Martensitic transformation and magnetic properties of Co–Ni–Al shape memory alloy ribbons

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Abstract

We report on the magnetic and martensitic transformation properties of $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ferromagnetic shape memory alloy ribbons. We found that the phase formation of $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ is strongly dependent on the method of preparation. The conventional as-cast ingot sample contains a large amount of the γ phase embedded in the primary β phase, while melt-spun ribbons contain the pure β phase. $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbons exhibit a perfect thermoelastic martensitic transformation from a cubic to a tetragonal structure at 240 K during cooling. The martensite structure can be well described by the L1_0 lattice, similar to that of Ni–Al alloys. The martensitic phase at 5 K exhibits a saturation magnetization of 48.67 emu g^{-1} and saturates at about 8000 Oe. A large increase in coercive force after ageing at 500°C for 1 h has been found due to the change in atomic chemical ordering. The temperature dependence of the saturation magnetization indicates that magnetization can be well interpreted by spin-wave theory at temperatures lower than 200 K. The material shows a recoverable strain of 500 ppm upon the martensitic transformation.

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) are expected to be useful as new magnetic–mechanical devices due to two of their useful functions: as magnetic-field-induced strain and field-controlled thermoelastic shape memory. The transformation in FSMAs can be triggered not only by changes in temperature and stress, as in conventional paramagnetic SMA NiTi, but also by applying a magnetic field. Many systems have been developed as FSMAs, such as Ni_2MnGa [1–4], Ni_2MnAl [5], Fe–Pd [6], Ni_2FeGa [7, 8] and Fe–Pt [9]. Very recently, Co–Ni–Al(Ga) alloys have been developed as new FSMAs [10, 11]. In contrast to the poor ductility of the well-known FSMA NiMnGa, the Co–Ni–Al(Ga) alloys have good ductility over a large temperature range, which is important for shape memory alloy applications. A systematic investigation has been carried out for Co–Ni–Al polycrystalline and single crystal samples [12–14]. In this work, we prepared our samples using the

melt-spinning technique. X-ray diffraction (XRD) confirmed that $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbons have the pure β phase, while a large amount of the γ phase has been observed embedded in the β matrix in as-melted ingots. Our study of the martensitic transformation, the basic magnetic properties and the shape memory effect of the ribbons is presented and discussed.

2. Experiment

The intermetallic compound $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ was prepared by two methods: one is the conventional method of arc melting under the protection of an argon atmosphere, followed by annealing at 800°C for 5 days, and the other is rapid quenching from the liquid state, spinning onto the surface of a rotating copper wheel. The wheel velocity was about 25 m s^{-1} . The thickness and width of the ribbon were $30 \mu\text{m}$ and 4 mm, respectively. The crystal structure was investigated by using XRD techniques. The martensitic phase transition was determined by an ac susceptibility measurement

with an ac field of 796 A m^{-1} and a frequency of 77 Hz. The magnetization curves were obtained using a SQUID (Quantum Design MPMS) magnetometer. The shape memory effect was measured in the ribbon length direction using a strain gauge.

3. Results and discussion

Figure 1 shows the XRD patterns of the $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbon and the precursor ingot. For the ribbon samples, as shown in figure 1(a), the characteristic peaks of the β structure, (220), (400) and (422), can be clearly seen. The lattice parameter was obtained as $5.6 \text{ \AA}$ by indexing these peaks. As seen from figure 1(b), in addition to the bcc β austenite phase, the characteristic peaks of the face-centred cubic γ phase are observed in the precursor ingot. We can speculate at this time that these alloys crystallize at a high temperature into the bcc structure (or β phase). For kinetic reasons, this β phase can be retained below its phase stability temperature range by means of suitable (fast enough) cooling because the precipitation of the equilibrium γ phase in the β parent matrix phase is a slow process that strongly depends on the cooling rate. Therefore, the single β phase can be obtained by our melt-spinning technique or quenching in ice water from temperatures as high as 1400°C [14]. These fast cooling methods can effectively minimize the time spent by the sample in a temperature range at which the equilibrium phase can grow, even impeding the formation of the γ phase, enforcing a rapid cooling of the liquid state directly into the solid state of the pure β phase. This phenomenon is rather similar to that observed in the Heusler alloy Ni_2FeGa [7, 8].

The temperature dependence of the ac susceptibility of the $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbon is shown in figure 2 (solid symbols). The martensite starting temperature, M_s , finishing temperature, M_f , the reverse transformation starting temperature, A_s , the finishing temperature, A_f , and the Curie temperature, T_C , are 240 K, 208 K, 230 K, 287 K and 350 K, respectively, and together with the large temperature interval M_s-M_f are known

Figure 1. XRD patterns for $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ melt-spun ribbon (a) and precursor ingot (b) taken at room temperature.

as the thermoelastic martensitic transformation. In contrast to the ribbon sample, the precursor ingot only shows weak and broad phase transitions in the first and second order, as shown in figure 2 by the open symbols. Moreover, the M_s of the ingot sample is lower than that of the ribbon sample. It is well known that the martensitic transformation and Curie transition strongly depend on the composition, the degree of atomic ordering and the presence of some amount of precipitates of the equilibrium phase. According to the XRD results, as discussed above, we have found that a large amount of γ phase is embedded in the β matrix phase for the ingot sample. Oikawa *et al* [12] pointed out that the fcc γ phase is a Co-rich phase, corresponding to the decrease in Co content in the matrix composition and the decrease in electron concentration. Thus the martensitic transformation in the ingot is lower than that in the ribbon samples. At the same time, the sharp first-order transformations and second-order magnetic transition in $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbon are further evidence of the high chemical ordering structure in the melt-spun sample.

In order to confirm the structure transition across the martensitic transformation, XRD patterns were obtained at 93 K for the $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbon, as shown in figure 3. An analysis of the XRD patterns indicates that the structure is the face-centred $L1_0$, as in Ni–Al and the non-modulated NiMnGa martensite system [15]. The lattice parameters are calculated to be $a_{L10} = b_{L10} = 3.79 \text{ \AA}$, and $c_{L10} = 3.15 \text{ \AA}$. On the other hand, the structure distortion can also be regarded as a B2-like order parent phase transformed to a body-centred tetragonal structure. They only differ in the selection of the crystallographic axes. The relationship of the lattice constants between the body-centred tetragonal structure and the $L1_0$ structure is as follows:

$$a_{L10} = \sqrt{2}a_{bct} = 3.79 \text{ \AA},$$

$$c_{L10} = c_{bct} = 3.15 \text{ \AA}.$$

Thus $a_{bct} = b_{bct} = 2.68 \text{ \AA}$, $c_{bct} = 3.15 \text{ \AA}$. Note that $c_{L10}/a_{L10} = 0.83$, while $c_{bct}/a_{bct} = 1.17 > 1$, which is different from the usually modulated martensite structure

Figure 2. Temperature dependence of ac magnetic susceptibility of $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbon (●) and ingot (○).

Figure 3. XRD patterns of $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ melt-spun ribbon taken at 93 K.

with $c_{\text{bct}}/a_{\text{bct}} < 1$. It is worth noting that $c_{\text{L10}}/a_{\text{L10}}$ is rather close to the value reported by Kainuma *et al* [16], $c_{\text{L10}}/a_{\text{L10}} = 0.8$.

Figure 4(a) shows the magnetization curves obtained at 250, 220, 200, 100 and 5 K for the ribbon sample. Examining the curves, we can see the evidence for the martensitic phase transition. Although the curves at 200 and 250 K differ by only 50 K, their saturation fields are rather different. At 200 K, the alloy is in the martensitic phase, and the in-plane moment does not saturate until we apply a field of 8000 Oe. In contrary, at 250 K, the alloy is at the parent phase with a saturation magnetic field of 3000 Oe. The dramatic decrease in the saturation field from 200 to 250 K is evidence of the structural transition from a magnetically hard martensitic phase to a magnetically soft austenitic phase. At the same time, the martensitic phase at 5 K exhibits a high-saturated magnetization of $48.67 \text{ Am}^2 \text{ kg}^{-1}$ and a high anisotropy field of 1 T, and both decrease to $29.48 \text{ Am}^2 \text{ kg}^{-1}$ and 0.3 T at 300 K.

The most striking magnetic property of the $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbons is that an unusually large hysteresis is found in ribbon samples after heat treatment. Figure 4(b) shows the magnetic loops obtained at 5 K for as-spun ribbons and ribbons annealed at 500, 600 and 700°C for 1 h. For the as-spun ribbons, the coercive force (H_c) is nearly zero and the hysteresis is very small, with a magnitude of 250 Oe. The hysteresis loop is greatly improved and the H_c reaches 2070 Oe after being treated at 500°C for 1 h. The increase in H_c is accompanied by a decrease in saturation magnetization from 48.67 to 40.52 emu g^{-1} . In contrast with the above observation, H_c is nearly unchanged if we anneal the ribbon at 700°C for 1 h, remaining at about 250 Oe. But the magnetization process changes a lot with a decrease in saturation magnetization. It has been found that the shape of the hysteresis loops depends on the amount of disorder [17, 18]. For low disorder, when sweeping the field from $-\infty$ to $+\infty$, the magnetization of the system reverses sharply at a given field, while for a high amount of disorder the path is smoother and extends over a wide range of fields. As mentioned above, the as-spun ribbon has a pure β phase and the alloy is structured in an ordered bcc structure. Therefore, a rather small hysteresis is obtained. The chemical ordering will be affected by the heat treatment. A change from sharp cycles to smooth is observed

Figure 4. (a) Magnetization as a function of magnetic field measured at 5, 100, 200, 220 and 250 K with the field axis in the ribbon plane and parallel to the long axis of the ribbon. (b) Magnetic hysteresis loops of the $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbon samples measured at 5 K with the field axis in the ribbon plane and parallel to the long axis of the ribbon. (c) Temperature dependence of the spontaneous magnetization, M_s , for $5 \text{ K} < T < 300 \text{ K}$. Inset graph shows the ribbon data, M_s , for $T < 200 \text{ K}$ as a function of $T^{3/2}$. The solid line in the inset graph is a linear fit to the $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ data, demonstrating the $T^{3/2}$ dependence of the magnetization for this low temperature range.

when annealing the ribbon sample at 500°C, which is related to the increase in configurational disorder. The decrease in the saturation magnetization provides powerful evidence for this. Anyway, we can see that the phase stability is prone to influence by heat treatment, rather than being stabilized in a wide temperature range, as in FSMA Ni–Mn–Ga. The phenomenon of a sharp increase in H_c is really similar to that observed in Cu–Mn–Al [19]. A more detailed study on the hysteresis increase mechanism is in progress and will be published elsewhere.

The area of the loops gives the dissipated energy per cycle. This material could be easily converted to a rather soft and a possible permanent magnet accompanied by a structure change if we select an appropriate heat treatment condition. In addition, the Co–Ni–Al ribbons have good ductility. These peculiarities render it a good candidate for practical use.

The spontaneous magnetization, $M(T)$, as a function of temperature is shown in figure 4(c). The spontaneous magnetization decreases smoothly and monotonically as the temperature increases. The shift in the magnetization curve near the martensitic transition temperature is not distinct. At low temperatures, $T < 200$ K, the magnetization curves follow the spin-wave theory with the functional form $M(T) = M(0)(1 - AT^{3/2})$. Fitting the data to this form yields a best-fit value for $M(0) = 47.77 \text{ emu g}^{-1}$ ($1.71\mu_B$), $A = 5.59 \times 10^{-5} \text{ }^{-3/2}$ (inset to figure 4(c)); that is, the spontaneous magnetization for the martensite is 47.77 emu g^{-1} at 5 K, very close to the direct measurement value, 48.67 emu g^{-1} . The spin-wave stiffness coefficient, D , from the spin dispersion law, $\hbar\omega = Dq^2$, may be calculated from the parameter A by using the relation $A = 2.612(V/S)(k_B/4\pi D)^{3/2}$, where V is the volume per magnetic atom, S is the spin and k_B is the Boltzmann constant. A calculation for $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ gives the value $D = 74 \text{ meV } \text{\AA}^2$.

The thermoelastic martensitic transformation observed in Co–Ni–Al ribbons implies the existence of a shape memory effect. Figure 5 shows the temperature dependence of strain. The strain measurement was performed in the longitudinal

direction of the ribbons without the assistance of the bias field. During the cooling run, one can easily see that the martensitic transformation starts at about 245 K and finishes at 210 K, causing the sample to shrink about 500 ppm in the ribbon direction. During the heating run, the reverse martensitic transformation occurs at about 230 K and the deformation is completely recovered. Here, a relatively large strain up to 500 ppm has been observed in Co–Ni–Al ribbons, which is composed of many small textured polycrystalline grains. Thus, we argue that the internal stresses generated from the melt-spinning process might play an important role in orienting variants. At the same time, the thin ribbon sample would minimize the ac eddy current losses and be good for working at a high frequency, making it a candidate material for sensors.

4. Conclusion

In summary, the intermetallic compound $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ was synthesized using the melt-spinning technique, showing a thermoelastic martensitic transformation from a cubic to a tetragonal structure at 240 K during cooling, with the anisotropy field increasing from 3000 Oe at 250 K to 8000 Oe at 200 K. The magnetic coercive force can be significantly increased from 250 to 2070 Oe by annealing at 500°C for 1 h. On increasing the annealing temperature to 700°C, the coercive force rapidly decreases to 250 Oe and is restored to the initial state. The change in coercive force is attributed to a decrease in the chemical ordering. At low temperatures, the magnetization decreases with decreasing temperature and follows the $T^{3/2}$ law, which can be interpreted well by spin-wave theory. The ribbons showed a recoverable strain of 500 ppm upon the martensitic transformation.

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Figure 5. Strain as a function of temperature measured in the ribbon direction without an external stress and field for $\text{Co}_{39}\text{Ni}_{33}\text{Al}_{28}$ ribbons.

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