Postprint of a Study on Martensitic Transformation and Strain Behavior of Ni50-xCoxMn39Sn11 (x=0, 2, 4, 6) Heusler Alloys

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Date: 2023-03-19T00:00:00+00:00

Abstract

Through structural and magnetic measurements, the crystal structure, phase transformation, and magnetic properties of Ni50-xCoxMn39Sn11 (x=0, 2, 4, 6) Heusler alloys were investigated. The results demonstrate that with increasing Co content, the martensitic transformation temperature of this alloy series decreases significantly, while the Curie temperature exhibits an upward trend, and different crystal structures are displayed at room temperature. Simultaneously, the increase in Co content leads to a rapid enhancement of magnetization in the austenite phase, whereas the magnetization in the martensite phase remains nearly unchanged, significantly increasing the magnetization difference (ΔM) between the two phases. Particularly when the Co content increases to x=4, the ΔM between the two phases reaches 40 $\mathrm{Am^2/kg}$, and characteristics of magnetic-field-induced martensitic transformation are exhibited. Furthermore, the strain behavior of Ni50-xCoxMn39Sn11 (x=0, 2, 4) samples during the martensitic transformation process was also investigated. Among them, the transformation strain of the x=4 sample reaches 0.17%, and through magnetic field cycling at 3 T, this sample displays reversible magnetically induced strain within the temperature range of 215-235 K. This reversible strain behavior can be attributed to the fact that partial martensitic transformation in the sample can be driven by an isothermal magnetic field.

Full Text

Study of Martensitic Transformation and Strain Behavior in $\mathrm{Ni_{50}}$ Co $\mathrm{Mn_{39}Sn_{11}}$ (x=0, 2, 4, 6) Heusler Alloys

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Abstract
The crystal structure, phase transformations, and magnetic properties of Ni_{50} Co $Mn_{39}Sn_{11}$ (x=0, 2, 4, 6) Heusler alloys have been systematically studied by means of structural and magnetic measurements. The results show that with increasing Co concentration, the martensitic transformation temperatures decrease significantly, while the Curie temperatures exhibit an upward trend, with the alloys displaying different crystal structures at room temperature. Simultaneously, increasing Co content leads to a rapid enhancement of magnetism in the austenite phase while the magnetism of the martensite phase remains nearly unchanged, substantially improving the magnetization difference (ΔM) between the two phases. Particularly when the Co content reaches x=4, the ΔM between the two phases achieves approximately 40 $A \cdot m^2/kg$ and exhibits magnetic field-induced martensitic transformation characteristics. Additionally, the strain behavior during martensitic transformation has been investigated for Ni_{50} Co $Mn_{39}Sn_{11}$ (x=0, 2, 4) samples. The phase transformation strain in the x=4 sample reaches 0.17%, and through magnetic field cycling at 3 T, this sample displays reproducible magnetically induced strain in the temperature range of 215–235 K. This reproducible strain behavior can be attributed to the fact that a partial martensitic transformation in the sample can be driven by an isothermal magnetic field.

Keywords Ni-Co-Mn-Sn, shape memory alloy, martensitic transformation, magnetostrain

1. Introduction

Conventional ferromagnetic shape memory alloys have attracted considerable attention in condensed matter physics and materials science as candidate materials for "magnetic sensing" and "magnetic actuation" due to their high response frequency and large recoverable strain. Ni-Mn-Ga ternary Heusler alloys represent the most typical ferromagnetic shape memory alloys, and their giant magnetic shape memory effect in the martensitic state has been extensively and systematically investigated over the past two decades [1–5]. The underlying mechanism can be interpreted as twin boundary movement or reorientation caused by the competition between the Zeeman energy provided by the magnetic field and the anisotropy energy between martensitic variants [4–6].

In 2004, Sutou et al. [7] first discovered thermoelastic martensitic transformation in Mn-rich Ni_2Mn_1 X (X=Sn, In, Sb) ferromagnetic Heusler alloys. During cooling, these alloys typically transform from a high-symmetry austenite structure to a low-symmetry martensite structure, accompanied by a sharp drop in magnetization. This metamagnetic transformation induces a large magnetization difference (ΔM) between the two phases. Consequently, the Zeeman energy provided by an isothermal magnetic field ($_0\Delta$M · H, where $_0$ is the vacuum permeability and H is the applied magnetic field strength) can also drive the martensitic transformation, namely "magnetic field-induced martensitic transformation" [8,9]. Accompanying this peculiar property, microscopic structural changes in Ni-Mn-based metamagnetic alloys produce macroscopic induced strain, referred to as "magnetically induced strain." In 2006, Kainuma et al. [10,11] first reported strain behavior studies on Ni-Co-Mn-In and Ni-Co-Mn-Sn alloys under applied prestress, observing 3% and 1% strain respectively through isothermal magnetic field induction of 0–8 T. Subsequently, researchers reported reproducible magnetically induced strain in Ni-Mn-based metamagnetic alloys under high magnetic fields (5 T) without applied prestrain, such as in Ni-Mn-In [12–14], Ni-Co-Mn-In [15,16], and Ni-Fe-Mn-In [17], attributing this to martensitic transformation driven by isothermal magnetic fields.

For non-stoichiometric Ni-Mn-Sn ternary alloys, the transformation strain during martensitic transformation is only 0.04% [18]. Moreover, due to the relatively low ΔM between the two phases in this alloy, the Zeeman energy provided by the magnetic field is insufficient to drive its martensitic transformation under isothermal conditions. However, recent studies [19–21] have shown that substituting Co atoms for Ni or Mn sites in Ni-Mn-Sn alloys can enhance ΔM between the two phases. Additionally, related research [14,22] has indicated that the transformation strain in Ni-Mn-based metamagnetic alloys is closely related to their composition. With this objective, the present work prepared polycrystalline Ni$_{50}$ Co Mn$_{39}$Sn$_{11}$ (x=0, 2, 4, 6) samples by substituting Co for Ni and systematically investigated the crystal structure, martensitic transformation, and magnetic properties of this alloy series. Based on these results, the strain behavior during martensitic transformation was further studied for Ni$_{50}$ Co Mn$_{39}$Sn$_{11}$ (x=0, 2, 4) samples, achieving reproducible magnetically induced strain in the x=4 sample under a 3 T magnetic field.

2. Experimental Methods

Polycrystalline samples with nominal composition Ni$_{50}$ Co Mn$_{39}$Sn$_{11}$ (x=0, 2, 4, 6, atomic fraction) were prepared using high-purity Ni, Mn, Co, and Sn elemental metals. The samples were melted using a WK2-type non-consumable high-vacuum arc furnace under high-purity Ar atmosphere protection, with a mass loss rate of less than 1% for the as-cast alloys. To homogenize the composition of the as-cast polycrystalline samples and achieve highly ordered atomic arrangement, the samples were sealed in vacuum quartz tubes and subjected to high-temperature annealing at 1173 K for 24 h, followed by quenching in ice water. To investigate the strain characteristics of the x=0, 2, and 4 samples, they were uniformly cut into plate-shaped specimens with dimensions of 6.5 mm

× 6.5 mm × 1 mm using a low-speed diamond cutter. The crystal structure at room temperature was characterized using a D/max-Ultima IV multifunctional X-ray diffractometer (XRD). Magnetic measurements were performed using a Versalab physical property measurement system, and strain data were collected using standard electrical resistance strain measurement techniques. The temperature range for collecting transformation strain data without applied magnetic field was 400-100 K, with the initial strain value of the sample normalized to zero before measurement. The experimental temperature range for magnetically induced strain was 300-100 K. The sample temperature was first decreased from 300 K to 100 K, then increased to the target temperature, and the initial strain value was normalized to zero before measurement.

2.1 Crystal Structure

Figure 1 [Figure 1: see original paper] presents the XRD spectra of Ni_{50} Co $Mn_{39}Sn_{11}$ (x=0, 2, 4, 6) samples at room temperature. Analysis reveals that the x=0 and 2 samples exhibit a 10M modulated orthorhombic martensite structure at room temperature, with lattice parameters of a=0.4314 nm, b=0.5692 nm, c=2.779 nm and a=0.4374 nm, b=0.5759 nm, c=2.1992 nm, respectively. In contrast, the x=4 and 6 samples display an $L2_1$-type austenite structure at room temperature, with lattice parameters of a=0.5977 nm and a=0.5952 nm, respectively. These results demonstrate that with increasing Co content, the samples gradually transition from a low-symmetry martensite structure to a high-symmetry austenite structure at room temperature.

2.2 Phase Transformation Characteristics

To investigate the phase transformation characteristics, Figure 2 [Figure 2: see original paper] shows the temperature dependence of magnetization (M) for Ni_{50} Co $Mn_{39}Sn_{11}$ samples under an applied magnetic field of 0.05 T. Throughout the cooling process, all samples exhibit paramagnetic behavior in the high-temperature region. As temperature decreases, the magnetization of the samples increases sharply at the austenite Curie temperature (T_C^A), demonstrating clear ferromagnetic behavior. However, when temperature further decreases, the magnetization of the x=0, 2, and 4 samples begins to drop significantly at the martensitic transformation start temperature (M_s), and stabilizes below the martensitic transformation finish temperature (M_f), corresponding to the start and completion of martensitic transformation. During subsequent heating, these three samples undergo reverse martensitic transformation starting at the austenitic transformation start temperature (A_s) until completion at the austenitic transformation finish temperature (A_f), accompanied by obvious thermal hysteresis ΔT, indicating that this metamagnetic martensitic transformation exhibits first-order structural phase transformation characteristics. The x=6 sample maintains constant magnetization throughout the entire temperature range after completing the austenite ferromagnetic transition, suggesting that excessive Co substitution for Ni suppresses martensitic transformation in Ni-Mn-Sn alloys.

Table 1 lists the characteristic temperatures of Ni_{50} Co $Mn_{39}Sn_{11}$ samples during martensitic transformation. It can be seen that as Co content increases, the four characteristic temperatures of the samples rapidly shift to lower temperatures, which can be interpreted as Co substitution suppressing the hybridization between the 3d orbitals of Ni atoms and the 3d orbitals of Mn atoms occupying Sn sites [23,24]. The table also shows that T_C of the samples exhibits an upward trend with increasing Co content, indicating enhanced ferromagnetic stability of the austenite state. Similar behavior has been observed in Ni_{50} Cu $Mn_{36}In_{14}$ alloys [25]. According to first-principles calculations [26], the magnetic exchange interaction in Ni-Mn-based metamagnetic alloys strongly depends on the Mn-Mn interatomic distance, and this exchange interaction is mediated by itinerant 3d electrons provided by other elements in the alloy. Combined with the XRD analysis results for the x=4 and 6 samples, the lattice constant of the austenite phase decreases with increasing Co content, which reduces the Mn-Mn interatomic distance to some extent. Such a result would normally weaken the ferromagnetic coupling between Mn-Mn pairs (as it is generally believed that overly close Mn-Mn interatomic distances tend to form antiferromagnetic exchange interactions [26]). However, considering that partial substitution of Co for Ni reduces the concentration of 3d conduction electrons in the alloy, the original electronic structure is altered, thereby enhancing the ferromagnetic exchange interaction in the austenite state.

2.3 Magnetization Behavior

Figure 3 [Figure 3: see original paper] shows the isothermal magnetization hysteresis loops for Ni_{50} Co $Mn_{39}Sn_{11}$ (x=0, 2, 4) samples during reverse martensitic transformation. Figure 3a presents the magnetization curves for the x=0 sample. When the sample is in the austenite state (300 K), its magnetization increases sharply at low fields due to ferromagnetic components, but fails to saturate even at high fields, displaying weak ferromagnetic or magnetically inhomogeneous behavior. This occurs because excess Mn atoms occupy Sn sites in the lattice, and according to neutron diffraction results [27], these Mn atoms tend to form antiferromagnetic exchange interactions with original Mn atoms. As temperature decreases, martensitic transformation induces changes in Mn-Mn spacing and redistribution of 3d conduction electrons, causing a slight increase in antiferromagnetic components and resulting in only a very small ΔM between the two phases in the x=0 sample (inset of Figure 3a). When a small amount of Co is substituted for Ni, the magnetization curves in Figure 3b show that the magnetization of the x=2 sample is significantly enhanced throughout the entire measurement temperature range and essentially reaches saturation, demonstrating that Co atoms act as "ferromagnetic activators" in the sample [28-30]. Particularly when Co content increases to x=4 (Figure 3c), the x=4 sample exhibits typical ferromagnetic behavior in both austenite and martensite phases. Compared with the x=2 sample (inset of Figure 3b), the magnetization in the austenite state increases by nearly 2 times, while the magnetization in the martensite state remains almost unchanged, resulting in a ΔM of approximately 40 $A \cdot m^2/kg$ between the two phases. Furthermore, unlike the x=0 and 2 samples, the magnetization curve in the transformation region (225 K) for the x=4 sample clearly shows (Figure 3c) obvious hysteresis during magnetization and demagnetization processes, which can be attributed to magnetic field-induced martensitic transformation.

2.4 Shape Memory Effect and Magnetically Induced Strain

Figure 4 [Figure 4: see original paper] shows the temperature dependence of spontaneous strain (λ) during martensitic transformation for Ni_{50} Co $Mn_{39}Sn_{11}$ (x=0, 2, 4) samples without applied magnetic field. During cooling, the λ of all samples decreases sharply with the occurrence of martensitic transformation, exhibiting volume contraction. During subsequent heating, the samples expand with the same strain magnitude and recover their original shape, demonstrating two-way shape memory effects controlled by temperature. The maximum transformation strains of the x=0 and 2 samples are nearly equal at approximately 0.04%, which is consistent with previous studies [18]. However, the maximum transformation strain of the x=4 sample reaches 0.17%, a value comparable to the transformation strain of Ni-Mn-In ternary alloys without applied magnetic field [12,13]. Considering that the macroscopic transformation strain in Ni-Mn-based metamagnetic alloys depends on microscopic changes in crystal structure between the two phases, this study suggests that appropriate Co substitution for Ni can effectively increase the unit cell volume change before and after martensitic transformation.

Since enhanced transformation strain was obtained in the x=4 sample and isothermal magnetization results indicated possible magnetic field-induced martensitic transformation in the transformation temperature region, it is promising to achieve magnetically induced strain driven by magnetic field in this sample. To confirm this, Figure 5 [Figure 5: see original paper] shows the magnetically induced strain curves for this sample at different temperatures. When the sample is in the martensite state (150 K), no obvious strain behavior is observed, which can be attributed to the very weak magnetic anisotropy energy of the martensite in this sample, such that the Zeeman energy provided by the external magnetic field cannot cause twin boundary movement or reorientation. However, as seen from the curve measured at 225 K, during initial magnetization, the λ of the sample increases slowly at low fields and rapidly increases by 0.045% in the magnetic field range of 0.5-3 T, demonstrating obvious magnetically induced strain without any pre-strain. This result is similar to the magnetization behavior exhibited by the x=4 sample at the same temperature, fully proving that the magnetically induced strain indeed originates from magnetic field-induced martensitic transformation.

During subsequent magnetic cycling, although the magnetically induced strain does not fully recover to its original state, approximately 0.012% of the strain in the sample can be completely driven by the magnetic field, showing reproducible magnetically induced strain. Similar curves are also observed at temperatures of 215 and 235 K (Figure 5), indicating that this reproducible strain characteristic can be displayed over a relatively wide temperature range. Such experimental results can be understood as follows: during initial magnetization, partial martensite in the sample transforms into austenite driven by Zeeman energy, displaying a relatively large macroscopic strain. However, during demagnetization, the thermal hysteresis caused by interfacial friction between the two phases consumes most of the Zeeman energy [31], resulting in only one-quarter of the previous austenite being able to transform back to martensite, thus observing only 0.012% reproducible magnetically induced strain in the x=4 sample.

In summary, the reproducible magnetically induced strain in the x=4 sample is mainly determined by the change in phase fraction between martensite and austenite driven by the magnetic field. It is well known that when changing the external magnetic field, the change in volume fraction between the two phases mainly depends on the variation amplitude of the phase transformation equilibrium temperature (T_0) with magnetic field, i.e., dT_0/dH. As shown in Figure 6 [Figure 6: see original paper], the martensitic transformation equilibrium temperature of the x=4 sample exhibits a basically linear decreasing trend with increasing applied magnetic field, with dT_0/dH reaching approximately -3 K/T, which is nearly twice that of Ni-Mn-Sn ternary alloys [18]. This is because appropriate Co substitution significantly increases ΔM between the two phases in the sample. According to thermodynamic theory [32], the minimum magnetic field required to drive a complete martensitic transformation can be described by $\Delta T/(dT_0/dH)$. For the x=4 sample, the complete martensitic transformation temperature span (i.e., M_s-M_f) reaches 70 K, which includes about 13 K of thermal hysteresis ΔT during forward and reverse martensitic transformation. However, the absolute change in T_0 under an applied magnetic field of 3 T is only 9 K, which is smaller than the thermal hysteresis of the x=4 sample. This seems to imply that it would be difficult to obtain reproducible magnetically induced strain through magnetic field cycling. To clarify this point, normalized thermomagnetic loops of the x=4 sample during partial martensitic transformation were measured, as shown in Figure 7 [Figure 7: see original paper]. Unlike the transformation from complete austenite to martensite, when the sample transforms from an intermediate state (coexistence of martensite and austenite) to the martensite state, its ΔT is significantly reduced. This phenomenon may be attributed to the fact that incomplete martensitic transformation weakens the interfacial friction energy consumption between austenite and martensite during the initial stage of transformation. Under these conditions, the Zeeman energy provided by an applied magnetic field of 3 T can completely drive a partially reversible martensitic transformation, thereby achieving reproducible magnetically induced strain in the x=4 sample without pre-strain.

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3. Conclusion

1. For Ni_{50} Co $Mn_{39}Sn_{11}$ (x=0, 2, 4, 6) Heusler alloys, as Co content increases, the martensitic transformation temperature gradually shifts to lower temperatures, while the austenite Curie temperature moves to higher temperatures, until excessive Co substitution suppresses martensitic transformation in the samples.
2. Appropriate substitution of Co atoms for Ni atoms not only increases the magnetization difference between the two phases but also enhances the unit cell volume change before and after transformation.
3. A transformation strain of nearly 0.17% was observed in the $Ni_{46}Co_4Mn_{39}Sn_{11}$ sample, which is comparable to that of Ni-Mn-In ternary alloys. Meanwhile, reproducible magnetically induced strain of approximately 0.012% was achieved in this sample under magnetic field cycling at 3 T. This characteristic suggests potential for such alloys as magnetic actuation devices.

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