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William M. Yuhasz
Iowa State University

Deborah L. Schlagel
Iowa State University, schlagel@iastate.edu

Qingfeng Xing
Iowa State University, qxing@ameslab.gov

Kevin W. Dennis
Iowa State University, dennis@ameslab.gov

R. William McCallum
Iowa State University, mccallum@ameslab.gov

See next page for additional authors

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Influence of annealing and phase decomposition on the magnetostructural transitions in Ni₅₀Mn₃₉Sn₁₁

Abstract

Magnetic and structural transitions in the Ni₅₀Mn_{50-x}Sn_x ($x = 10-25$) ferromagnetic shape memory alloys are currently of interest. As in Ni-Mn-Ga, these alloys feature high-temperature austenite and low-temperature martensite phases, where the magnetic state is strongly composition dependent. To study the role of chemical ordering in fine-tuning their magnetostructural properties, they were first annealed for 4 weeks/1223 K to achieve structural and compositional homogeneity, and were then further annealed for 1 week (~ 150 K below the reported $B2$ to $L2_1$ transition) at 773 K to increase the degree of chemical ordering. For $x = 11$, this anneal resulted in a dramatic change in the magnetic ordering temperature. Following the 1223 K anneal, the sample exhibited ferromagnetic ordering at 140 K. After the 773 K anneal, the ferromagnetic transition is at 350 K, a characteristic of the ferromagnetic austenite phase with $15 < x < 25$. Consistent with the magnetization data, transmission electron microscopy examination confirms that the alloy decomposed into two phases with $x = 20$ and 1. From this result one can conclude that the martensitic transformation occurs only in those compositions where the single phase $L2_1$ has been retained in a metastable state on cooling.

Keywords

annealing, ferromagnetic materials, magnetic transitions, magnetisation, manganese alloys, martensitic transformations, nickel alloys, shape memory effects, solid-state phase transformations, tin alloys, transmission electron microscopy

Disciplines

Condensed Matter Physics | Metallurgy

Comments

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Authors

William M. Yuhasz, Deborah L. Schlagel, Qingfeng Xing, Kevin W. Dennis, R. William McCallum, and Thomas A. Lograsso

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Influence of annealing and phase decomposition on the magnetostructural transitions in $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$

W. M. Yuhasz, D. L. Schlagel, Q. Xing, K. W. Dennis, R. W. McCallum, and T. A. Lograsso^{a)}

Materials Sciences, Ames Laboratory, Ames, Iowa 50011, USA

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Magnetic and structural transitions in the $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sn}_x$ ($x=10-25$) ferromagnetic shape memory alloys are currently of interest. As in Ni–Mn–Ga, these alloys feature high-temperature austenite and low-temperature martensite phases, where the magnetic state is strongly composition dependent. To study the role of chemical ordering in fine-tuning their magnetostructural properties, they were first annealed for 4 weeks/1223 K to achieve structural and compositional homogeneity, and were then further annealed for 1 week (~ 150 K below the reported $B2$ to $L2_1$ transition) at 773 K to increase the degree of chemical ordering. For $x=11$, this anneal resulted in a dramatic change in the magnetic ordering temperature. Following the 1223 K anneal, the sample exhibited ferromagnetic ordering at 140 K. After the 773 K anneal, the ferromagnetic transition is at 350 K, a characteristic of the ferromagnetic austenite phase with $15 < x < 25$. Consistent with the magnetization data, transmission electron microscopy examination confirms that the alloy decomposed into two phases with $x=20$ and 1. From this result one can conclude that the martensitic transformation occurs only in those compositions where the single phase $L2_1$ has been retained in a metastable state on cooling. © 2009 American Institute of Physics. [DOI: [10.1063/1.3067855](https://doi.org/10.1063/1.3067855)]

I. INTRODUCTION

There has been a great deal of research into the ferromagnetic (FM) Heusler alloys as potential FM shape memory alloys (FSMAs).¹ Several of these systems can be tuned such that they undergo field-induced structural transformations from a low-temperature (T) martensite phase to a high- T austenite phase near room temperature. There are numerous applications for FSMAs ranging from magnetically driven actuators to magnetic refrigeration.^{2,3} The Ni–Mn–Ga alloy series is one such FM Heusler system that has garnered much interest.^{4,5} This system features martensitic transformations from a high- T FM $L2_1$ austenite phase to a low- T paramagnetic modulated 10M, 14M, or $L1_0$ martensite phase depending on the composition. In this system, the degree of chemical ordering in the $L2_1$ phase is known to have an effect on the transition temperatures and is controlled by the thermal history of the sample.^{6–8} The degree of ordering can be improved with annealing such that the hysteresis of the structural transformation narrows and both the structural and magnetic transformations sharpen.

In an effort to further study these FM Heusler magnetic shape memory materials, the Ni–Mn–Sn alloy system has been investigated.^{9–11} Much like Ni–Mn–Ga, Ni–Mn–Sn alloys feature high- T austenite and low- T martensite phases; however, in Ni–Mn–Sn both the austenite and martensite phases can display FM ordering depending on the composition. Investigations of the alloy series $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sn}_x$ for $x=10-25$ have shown martensitic transformations for $x \leq 15$ with FM ordering in both the austenite and martensite phases

for $x=13-15$.^{9–11} The ordering in the FM austenite phase reaches a maximum value of 340 K for $x=25$ and monotonically decreases to 311 K as x approaches 13. The FM ordering in the martensite phase, first observed in $x=15$, quickly drops from a high of 230 to 137 K by $x=10$. The transformation from austenite to martensite, observed at 190 K for $x=15$ increases to 445 K by $x=10$.¹¹

In apparent disagreement with previous works by Krenke *et al.*¹¹ and Sutou *et al.*,¹⁰ which indicate that a single phase microstructure could be attained after as little as 2 h at 1273 K, attempts to grow single crystals of $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ revealed multiphase solidification behavior.¹² We recently demonstrated that while single phase microstructures may be achieved by short anneals, long term annealing (1223 K/4 weeks) is required to attain chemical homogeneity,¹² underscoring the importance of elemental analysis within the solid solution when interpreting the magnetostructural behavior of these alloys.¹³ It should also be noted that the FM transition in the $x=25$ austenite phase is closer to 370 K following the long term anneal.¹³ The other transition temperatures did not shift significantly from the values reported above. Along with structural and chemical homogeneities, atomic ordering may also play a significant role in fine-tuning the magnetostructural properties of the Ni–Mn–Sn alloys within the $L2_1$ structure.⁸ To study the effect of atomic ordering in Ni–Mn–Sn alloys, homogenized samples were subjected to an extended anneal at 773 K for one week, ~ 150 K below the $B2$ to $L2_1$ transition. In this paper we report that annealing $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ resulted in phase decomposition rather than an increase in atomic ordering. Differential scanning calorimetry (DSC) and magnetization measurements pre- and post-anneal originally intended to gauge the degree of atomic or-

^{a)}Electronic mail: lograsso@ameslab.gov.

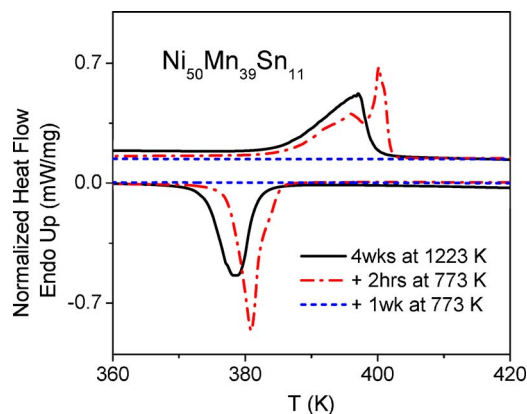


FIG. 1. (Color online) DSC data as a function of temperature for $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ showing the change in the martensite transition temperatures resulting from sample decomposition after annealing at 773 K.

dering, but instead revealed dramatic changes in the magnetic and structural phase transitions. The source of these postanneal changes were determined by transmission electron microscopy (TEM) and x-ray powder diffraction (XRD) experiments to be due to the decomposition of $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ during the 773 K anneal.

II. EXPERIMENTAL

An ingot of the $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ alloy was prepared by the Materials Preparation Center¹⁴ at Ames Laboratory using Ni (99.95 wt % purity), Sn (99.99%), and Mn (99.8%). The commercially available Mn had been further refined before use by distillation and all metals were etched before use. A button of Ni–Mn–Sn was arc melted several times under an argon atmosphere to ensure homogeneity and then chill cast into a 12.5 mm diameter rod. Cross sections of the ingot were made for microstructural characterization, thermal analysis, and physical properties measurements following a series of anneals. All the samples were first sealed in quartz tubes under 500 Torr (67 kPa) high purity Ar and heat treated at 1223 K for 4 weeks, quenched in water, and then annealed at 773 K for various times from 2 to 168 h. DSC was done in a PerkinElmer Pyris 1 unit. Small pieces were spark cut from the annealed cross sections and one side finely ground for good thermal contact with the aluminum pan. Scan rates of 10 K/min were used for all DSC runs. Magnetization measurements were performed using a 5 T Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer from 10 to 400 K in fields of 100 Oe. TEM samples were prepared by ion milling. TEM work was performed on an FEI Tecnai F20-XT microscope operated at 200 kV. XRD measurements on $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ were performed using a Panalytical X'Pert diffractometer with Cu $K\alpha$ radiation.

III. RESULTS AND DISCUSSION

DSC measurements were made on $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ following heat treatments for 4 weeks at 1223 K, 4 weeks at 1223 K+2 h at 773 K, and 4 weeks at 1223 K+1 week at 773 K. The resulting DSC measurements displayed in Fig. 1 from 360 to 420 K for the homogenized (1223 K/4 weeks)

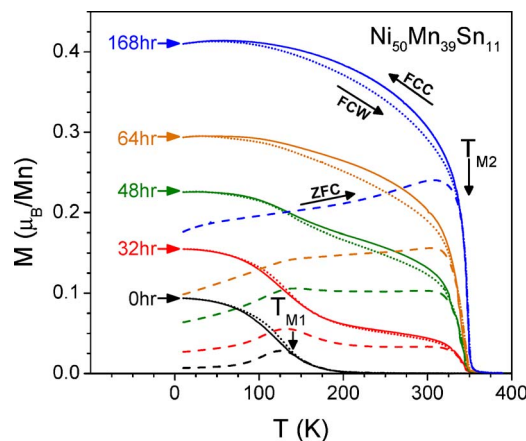


FIG. 2. (Color online) ZFC, FCC, and FCW $M(T)$ at $H=100$ Oe for $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ in the as-homogenized state (1223 K/4 weeks) and after additional heat treatments ranging from 32 to 168 h at 773 K.

sample show an endothermic peak on heating at 397 K due to a martensitic transition and on cooling; an exotherm is observed for the austenite to martensite transition at 379 K. When the homogenized sample is further annealed at 773 K for 2 h, the original endothermic peak splits into two peaks, a broad peak at the original transition temperature and a much sharper peak at 400 K, followed on cooling by a single sharp exotherm at 381 K. Once the sample has been annealed for 1 week, the original structural transition is absent, indicating that the martensitic transition has either shifted to a temperature out of the measured range or the sample no longer transforms.

Magnetization as a function of temperature $M(T)$ measurements were performed on $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ in the as-homogenized state and after consecutive heat treatments on the same sample for up to 1 week at 773 K. The measurements displayed in Fig. 2 include zero-field cooling (ZFC), field-cooled cooling (FCC), and field-cooled warming (FCW) curves from 10 to 400 K in an applied field $H=100$ Oe for each heat treatment. After 32 h at 773 K a second magnetic ordering temperature T_{M2} has clearly developed around 350 K. This transition increases in magnitude with further annealing and eventually dominates the $M(T)$ such that the original magnetic transition T_{M1} , with a Curie temperature of 140 K, can no longer be distinguished. There is also a significant change in the magnitude of the magnetization with annealing as the saturation magnetization shifts from $\sim 0.5\mu_B/\text{Mn}$ in the homogenized state to $\sim 1.4\mu_B/\text{Mn}$ after 1 week at 773 K. During this annealing process the transition at T_{M1} does not shift significantly in temperature, but rather is obscured by the transition that develops at T_{M2} . Splitting between the ZFC and both FC curves near T_{M1} also shifts quickly to just below T_{M2} with annealing. It is also interesting to note the behavior of the FCW and FCC curves, where at the ordering temperatures, T_{M1} and T_{M2} , a shift occurs between the FCW and FCC curves as the annealing progresses. Below T_{M1} , the FCW run has a larger magnetization and near T_{M2} , the FCC run has the larger magnetization. This difference is most apparent after 24 h at 773 K where the FCC and FCW curves cross between T_{M1} and T_{M2} .

TEM characterization results reveal that after the 1 week

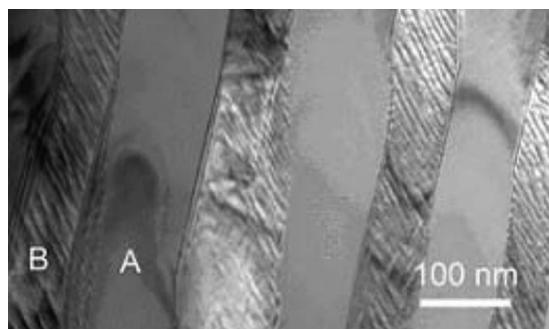


FIG. 3. TEM micrograph of $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ after 773 K/1 week anneal showing the presence of two lamellar phases. Energy dispersive x-ray spectroscopy measurements indicate that A and B have compositions of $\text{Ni}_{50}\text{Mn}_{30}\text{Sn}_{20}$ and $\text{Ni}_{54}\text{Mn}_{45}\text{Sn}_1$, respectively.

anneal $\text{Ni}_{50}\text{Mn}_{30}\text{Sn}_{11}$ decomposed into two lamellar phases of composition $\text{Ni}_{50}\text{Mn}_{30}\text{Sn}_{20}$ and $\text{Ni}_{54}\text{Mn}_{45}\text{Sn}_1$ (Fig. 3) with nanotwins or stacking faults in the $\text{Ni}_{54}\text{Mn}_{45}\text{Sn}_1$ phase. Rietveld refinement of the powder XRD spectra was consistent with the TEM results: the XRD spectra could be fit by a binary Ni–Mn theta phase and a cubic $L2_1$ phase with a lattice parameter consistent with $x=19$.¹¹

The calorimetry and magnetization data described earlier are consistent with the decomposition of $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ into $\text{Ni}_{50}\text{Mn}_{30}\text{Sn}_{20}$ and $\text{Ni}_{54}\text{Mn}_{45}\text{Sn}_1$ at 773 K. The magnetization data reveals that the magnetic transition at T_{M1} (140 K) for $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ shifts to T_{M2} (350 K) after the 1 week anneal at 773 K clearly showing the development of a second phase. In the Ni–Mn–Sn alloy system the 350 K transition temperature is consistent with an austenite phase with a composition between $x=15$ and 25. The DSC data indicate that after 2 h at 773 K, the peak of the original martensitic transition decreases in magnitude, while a second peak with a higher transition temperature appears. This is in agreement with a portion of the original $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$ decomposing to a composition with lower Sn content, as the martensitic transition temperature has been previously shown by Krenke *et al.*¹¹ to increase with decreasing Sn content. After 1 week the original martensitic transition is no longer observed in the measured temperature range consistent with the observed phases and the work of Krenke *et al.*,¹¹ which showed that there is no transformation for $x=20$ and that $x=1$ would transform at a temperature above the displayed temperature range (700 K).

IV. CONCLUSION

Previous work has shown that an extended anneal at 1223 K is required to achieve chemical and structural homogenizations for $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sn}_x$ ($x=11-15$). An attempt was made to build on this work with a low temperature anneal in order to improve the local atomic ordering of these alloys. Instead of improving the magnetostructural behavior of $\text{Ni}_{50}\text{Mn}_{39}\text{Sn}_{11}$, the low temperature anneal resulted in phase decomposition. This decomposition first observed in DSC and magnetization measurements was verified by both TEM and XRD results. The as-homogenized $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sn}_x$ ($x=11$) was found to decompose to compositions close to $x=1$ and 20. This result leads to the conclusion that $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sn}_x$ is metastable over the composition range where the martensitic transformation is observed below 400 K and suggests that the FSMA behavior is associated with this metastability.

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- ¹⁴Materials Preparation Center, Ames Laboratory US-DOE Basic Energy Sciences, Ames, IA, USA, available from www.mpc.ameslab.gov.