Investigation of magnetic phase transition and magnetocaloric effect of (Ni,Co)-Mn-Al melt-spun ribbons

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Abstract. Magnetic phase transition, magnetocaloric effect and critical parameters of Ni50-Co5Mn31-Al, (x = 5 and 10; y = 17, 18 and 19) rapidly quenched ribbons have been studied. X-ray diffraction patterns exhibit a coexistence of the L2_1 and 10M crystalline phases of the ribbons. Magnetization measurements show that all the samples behave as soft magnetic materials with a low coercive force less than 60 Oe. The shape of thermomagnetization curves considerably depends on Co and Al concentrations. The Curie temperature (Tc) of the alloy ribbons strongly increases with increasing the Co concentration and slightly decreases with increasing the Al concentration. The Ni55Co20Mn25Al10 and Ni50Co40Mn30Al15 ribbons reveal both the positive and negative magnetocaloric effects. Under magnetic field change (∆H) of 13.5 kOe, the maximum magnetic entropy change (∆Sm) of the Ni55Co20Mn25Al10 ribbon is about 2 and -1 J kg⁻¹K⁻¹ for negative and positive magnetocaloric effects, respectively. Basing on Arrott - Noakes and Kouvel - Fisher methods, critical parameters of the Ni50-Co5Mn31Al19 ribbon were determined to be Tc = 290 K, β = 0.58, γ = 0.92 and δ ≈ 2.59. The obtained values of the critical exponents indicate that the magnetic order of the alloy ribbon is close to the mean-field model.

1. Introduction

The magnetocaloric effect (MCE) is an intrinsic property of the magnetic material. Basically, magnetocaloric effect is the conversion of magnetic energy into heat energy when the material is exposed in changing magnetic field. This effect appears at all materials with different intensities and is assessed by the magnetic entropy change (∆Sm) and adiabatic temperature variation (∆Tad). MCE has been widely utilized in magnetic materials to reach low temperatures. Recently, the giant magnetocaloric effect (GMCE) at room temperature in magnetic materials to reach low temperatures. Recently, interesting properties were also observed [6 - 9]. In the Ni-Mn-Al alloys, the Neel temperature

Recently, it was reported that Co doping had a strong effect on the magnetic phase transformation of materials. Partial substitution of Co for Ni in the alloys leads to the significant increase of the magnetization change at the martensitic transformation (AM) which greatly enhanced the MCE [11-13]. The martensite-austenite temperature decreases gradually, while the Curie temperature increases greatly with increasing the Co concentration. Substitution of Co for Ni will reinforce the magnetic exchange interactions and the ferromagnetic phase of alloys [14-17]. However, the magnetic phase transitions and MCEs of the (Ni,Co)-Mn-Al bulk alloys are very sensitive to crystallize structure and it normally takes a long time (several days) to make structure stable [18-20]. Comparing the ribbon samples with bulk samples of the same composition, they have different structure and magnetic properties. Specifically, martensitic transformation temperature in Ni50-Co5Mn31-Al19, (x = 5, 10) ribbon alloys is significantly lower bulk alloys. As compared to a weakly magnetic of the Ni55Mn30Al15 ribbon, the Ni50Co5Mn31Al19, (x = 5, 10) ribbons demonstrate ferromagnetic properties. The Ni55Co5Mn31Al19 ribbon was found to exhibit a well-defined martensitic-austenitic phase transition [20-23].

In this work, we investigated magnetic, magnetocaloric and critical properties of Ni50-Co5Mn31-Al, (x = 5 and 10; y = 17, 18 and 19) rapidly quenched ribbons.

2. Experiment

Six alloy ingots with nominal compositions of Ni50-Co5Mn31-Al, (x = 5 and 10; y = 17, 18 and 19) were prepared from pure elements (99.9%) of Ni, Co, Mn and Al.
by using arc-melting method in Argon gas. Melt-spinning method was then used to fabricate the alloy ribbons with tangential velocity of copper wheel of 40 m/s. The thickness and width of the ribbons are about 20 µm and 1.5 mm, respectively. The structure of the alloys was investigated by powder X-ray diffraction (XRD) method. The magnetic properties and magnetocaloric effect of the alloys were characterized on a vibrating sample magnetometer.

### 3. Result and discussion

XRD patterns of the Ni_{50-x}Co_{x}Mn_{50-y}Al_{y} (x = 5 and 10; y = 17, 18 and 19) ribbons measured at room temperature are shown in figure 1. Structural analyses revealed that besides the main phase associated with an austenitic L2₁ structure (space group: Fm3m), some XRD peaks with low intensity corresponding to martensitic 10M (space group: Pmma) phase is also present. With high concentration of Al, the 10M phase develops strongly in the alloy ribbons. It should be noted that, a small change of structure in this kind of materials can greatly affect on magnetic properties of the ribbons as presented below.

![Fig. 1. XRD patterns of Ni_{50-x}Co_{x}Mn_{50-y}Al_{y} ribbons with x = 5 (a) and x = 10 (b).](image)

The magnetic properties of the samples were characterized by the magnetization measurements (figure 2). The results show that all the samples with Co-concentration of 10 at% behave as the soft magnetic material with a coercivity less than 2 Oe (figure 2a). The temperature dependence of magnetization, M(T), for the ribbons in the field 100 Oe are showed in figure 2(b). One can see that the shape of thermomagnetization curves considerably depend on both the concentrations of Co and Al. As for examples, the magnetization of the samples with x = 5 is increased from ~0.1 emu/g (for y = 17) to ~4.7 emu/g (for y = 19). In addition, the Ni_{45}Co_{5}Mn_{31}Al_{19} and Ni_{40}Co_{10}Mn_{33}Al_{17} ribbons reveal both the first-order (FOPT) and second-order (SOPT) magnetic phase transition. While the FOPT is strongly influenced by Al-concentration, the SOPT (FM-PM) is almost unchanged. By increasing the Co-concentration from 5 at% to 10 at%, the Curie temperature (T_C) is strongly increased from ~290 K (for x = 5 and y = 19) to ~393 K (for x = 10 and y = 19). The magnetization of the alloy ribbons is also increased considerably with the Co-concentration.

![Fig. 2. M(H) loops at room temperature (the inset enlarges the typical loops at low magnetic field) (a), M(T) curves measured in magnetic field of 100 Oe (the inset enlarges M(T) curves at low magnetization) (b) of Ni_{50-x}Co_{x}Mn_{50-y}Al_{y} (x = 5 and 10; y = 17, 18 and 19) ribbons.](image)

The different influence of Co and Al on T_c can be explained by the dependence of T_c on the exchange interaction in the materials. The ferromagnetic exchange interaction between Ni and Mn atoms in the (Ni,Co)-Mn-Al alloys essentially decides value of their T_c [24, 25]. Partial substitution of Mn by Al (paramagnetic material) hardly affects the exchange interaction of Ni and Mn atoms. But the substitution of Ni by Co (ferromagnetic material) enhances the exchange interaction of the alloy resulting in the large change of T_c. As compared to the Ni_{50}Co_{5}Mn_{50}Al_{19} bulk alloy with annealing at 1370 K for 24 h, martensite transformation temperature in ribbon is significantly higher, while Curie temperature is almost unchanged [20].

Among this series, the Ni_{45}Co_{5}Mn_{31}Al_{19} sample shows two strong magnetic phase transitions near room temperature region. Therefore, it was chosen as a representative one for analyzing magnetic properties. For further understanding the type of the phase transition and MCE of the alloy ribbons, the isothermal magnetization curves, M(H), with magnetic field up to 13.5 kOe were performed. Figure 3a shows M(H) curves at various temperatures of the Ni_{45}Co_{5}Mn_{31}Al_{19} sample.

The magnetic orders in a second-order magnetic phase transition of the material can be additionally understood by determining the critical parameters upon using Arrott plots [26]. The Arrott plots, H/M versus M² (figure 3b), were constructed from M(H) data. The M²–H/M curves are non-linear at low magnetic field and linear at high magnetic field. Values of the spontaneous magnetization (M_s) and the inverse initial susceptibility (χ_0⁻¹) at different temperatures were derived from Arrott plots.
The critical parameters of $\beta$, $\gamma$ and $\delta$ relate to the two above quantities by following equations [26, 27]:

\[ M_S(T) = M_0(-\epsilon)\beta \quad \epsilon < 0 \]  
\[ H = DM^\delta \quad \epsilon = 0 \]  
\[ \chi_0^{-1}(T) = H_0^\gamma \quad \epsilon > 0 \]  
\[ \delta = 1 + \frac{\gamma}{\beta} \quad \text{(4)} \]

where $M_0$, $H_0$ and $D$ are the critical amplitudes and $\epsilon = (T - T_C)/T_C$ is the reduced temperature.

\[ 0(\epsilon)H(M) \to \mathcal{M} \quad \text{as} \quad \epsilon \to 0 \]  
\[ \mathcal{M} = 0 \quad \text{as} \quad \epsilon > 0 \]

The linear extrapolation from high field to the intercepts with the $M$ and $H/M$ axes gives the values of $M_S(T)$ and $x_0^{-1}(T)$, respectively. The critical parameter $T_C$, $\beta$ and $\gamma$ obtained from fitting $M_S(T)$ and $x_0^{-1}(T)$ data (figure 4a) by using the according formulas (1) and (3), while $\delta$ was calculated by using the Widom scaling relation, equation (4) [27, 28]. As resulted, the $Ni_{5}Co_{5}Mn_{31}Al_{19}$ ribbon possesses $T_C \approx 290$ K, $\beta \approx 0.59$, $\gamma \approx 0.92$ and $\delta \approx 2.56$. The critical parameters are quite close to mean-field theory ($\beta = 0.5$, $\gamma = 1$ and $\delta = 3$) [28].

Alternatively, the critical parameters can be obtained more accurately by the Kouvel - Fisher method [29]. Similarity with Arrott - Noakes method, $M_S(T)$ and $x_0^{-1}(T)$ are determined by plotting $M^\beta$ versus $(H/M)^\gamma$ curves. The critical parameters of $\beta$ and $\gamma$ relate to the two above quantities by these equations:

\[ M_S(T) \left[ dm_S/d[T] \right] = (T - T_C)/\beta \quad \text{(5)} \]
\[ x_0^{-1}(T) \left[ dx_0^{-1}(T)/dT \right] = (T - T_C)/\gamma \quad \text{(6)} \]

Assessing the reliability of the critical parameters can be carried out by using the static-scaling theory [28, 30]. The isothermal magnetization is determined by the formula:

\[ M(H, \epsilon) = \epsilon^\beta f_+ (H|x|^{-\beta \gamma}) \quad \text{(7)} \]

Where $f_+$ and $f_-$ are regular functions for temperatures $T > T_C$ and $T < T_C$, respectively.

Figure 5 shows the static-scaling plots of $M|x|^{-\beta}$ versus $H|x|^{-\beta \gamma}$ in the log scale with the obtained critical parameters. We can see that points of the data fall on two universal branches with $T > T_C$ and $T < T_C$. Consequently, the critical values in our study are reliable results.

Magnetocaloric effect in the alloys was assessed by the magnetic entropy change ($\Delta S_m$). This value was calculated basing on the isothermal magnetizations (figure 3a). Fig 6 shows $\Delta S_m(T)$ curves of the $Ni_{5}Co_{5}Mn_{31}Al_{19}$ ribbon under several magnetic field change ($\Delta H = 2, 6, 10$ and $13.5$ kOe). With $\Delta H = 13.5$ kOe, the maximum magnetic entropy change are about 2.59 kJ/kgK.
and \(-1\) J kg\(^{-1}\) K\(^{-1}\) for negative and positive magnetocaloric effects, respectively. These results are similar to reports by Y. Kim et al [18, 19]. In addition, the \(\Delta S_m/\Delta m\) value increases with increasing the magnetic field (the above inset of figure 6).

The temperature dependence of \(\Delta S_m\) under different applied field for the second-order phase transition of materials can be described by the universal master curves [31, 32]. Basing on the \(\Delta S_m(T)\) curve, the \(\Delta S_m/\Delta S_{m\max}\) versus \(T\) plots are constructed. White \(\theta\) value is determined by the formula:

\[
\theta = \left\{ \begin{aligned}
& (T - T_{r1}) / (T_{r1} - T_{r2}), \quad T \leq T_{r1} \\
& (T - T_{r2}) / (T_{r2} - T_{r1}), \quad T > T_{r1}
\end{aligned} \right.
\]

(8)

Where \(T_{r1}\) and \(T_{r2}\) are the temperature of the two reference points. For the present study, they are selected as those corresponding to \(\Delta S_m(T_{r1,2}) = k \Delta S_{m\max}\) (\(k = 0.5\)). This choice of \(k\) does not affect the actual construction of the universal curve, as it implies only proportionality constant. The below inset of figure 6 shows the universal master curve of the Ni\(_{50}\)Co\(_{20}\)Mn\(_{20}\)Al\(_{10}\) ribbons. All \(\Delta S_m(T)\) data under different applied fields are collapsed into a universal master curve. This is an interesting property of the second-order phase transition of materials.

4. Conclusion

Structure of the Ni\(_{50-y}\)Co\(_{20}\)Mn\(_{20}\)Al\(_y\) (\(y = 5\) and 10; \(y = 17\), 18 and 19) ribbons exhibits multi-crystalline phases of the L2\(_1\) and 10\(M\) types. All the alloy ribbons behave as the soft magnetic materials and their Curie temperature strongly increases with increasing the Co-concentration and hardly changes with increasing the Al-concentration. The maximum magnetic entropy change with variation of magnetic field of 13.5 kOe for the Ni\(_{50}\)Co\(_{20}\)Mn\(_{20}\)Al\(_{10}\) ribbon is about 2 and \(-1\) J kg\(^{-1}\) K\(^{-1}\) for negative and positive magnetocaloric effects, respectively. Critical parameters of the alloy are close to those of the mean-field model for long-range ferromagnetic orders.

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