77% of the prestrain of 1.3%. This result means that the NiCoMnSn alloy system, in addition to the NiCoMnIn alloy system,[12] may also be a metamagnetic shape memory alloy. On the other hand, a spontaneous length change of about 0.3% was detected in the releasing process of the magnetic field, and a reversible, namely, two-way shape memory effect (TWME), induced by the magnetic field was confirmed as shown in Fig. 4. Not being observed in the single crystal of the NiCoMnIn alloy,[12] such a behavior may be brought about by a fact that the stabilized martensite plates which serve as nuclei for the TWME is formed near the grain boundary by constraint stress from surrounding grains[22] in the present polycrystalline NiCoMnSn alloy. Finally, the reason why the MMSME was hardly obtained at 300 K may be explained by the increase of the reverse transformation temperature induced by the predeformation, which is observed in the NiTi-based and Cu-based shape memory alloys.[23]

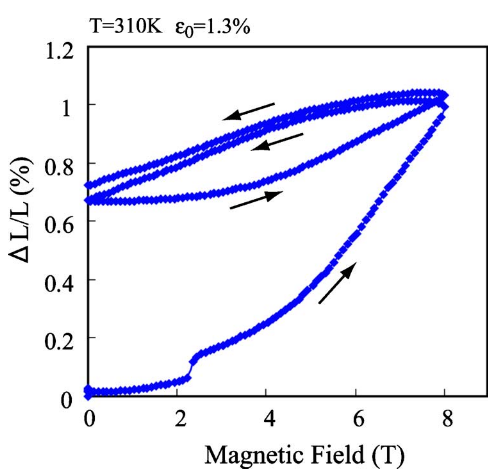

FIG. 4. (Color online) Recovery strain at 310 K induced by a magnetic field for the $Ni_{43}Co_7Mn_{39}Sn_{11}$ polycrystalline specimen. A compressive prestrain of about 1.3% was applied at room temperature, with the magnetic field applied parallel to the compressive axis of the specimen; the length change parallel to the compressive axis was cyclically measured.

In conclusion, magnetic and martensitic transformation behaviors of NiCoMnSn Heusler alloys were investigated, and martensitic transformation associated with metamagnetic transition was observed in this alloy system from the antiferromagneticlike martensite phase to the ferromagnetic parent phase. Magnetic-field-induced reverse martensitic transformation was experimentally confirmed. Furthermore, it was confirmed that the NiCoMnSn alloy is the second alloy system showing the MMSME, following the NiCoMnIn system, and that the MMSME occurs not only in a single-crystalline specimen, but also in a polycrystalline specimen. TWME was also confirmed in this study.

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