Magnetostructural transition in NiCuCoMnGa alloys*

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The effects of the addition of Co on the martensitic transformation and Curie transition temperatures of polycrystalline $Ni_{46-x}Cu_4Co_xMn_{33.5}Ga_{16.5}$ ($x = 0$, 1, 3, 5) alloys are investigated. An abrupt decrease in the martensitic transformation temperature and an obvious increase in the Curie transition temperature of austenite (T_C^A) are observed when Co is doped in the NiCuMnGa alloy. As a result, the composition range for obtaining the magnetostructural transition is extended. Furthermore, the effect of a strong magnetic field on the magnetostructural transition is analyzed. This study offers a possible method to extend the composition range for obtaining magnetostructural transition in Heusler alloys.

Keywords: magnetostructural transition, Heusler alloys, NiCuCoMnGa

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1. Introduction

The phenomenon of magnetostructural coupling has been in the spotlight since many magnetoresponsive effects were reported in the so-called "magnetostructural alloys", such as NiMnIn, NiMnSn, NiMnSb, and NiCoMnGa. These magnetoresponsive effects, including magnetocaloric, magnetoresistance, and magnetostrain effects,[1–5] make the magnetostructural alloys promising candidates for future magnetic refrigerants, recording materials, and actuators, respectively.[6–10] In general, magnetostructural coupling is a phenomenon where the structural transformation is accompanied by magnetic transition, which is a first-order magnetic transition. Large magnetization variation across the phase transformation, different lattice entropies, various types of electron transfers, and changes in the crystal structures between the two different phases, serve as the preconditions of the magnetoresponsive effects.[11,12]

Up to now, there have been many reports on magnetostructural coupling phenomena at room temperature, including those in NiMnX (X = In, Sn, Sb) alloys.[2,11,13] However, the composition window of magnetostructural coupling is limited to less than one atom percentage in these alloys, which is an obstacle to the applications of the magnetostructural alloys. In our attempt to identify promising magnetoresponsive materials suitable for engineering, we study the magnetostructural transition of the quinary alloy: NiCuCoMnGa. We find that doping Co in the NiCuMnGa alloy is an efficient way to expand the composition range of the magnetostructural transition. Our results indicate that NiCuCoMnGa is a promising alloy system in the application of multifunction materials.

2. Experiment

The polycrystalline samples of $Ni_{46-x}Cu_4Co_xMn_{33.5}Ga_{16.5}$ ($x = 0$, 1, 3, 5) were prepared by arc melting. The ingots were homogenized at 1173 K for 48 h and then quenched into water. The differential scanning calorimetry (DSC) Netzsch STA 449 was used to measure the latent heat upon martensitic transformation at heating and cooling rates of 5 K/min. The DSC measures the temperatures and heat flows associated with the transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about the physical and chemical changes that involve endothermic or exothermic processes, or the changes in heat capacity. The magnetization measurements were performed on a physical properties measurement system (PPMS) (Quantum Design) at heating and cooling rates of 10 K/min. The PPMS measures the DC resistivity, AC transport (AC resistivity, Hall coefficient, I–V curve, and critical current for superconductors), and the heat capacity for small samples under user-controlled magnetic field, pressure, gas composition, and temperature. The magnetic field may be programmed anywhere from 0 to +/– 7×10^4 Oe (1 Oe = 79.5775 A·m^{-1}) and the sample temperature can be programmed from 1.9 K to 400 K.

3. Results and discussion

Figure 1 shows the thermo-magnetization curves of $Ni_{46-x}Cu_4Co_xMn_{33.5}Ga_{16.5}$ ($x = 0$, 1, 3, 5) alloys measured at a magnetic field of 300 Oe. The samples were first cooled from 400 K to 200 K, and then heated. The values of the martensitic

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start temperature (M_s), martensitic finish temperature (M_f), austenite start temperature (A_s), austenite finish temperature (A_f), Curie temperature of austenite (T_C^A), and Curie temperature of martensite (T_C^M), are shown in Table 1. The large transformation hysteresis might be due to the fast heating/cooling speed of 10 K/min.

Table 1. Values of martensitic start temperature (M_s), martensitic finish temperature (M_f), austenite start temperature (A_s), austenite finish temperature (A_f), Curie temperature of austenite (T_C^A), Curie temperature of martensite (T_C^M), magnetization change (ΔM), and entropy change (ΔS) across the martensitic transformation, the effect of the magnetic field on the martensitic transformation temperatures (dT/dH), and the valence electron concentration (e/a) for various NiCuCoMnGa alloys.

Composition	M_s/K	M_f/K	A_s/K	A_f/K	T_C^A/K	T_C^M/K	ΔM/emu·g^{-1}	ΔS/J·kg^{-1}·K^{-1}	(dT/dH)/K·T^{-1}	e/a
$Ni_{46}Cu_4Mn_{33.5}Ga_{16.5}$	349	342	362	369	359	285	...	33.8	...	7.88
$Ni_{45}Cu_4Co_1Mn_{33.5}Ga_{16.5}$	339	332	352	359	364	294	20	27.8	0.8	7.87
$Ni_{43}Cu_4Co_3Mn_{33.5}Ga_{16.5}$	309	302	322	330	369	283	28	26.3	1.1	7.85
$Ni_{41}Cu_4Co_5Mn_{33.5}Ga_{16.5}$	256	251	270	275	389	...	15	...	1.6	7.83

As for the $x = 0$ sample, upon heating, the sample first goes through a "ferromagnetic martensite (FM)–paramagnetic martensite (PM)" transition and then undergoes an incomplete "paramagnetic martensite (PM)–ferromagnetic austenite (FA)" transition, and subsequently a "ferromagnetic austenite (FA)–paramagnetic austenite (PA)" transition. Both the martensitic transformation and the reverse martensitic transformation are partial, and result in the large peak at 350 K on cooling and the small peak at 370 K on heating. When substituting 1 at% Co for Ni, M_s decreases while T_C^A and T_C^M increase. In this way, substituting Ni by Co stabilizes the ferromagnetic austenite phase. Therefore, the M–T curve of $x = 1$ shows a more clear transition sequence of "FM–PM–FA–PA" on heating and is reversible on cooling. Furthermore, when increasing x to 3, M_s decreases, T_C^A increases, whereas T_C^M decreases. It is also seen from the M–T curve of $x = 3$ that the "FM–PM" transition for this sample is not complete. This sample also shows the magnetostructural transition "PM–FA" on heating. When x reaches 5, no "FM–PM" transition is observed. The curve shows an "FM–FA–PA" transition on heating, and no magnetostructural transition is found.

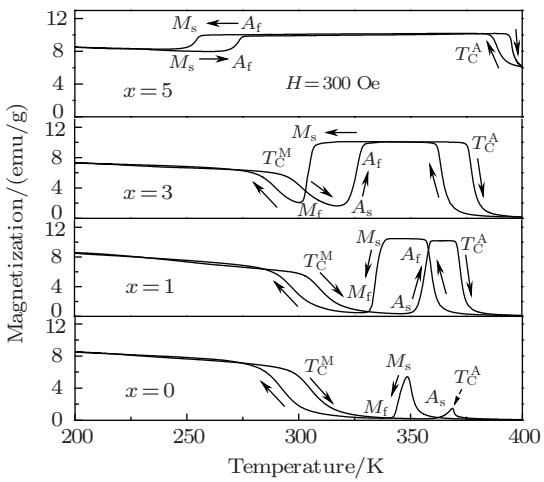


Fig. 1. The thermo-magnetization curves for the alloys $Ni_{46-x}Cu_4Co_xMn_{33.5}Ga_{16.5}$ ($x = 0$, 1, 3, 5), showing the magnetostructural transitions at 300 Oe.

In conclusion, when Co is substituting Ni, M_s decreases heavily, T_C^A slightly increases, and there is no obvious variation in T_C^M. That is, Co can enhance the magnetization of austenite and reduce the martensitic transformation temperature, while having little influence on the magnetization of martensite.

To identify the first-order nature of the structural transition, DSC measurement is usually taken to measure the latent heat upon transformation. Each of the DSC curves shows an apparent endothermic peak on heating and an exothermic peak on cooling; the relevant curves are not shown here. The entropy change across the structural transformation is calculated from the DSC curve according to the following formula:

$$\Delta S = \frac{\Delta H}{T_0}, \tag{1}$$

where ΔH is the latent heat upon transformation, and $T_0 = (M_s + A_f)/2$ is the temperature at which the parent and martensite phases are in equilibrium by the Gibbs energy. The value of ΔS is shown in Table 1. ΔS decreases when Co is substituted for Ni.

Figure 2 shows the trends in variation of T_M, T_C^A, T_C^M with different Co concentrations. T_M is usually calculated as $(M_s + A_s)/2$. T_M decreases significantly by 18.5 K/at%, T_C^A increases by 5.7 K/at%, while T_C^M slightly decreases by 1.4 K/at%. It has been reported in FSMAs that the characteristic temperatures of the martensitic transformation increase with increasing valence electron concentration (e/a).[14,15] In the present alloy, the decrease in M_s may be due to the reduced valence electron concentration (e/a) when Co ($3d^74s^2$) is substituted for Ni ($3d^84s^2$), as shown in Table 1. It has also been suggested that the Co substitution is conducive to the aligning of Mn moments in ferromagnetic ordering, thereby increasing the magnetism in the austenitic phase and also increasing the value of T_C^A,[16,17] which is verified by the present observation. The compositions in the shadow area exhibit a magnetostructural transition sequence of "FM–PM–FA–PA" on heating and the reverse on cooling. The magnetostructural transitions from PM to FA exist in a Co content range from about 0 to 4.3 at% in the $Ni_{46-x}Cu_4Co_xMn_{33.5}Ga_{16.5}$ ($x = 0$, 1, 3,

5) alloys. This composition range is larger than that reported previously,[18] which suggests that doping Co is an effective way to broaden the composition range for obtaining the magnetostructural transition from PM to FA. This observation indicates that NiCuCoMnGa is a promising alloy system to perform magnetostructural transition in engineering.

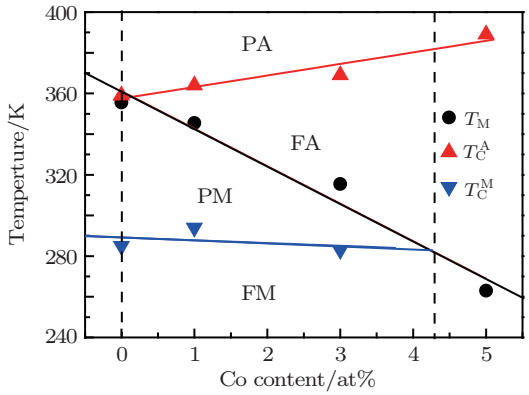


Fig. 2. (color online) The transition sequences depending on the Co content in the NiCuCoMnGa alloys. Here, FM, PM, FA, and PA denote ferromagnetic martensite, paramagnetic martensite, ferromagnetic austenite, and paramagnetic austenite, respectively.

To investigate the magnetostructural transition in a strong magnetic field, a magnetic field of 9×10^4 Oe is used when measuring the thermo-magnetization curves as shown in Fig. 3. For comparison, the thermo-magnetization curves in 300 Oe are also shown. As seen in this figure, the martensitic transformation temperatures decrease when the applied magnetic field strength increases from 300 Oe to 9×10^4 Oe. The dashed line denotes the change in extent. The effects of the magnetic field on the transformation temperature ($\mathrm{d}T/\mathrm{d}H$) for various NiCuCoMnGa alloys are shown in Table 1. The value of $\mathrm{d}T/\mathrm{d}H$ increases when x rises. This indicates that the addition of Co can enhance the magnetic field effect on the transformation temperature. This phenomenon can be illustrated by the Clausius–Clapeyron equation:[5]

$$\frac{\mathrm{d}T}{\mathrm{d}H} = \frac{\Delta M}{\Delta S}. \tag{2}$$

As shown in Table 1, doping Co increases the magnetization change (ΔM) and reduces the entropy change (ΔS) across the martensitic transformation. Thus, $\Delta M/\Delta S$, or $\mathrm{d}T/\mathrm{d}H$ increases as the Co content rises.

On the other hand, the magnetization change (ΔM) across the martensitic transformation increases from 20 emu/g for $x = 1$ to 28 emu/g for $x = 3$, whereas it decreases to 15 emu/g for $x = 5$. This decrease may be due to the absence of T_C^M, as mentioned above. This is because the martensitic temperature is lower than T_C^M, and therefore, the sample does not transform to paramagnetic martensite before the austenite transformation. The transformation here is the conversion from ferromagnetic martensite into ferromagnetic austenite.

Furthermore, the significant increases of the saturation magnetizations for martensite and the austenite phase in 9×10^4 Oe from $x = 1$ to $x = 5$ indicate that doping Co is a very effective method to enhance magnetization.

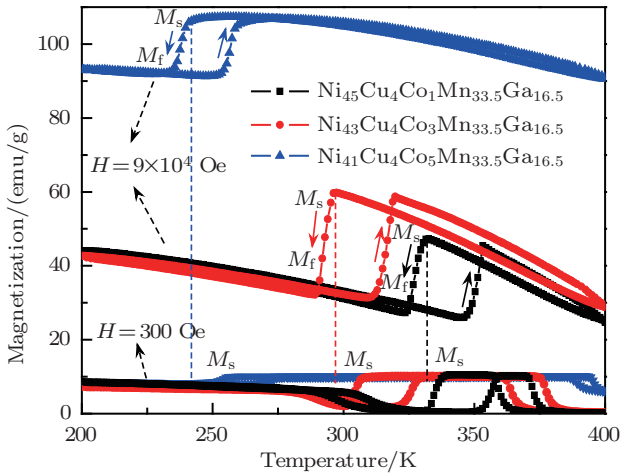


Fig. 3. (color online) Comparisons of the thermo-magnetization curves of $Ni_{46-x}Cu_4Co_xMn_{33.5}Ga_{16.5}$ ($x = 1$, 3, 5) alloys at magnetic fields of 300 Oe and 9×10^4 Oe.

For the austenite and martensite phase, the magnetization under 9×10^4 Oe for $x = 5$ is much higher than for $x = 1$ and $x = 3$. This means that the effect of doping Co on the increase in magnetization is not linear. In particular for $Ni_{41}Cu_4Co_5Mn_{33.5}Ga_{16.5}$, due to the substitution of Co for Ni, the ferromagnetic parent phase shows a saturation magnetization higher than 100 emu/g, which is much higher than the value reported previously for NiMnGaCu.[18–20] The enhanced magnetization of Co substitution for Ni in NiCuMnGa can be analyzed from the following aspects. First, each Co atom at the site of Ni contributes a magnetic moment of $\sim 1.0\ \mu_B$, whereas the Ni atoms each have a magnetic moment of less than $0.31\ \mu_B$, based on *ab initio* calculation and magnetization measurement at nearly 0 K.[21] On the other hand, as reported by Feng *et al.*[22] and Tan *et al.*,[23] the Co–Mn ferromagnetic exchange interaction may exist in this NiCuCoMnGa alloy. As reported in Ref. [22], the Co–Mn ferromagnetic exchange interaction is a short-range effect that is more effective at a short distance. In other words, the Co–Mn interaction is not linear to Co content, and therefore the magnetization values of $x = 1$, 3, 5 are not linear to the Co content.

4. Conclusions

Doping Co is an effective way to broaden the composition range in which the PM phase transforms to the FA phase. With the increase in Co concentration, the martensitic temperature decreases rapidly, T_C^A increases linearly and the magnetization increases heavily.

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