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Magnetic entropy and magnetocaloric effect of ferromagnetic Heusler alloys $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2MnGa_{0.88}Cu_{0.12}$

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ABSTRACT

The magneto-structural transformation and the associated magnetic entropy change were studied in the ferromagnetic shape memory alloys $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2MnGa_{0.88}Cu_{0.12}$ by using magnetization measurements performed around the martensite transformation temperature T_M and the Curie temperature T_C. The direct transition from the paramagnetic austenite phase (PM phase) to the ferromagnetic martensite phase (FM phase) was observed in both alloys. In a magnetic field of 2.0 T, the $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2MnGa_{0.88}Cu_{0.12}$ alloys showed large magnetic entropy changes of $-\Delta S_M = 15.2$ J/kg K at 302 K and -7.5 J/kg K at 333 K, respectively. The magnetic entropy change of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ is larger than that of the polycrystalline $Ni_{2.19}Mn_{0.81}Ga$ alloy. Theoretical calculations were also performed, and they agreed well with the experimental determinations of $-\Delta S_M$.

1. Introduction

1.1. Structural and magnetic properties of Ni–Mn–Ga Heusler alloys

Recently, ferromagnetic shape memory alloys (FSMAs) have been studied by many researchers as potential candidates for smart materials. Ni_2MnGa is the most familiar alloy [1]. It has a cubic $L2_1$ Heusler structure (space group) $Fm\bar{3}m$ with lattice parameter $a = 5.825$ Å at room temperature, and orders ferromagnetically at the Curie temperature $T_C \approx 365$ K [2,3]. Upon cooling from room temperature, martensitic transformation occurs at the martensitic transformation temperature $T_M \approx 200$ K. Below T_M, a superstructure forms because of lattice modulation. For Heusler Ni–Mn–Ga alloys, T_M varies from 200 to 330 K as the concentrations of composite elements change non stoichiometrically.

1.2. Magnetic properties of $Ni_{50+x}Mn_{12.5}Fe_{12.5}Ga_{25-x}$ alloys

Kikuchi et al. reported the magnetic properties of $Ni_{50+x}Mn_{12.5}Fe_{12.5}Ga_{25-x}$ ($0 \leqslant x \geqslant 5.5$) ferromagnetic alloys, which were produced by replacing with Ni in the $Ni_{50}Mn_{12.5}Fe_{12.5}Ga_{25}$ alloy [4]. Measurements of the temperature dependence of the magnetization for this alloy series were performed. It was observed that T_C gradually decreases with concentration x, while T_M and the reverse martensitic transformation temperature T_R increases with x and exhibit saturation behavior for $x \geqslant 3.0$. Kataoka et al. reported the magnetic properties of $Ni_2Mn_{1-x}Cu_xGa$ ($0 \leqslant x \leqslant 0.40$) alloys, which were obtained by replacing Mn with Cu in the Ni_2MnGa alloy [5]. Samples with $0.23 \leqslant x \leqslant 0.30$ show the martensite transition at approximately 300 K. The magnetic and crystal states above and below T_M are the paramagnetic austenite (Para-A) phase and the ferromagnetic martensite (Ferro-M) phase, respectively. Such Heusler alloys show the martensitic transformation above room temperature. Therefore, they are candidates for smart materials. The thermal strain and magnetization measurements of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ were performed [6]. These measurements were performed after zero-field cooling at 323 K in the austenite phase. The linear strain $\Delta\varepsilon$ at T_M was -3.0×10^{-3} (-0.30%). The minus sign ($-$) indicates that shrinking occurred at the martensite transition temperature when cooling from the austenite phase. Below T_M, the magnetization exhibits ferromagnetic properties, whereas above T_M it exhibits paramagnetic properties. This is consistent with the permeability result in Ref. [6]. The Arrott plots of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ indicate that the spontaneous magnetization at 300 K in the Ferro-M state is 42.4 J/$\mu_0$kg T. The obtained T_C of the martensite phase is 307 K, which is almost the same as $T_M = 308$ K; this is consistent with the x–T phase diagram of

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$Ni_2Mn_{1-x}Cu_xGa$ obtained from experimental and theoretical calculations [5].

1.3. Magnetic properties of $Ni_2MnGa_{1-x}Cu_x$ alloys

Endo et al. prepared $Ni_2MnGa_{1-x}Cu_x$ ($0 \leqslant x \leqslant 0.35$) alloys [7]. The T_M increases with increasing Cu content x. On the contrary, The Curie temperature T_C decreases with increasing x. For $0.10 < x < 0.15$, the T_M and T_C are almost the same. The thermal strain and magnetization measurements of $Ni_2MnGa_{0.88}Cu_{0.12}$were performed [8]. The linear strain $\Delta\varepsilon$ at T_M was -1.3×10^{-3} (-0.13%) for $Ni_2MnGa_{0.88}Cu_{0.12}$. The *M*–*B* curves show ferromagnetic behavior below 333 K. A prominent decrease in the magnetization occurs between 333 and 336 K. The temperature dependence of the magnetization *M*–*T* at 0.5 and 1 T, which was obtained by magnetization measurements in a pulsed magnetic field, suddenly decreases between 333 and 336 K for each field This temperature region corresponds to a sharp increase in the permeability when heating from a low temperature, and is just below T_M, which was obtained from the linear expansion measurement in Ref. [8]. The *M*–*T* curve shows a shallow depression between 310 and 330 K, which corresponds to a dip in the permeability and the linear expansion results. The Arrott plots of $Ni_2MnGa_{0.88}Cu_{0.12}$ indicate that the spontaneous magnetization at 289 K in the Ferro-M state is 47.1 J/$\mu_0$kg T. The T_C of the martensite phase obtained from the Arrott plots is 340 K, which is almost the same as T_M = 337 K. This is consistent with the *x*–*T* phase diagram of $Ni_2MnGa_{1-x}Cu_x$ shown in Ref. [7].

1.4. Magnetocaloric effect

Buchelnikov studied the magnetocaloric effect (MCE) in a polycrystalline $Ni_{2.19}Mn_{0.81}Ga$ sample, which shows the martensite and ferromagnetic transitions at the same temperature, $T_M = T_C$ = 340 K, and the magnetic entropy change is 11 J/kg K in a magnetic field of 2.6 T [9]. For Ni_2MnGa type alloys, a temperature change due to the MCE is expected.

The purpose of this study is to investigate the magneto-structural transformation and the associated magnetic entropy change caused by the martensitic transformation. Two Heusler alloys were selected in which the martensitic transition occur at the Curie temperature of the martensite phase T_C. The chosen alloys were $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2MnGa_{0.88}Cu_{0.12}$, which show a transition from the Para-A phase to the Ferro-M phase at T_M = 308 and 337 K, respectively [5,7]. The structural and magnetic properties of these alloys were shown above. Results from the magnetic measurements of these alloys were used to calculate the magnetic entropy change, and a thorough investigation of the correlations among the magnetic transition, martensite transformation, and magnetocaloric effect was performed. We also compared the MCE effects with $LaFe_{13}$-type alloys, which show large MCE effects [10–19].

2. Experimental

The $Ni_2Mn_{0.75}Cu_{0.25}Ga$, and $Ni_2MnGa_{0.88}Cu_{0.12}$ alloys were prepared by the arc melting of 99.9% pure Ni, Mn, and Cu, 99.95% pure Fe, and 99.9999% pure Ga in an argon atmosphere. To obtain homogenized samples, the reaction products were sealed in double-evacuated silica tubes, which were annealed at 1123 K for 3 days, and then quenched in cold water. The samples obtained for these three alloys were polycrystalline.

Magnetization measurements were performed using a Bitter-type water-cooled pulsed magnet at Akita University after zero-field cooling from the austenite phase. The *M*–*B* curves are shown for increasing field processes in a pulsed magnetic field.

3. Results and discussion

The magnetic entropy change ΔS_M is an important parameter in quantifying the MCE in such a specific class of materials that have simultaneously occurring magneto-structural phase transitions. Note that in the $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2MnGa_{0.88}Cu_{0.12}$ alloys, the isothermal magnetization, which was mentioned in Sections 1.2 and 1.3, decreases as the temperature increases, and it discontinuously decreases near the transition temperature. The discontinuous change in the magnetization occurs around 305 and 334 K in $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2MnGa_{0.88}Cu_{0.12}$, respectively.

Results of the isothermal magnetization measurements were used to estimate the ΔS_M values. The ΔS_M values were estimated from the isothermal magnetization results using the Maxwell relation:

$$\Delta S_M(T,H) = \int_{H_1}^{H_2} \left(\frac{\partial M(H,T)}{\partial T} \right)_H dH, \quad (1)$$

where M is the magnetization at field $H = B/\mu_0$ and temperature T, H_1 and H_2 indicate the initial and final magnetic fields, respectively.

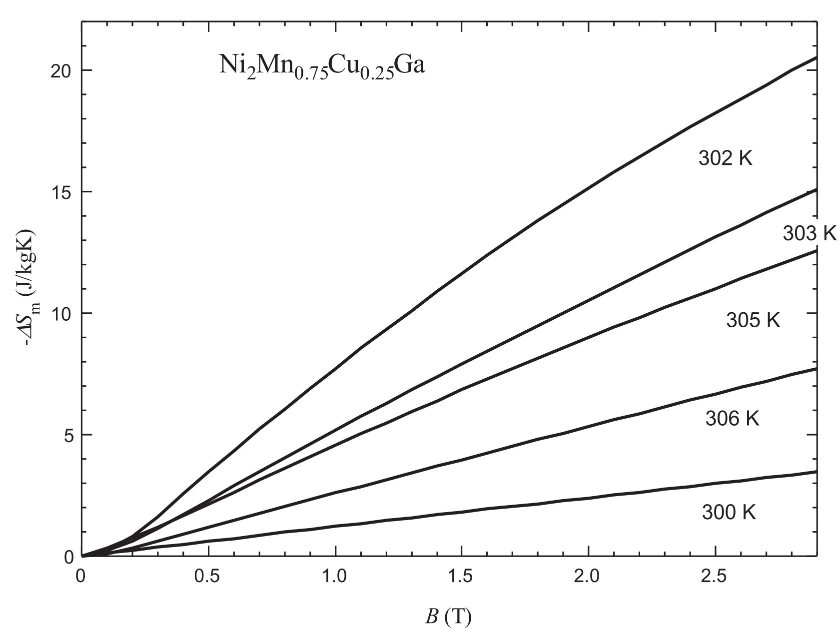

Fig. 1. Magnetic entropy change of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ in an isothermal process.