Magnetic and structural transitions in the melt-spun Heusler alloy Ni$_{53}$Mn$_{25}$Al$_{22}$

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Abstract

We report on the magnetic properties and structural transitions of the melt-spun ribbon Ni$_{53}$Mn$_{25}$Al$_{22}$ alloy by means of resistance, differential scanning calorimetry (DSC) and magnetization measurements. The Ni$_{53}$Mn$_{25}$Al$_{22}$ ribbon having a B2 structure exhibits a magnetic transition from antiferromagnetic to paramagnetic state, and a structural transition of austenitic–martensitic character with a $M_s$ of 278 K. The calculated effective paramagnetic moment of 4.47 $\mu_B$ per formula unit reveals that the Mn atoms contribute to the paramagnetism of the B2 phase in this alloy.

Keywords: Martensitic transformation; Magnetic transition; Melt-spinning technique; Heusler alloy

1. Introduction

Heusler alloys have stimulated much research interest since the discovery of a large magnetic shape memory effect in Heusler compounds Ni$_2$MnGa [1]. Up to now, several candidates for magnetic shape memory alloys have been developed, including Ni–Co–Al [2], Ni$_2$FeGa [3,4], Co–Ni–Ga [5] and Ni–Mn–Al [6–13] systems. Among them, Ni–Mn–Al alloys are particular in that martensitic transformations only occur in slightly off-stoichiometric compounds. Having a high $M_s$ temperature in the B2 phase and exhibiting different crystal structures of martensite like the 14M, 10M, L1$_0$ phase of the Ni–Mn–Al system alloys has brought much attention to these materials as potential high-temperature shape memory alloys. In previous investigations it has been established that the martensitic transformations of these compounds depend sensitively on the concentration and the structure of the parent phase. Kainuma et al. found that the Ni–Mn–Al B2 phase transforms to the L1$_0$ martensite for low-Al and low-Mn content, while the 10M and 14M phases appear in the high-Al and high-Mn alloys [6]. Morito et al. and Mañosa et al. proposed that the formation of the L2$_1$ phase can suppress martensitic transformation which is able to take place in single B2 structure [7,8]. Acet et al. found that a single L2$_1$ phase is not readily stabilized but rather a mixed L2$_1$ + B2 state is present in stoichiometric Ni$_2$MnAl [9]. Kainuma et al. found that $M_s$ temperatures decrease when the parent phase is the L2$_1$ structure, and the B2/L2$_1$ ordering temperatures affect $M_s$ strongly [10]. In the present study, the magnetic properties and structural transitions of the Ni$_{53}$Mn$_{25}$Al$_{22}$ alloy synthesized by melt-spinning technique were investigated in detail. X-ray diffraction (XRD) measurements indicate that this alloy has a B2 structure at room temperature. The results of magnetization, resistance and differential scanning calorimetry (DSC) measurements reveal the occurrence of a thermoeelastic martensitic transformation, and a magnetic transition from antiferromagnetic to paramagnetic state. Furthermore, we calculate the effective paramagnetic moment and conclude that the Mn atoms mainly carry the magnetic moment in the parent phase.
2. Experimental

We prepared the precursor ingot by repeatedly melting high purity Ni, Mn and Al metals in appropriate proportion in an induction furnace under the argon atmosphere. Subsequently the ingots were homogenized by annealing in a quartz tube at 1073 K for 3 days and rapidly cooled by spinning onto a copper wheel at a linear velocity of about 25 m/s, a process which was also performed under an Ar protection. X-ray diffraction measurements were performed to identify the structure of the polycrystalline samples. The magnetizations were measured using both a physical property measurement system (Quantum Design PPMS, USA) and a superconducting quantum interference device (SQUID). The resistance measurements were carried out by means of a standard ac four-point technique at temperatures ranging from 5 to 350 K employing the physical property measurement system. The transformation temperatures were determined by differential scanning calorimetry at a rate of 10 K/min.

3. Results and discussion

The phase structure was identified at room temperature by X-ray diffraction using Cu Kα radiation. The power X-ray diffraction pattern is shown in Fig. 1, where the strongest peaks have been indexed and marked. One can see that, in the experimental alloys Ni$_{53}$Mn$_{25}$Al$_{22}$ parent phase, the specimens show a B2 structure with four characteristic reflection peaks (2 0 0), (2 2 0), (4 0 0), (4 2 2), while the odd number peaks (1 1 1) and (3 1 1), which represent the existence of L2$_1$ structure are not obviously present. For most Heusler alloys, the conventional synthesis is arc-melting followed by annealing at a specific temperature to achieve a structure transition from B2 to L2$_1$. However, some reports have shown that even with long time annealing only a mixed L2$_1$ + B2 state is obtained in Ni–Mn–Al alloys. Because the B2–L2$_1$ transformation occurs at a temperature where diffusion kinetics in a solid are slow, this enables the high-temperature B2 phase to be readily retained at room temperature as a metastable state rather than the thermodynamically more favorable L2$_1$ phase [9]. This is in contrast to Ni–Mn–Ga alloys for which the B2–L2$_1$ transition occurs very easily. The lattice constant of the B2 phase is estimated to be $a = 0.2899$ nm, which is similar to that of the Ni$_2$MnAl alloy with a B2 structure [14].

![Fig. 1. X-ray diffraction pattern at room temperature for the melt-spun ribbons Ni$_{53}$Mn$_{25}$Al$_{22}$.](image)

The magnetization was measured over a temperature range of 5–350 K using the PPMS at a magnetic field of 5T, as shown in Fig. 2. We can see an increase of magnetization with decreasing temperature with two exceptions: the curve slope changes direction in the low-temperature region where a hump peak is present, and in the vicinity of 280 K where a distinct peak is found, which implies the possible existence of transitions. In order to achieve further understanding of this behavior, we measured the temperature dependence of the magnetization under 500 Oe during cooling and heating progress using a SQUID, and the results are shown in Fig. 3. It is clearly visible that the heating data do not retrace the cooling data around 280 K but show a narrow hysteresis (see the inset of Fig. 3), indicating the occurrence of a first-order transition.

![Fig. 2. Temperature dependence of magnetization at the constant magnetic field of 50 kOe for Ni$_{53}$Mn$_{25}$Al$_{22}$ ribbons.](image)

![Fig. 3. The magnetization curves in the melt-spun Ni$_{53}$Mn$_{25}$Al$_{22}$ specimen which were finite field cooled. Field cooling and heating measurements were carried out under 500 Oe. Inset graph shows the magnified hysteresis near the martensitic transition.](image)
known martensitic transformation behavior in off-stoichiometry Heusler alloy Ni$_2$MnAl, the behavior near 280 K in our sample can be identified as a martensitic transformation. We herein have to point out that the details about the structure of martensitic phase cannot be presented since a low-temperature X-ray diffraction apparatus was not available. Differentiating the resistance data with respect to temperature gives 280 K ($M_s$), 268 K ($M_f$), 272 K ($A_s$) and 286 K ($A_f$) for the martensitic transition temperatures, respectively (see the inset (a) of Fig. 4). As we know, the transition temperatures $M_s$, $M_f$ and the hysteresis width $\delta T$ can be determined by the corresponding peak positions of the DSC measurements. Our DSC measurement results are shown in Fig. 5. It can be seen that the DSC traces exhibit large exothermic and endothermic peaks, which is in good correspondence with martensitic and reverse transformations at around 260–290 K. More precise values of the transition temperatures can be obtained using the crossing point between the extrapolation lines of these peaks and the base line, i.e., $M_s = 278$ K, $M_f = 267$ K, $A_s = 274$ K and $A_f = 284$ K. The $M_s$ temperature is similar with that in Ref. [10] where synthesis by other methods was used, but $\delta T = A_f - M_s \approx 6$ K is comparatively smaller. Chernenko has reported that the $M_s$ temperatures and the electron concentration $e/a$ are correlated when assuming that the numbers per atom in Ni–Mn–Ga alloys are Ni = 10, Mn = 7 and Ga = 3 [15]. This type of normalization can be extended to the Ni–Mn–Al system as well if the alloys are in the restricted region near the Ni$_2$MnAl stoichiometric composition under the assumption that the numbers of valence electrons per atom are 10, 7 and 3, for Ni, Mn and Al, respectively. For our sample, the $e/a$ ratio is 7.71, and the transition temperature is in good agreement with the data in Refs. [8,16].

The inverse magnetic susceptibility as a function of temperature is shown in Fig. 6. It is clear from the figure that the data points fall on a straight line which appears to show a Curie–Weiss variation above 290 K. This, together with the linear character of the magnetic field dependence of the magnetization at 300 K (see the inset (a) of Fig. 6), shows that the parent phase is paramagnetic in this temperature section. We know that in Ni–Mn–Al alloys, the L2$_1$ phase is ferromagnetic, and the B2 phase is conical antiferromagnetic. It can be seen in the figure that the isothermal $M$ versus $H$ curve at 150 K has no substantial curvature up to the highest magnetic fields, which shows that an antiferromagnetic exchange dominates. So the marked small peak in the DSC curve at about 290 K near the endothermic peak should be a result of the magnetic transition from the paramagnetic to antiferromagnetic state. However, we did not find such a salient peak representing the Néel temperature like Morito et al. and Ziebeck et al. reported in both Ni$_{50}$Mn$_{30}$Al$_{20}$ and Ni$_2$MnAl alloys [7,14]. This feature is not observable in our alloy possibly owing to the close-lying $T_N$ and $M_s$ temperatures, and consequently the hump in the curve around $T_N$ (see Fig. 3) is somewhat rounded out and not as sharp as in Refs. [7,14]. Accompanying the martensitic transformation, the mag-
netic anisotropy will change, so that the magnetization increases with decreasing temperature, which suggests that some magnetic ordering is present. And ferromagnetism in the martensitic state is necessary for a magnetic shape memory effect to occur.

It can be seen from Fig. 3 that the slope of the magnetization curve changes at about 80 K. Since there is no temperature hysteresis in the resistance measurement, we cannot attribute this to the structure transformation. Previously, a hump-like peak was found in Fig. 2 when cooling under zero field at low temperatures, and an apparent hysteresis was also observed in magnetization $M(H)$ curve in the middle temperature region (40 K) of FC (see the inset (b) of Fig. 6). Similar behaviors have also been observed in the Ni50Mn30Al20 alloy and are attributed to the spin-glass transition [7]. In the case of the Ni$_{53}$Mn$_{25}$Al$_{22}$ ribbon, structural defects or compositional inhomogeneity can bring about a spin-glass-like phase transition arising from the competition between the ferromagnetic and antiferromagnetic exchange interactions.

In Heusler alloys Ni$_2$MnZ, many works indicated that an indirect d–d coupling by conduction electrons makes Mn atoms coupled as ferromagnetic with a large magnetic moment [17]. For the Ni$_{53}$Mn$_{25}$Al$_{22}$ ribbon, a least-squares fit of the $\chi(T)$ data above 290 K to $\chi(T) = C/(T - \theta)$, where $C = N_A \mu_{\text{eff}}^2/(3 K_B)$, $N_A$ the Avogadro number, $\mu_{\text{eff}}$ the effective moment per formula unit, $K_B$ the Bohr magneton and $\theta$ is the Curie–Weiss temperature, yields $\mu_{\text{eff}} \approx 4.47 \mu_B$. This is close to the theoretical value of Mn$^{3+}$ atom $4.9 \mu_B$. Our calculation shows that Mn atoms are dominant in the paramagnetism of the B2 melt-spun Ni$_{53}$Mn$_{25}$Al$_{22}$ alloy.

4. Conclusion

Summarizing the XRD, magnetization, DSC and electrical resistance measurements, we have found that the ternary melt-spun Ni$_{53}$Mn$_{25}$Al$_{22}$ alloy has a B2 structure, and thermoelastic martensitic transformation with a $M_s$ of 278 K was observed which is characterized by significant thermal hysteresis in all measured quantities. Additionally, a magnetic phase transition from antiferromagnetic to paramagnetic state also exists. Below 80 K, the magnetic state takes on a spin-glass-like character. A value of 4.47 $\mu_B$ per formula unit of effective paramagnetic moment is estimated.

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References