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Effect of Co addition on the martensitic transformation and magnetocaloric effect of Ni–Mn–Al ferromagnetic shape memory alloys

H.C. Xuan [a,*], F.H. Chen [b], P.D. Han [a], D.H. Wang [c], Y.W. Du [c]

[a] College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China
[b] Department of Physics, Taiyuan University of Science and Technology, Taiyuan 030024, People's Republic of China
[c] National Laboratory of Solid State Microstructures and Key Laboratory of Nanomaterials for Jiang Su Province, Nanjing University, Nanjing 210093, People's Republic of China

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ABSTRACT

A series of $Ni_{50-x}Co_xMn_{32}Al_{18}$ (x = 3, 4, 5, 6, 7, and 8) alloys were prepared by the arc melting method. The martensitic transformation (MT) shifts to a lower temperature with increasing Co concentration and can be tuned to occur from a ferromagnetic austenite to a weak-magnetic martensite in the range of $6 \le x \le 8$. The field-induced metamagnetic behavior was realized in $Ni_{42}Co_8Mn_{32}Al_{18}$ sample in which a large magnetic entropy change of 7.7 J/kg K and an effective refrigerant capacity value of 112 J/kg were obtained under the field of 60 kOe. The large magnetocaloric effect and adjustable MT temperature suggest that Ni–Co–Mn–Al alloys should have promising potential as magnetic refrigerants.

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) are interesting materials showing shape memory effect and magnetism simultaneously, owing to the strong coupling between the crystal structure and magnetism [1]. The magnetic shape memory effect in these alloys arises from a magnetic-field-induced reorientation of twin-related martensitic variants and can be induced by temperature, stress, or magnetic field. Recently, some FSMAs have drawn more and more attention, such as Ni–Mn–X (X = Ga, In, Sn, Sb) [1–3], Ni–Mn–Al [4,5], Ni–Co–Al [6], and Ni–Fe–Ga [7], due to their several interesting physical properties and promising applications. With the decreasing temperature, these alloys undergo a first-order martensitic transformation (MT) from a high symmetry phase (austenite) to a low symmetry phase (martensite) along with the change of magnetization. Since the austenite and martensite have different crystal structures and magnetizations, large magnetocaloric effects (MCE) [8,9], magnetoresistance (MR) [10,11], and magnetic-field-induced strain [3] can be observed in some FSMAs. These multifunctional properties are related to the field-induced MT associated with the drastic change in the magnetization between the austenite phase and the martensite phase, i.e., metamagnetic transformation. The magnetic driving force for such metamagnetic phase transformation is provided by the Zeeman energy $E_{Zeeman} = \mu_0 \Delta M H$, where ΔM is the saturation magnetization difference between the austenite and martensite and H corresponds to the strength of the applied field. Therefore, the magnitude change of ΔM is of great importance for the use of the magnetic-field-induced MT. Up to now, the exploration for more FSMAs possessing a large value of ΔM around the MT is still in rapid progress.

Compared with Ni–Mn–X (X = Ga, In, Sn, Sb) FSMAs, Ni–Mn–Al system has not received much attention up to now. Stoichiometric Ni_2MnAl is structurally stable down to the lowest temperatures, but MT occurs within a certain range of compositions close to stoichiometric compounds [12]. Previous studies have revealed that Ni–Mn–Al system consists of a mixed $B2 + L2_1$ phase, which includes ferromagnetic and antiferromagnetic parts [12–14]. The magnetic ordering in the metastable $B2$ phase is conical antiferromagnetic, while the $L2_1$ phase is in a ferromagnetic ordering [12,13]. Therefore, MT in off-stoichiometric Ni–Mn–Al alloys always occurs from the paramagnetic or mixed ferromagnetic–antiferromagnetic state to the weak-magnetic state. Correspondingly, the magnitude change of ΔM was restricted to a small value, which significantly hinders their practical applications as magnetic functional materials. Moreover, a complete reversible metamagnetic

* Corresponding author. Tel./fax: +86 351 6018843.
E-mail address: xuanhaicheng@tyut.edu.cn (H.C. Xuan).

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transformation is yet to be achieved in undoped Ni–Mn–Al alloys due to the low ΔM. Recently, Co doping has been reported to have prominent effect on increasing ΔM in Ni–Mn–X (X = In, Sn, Sb) FSMAs due to its effect on promoting ferromagnetic alignment of the moments of the nearest neighboring Mn atoms [15–17]. Yu et al. reported that the partial substitution of Co for Ni turns the antiferromagnetically aligned Mn moments in the $Ni_{50}Mn_{39}Sb_{11}$ alloy into a ferromagnetic order, and the magnetization at room temperature is significantly enhanced for $Ni_{41}Co_9Mn_{39}Sb_{11}$ alloy, leading to the magnetic field-induced MT [17]. In addition, a magnetic field-induced shape recovery through reverse MT in $Ni_{42}Co_8Mn_{39}Sn_{11}$ polycrystalline alloy and $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ single crystalline alloy was observed at room temperature [3,15,16]. In the case of Ni–Mn–Al FSMAs, the magnetic and thermal properties have been disclosed in detail in earlier studies [18–20]. However, research on the field-induced MT and related physical properties in the Ni–Mn–Al alloys is still in its early stages [12–14]. In this work, we report the magnetic field-induced MT in $Ni_{50-x}Co_xMn_{32}Al_{18}$ (x = 3, 4, 5, 6, 7, and 8) alloys by substituting a small amount of Co for Ni. The magnetization of the parent phase is effectively enhanced and a large ΔM is obtained, which endows the system with a metamagnetic behavior. The magnetic phase diagram was established and a large inverse MCE around MT in Ni–Co–Mn–Al alloys was obtained.

2. Experimental procedures

Polycrystalline $Ni_{50-x}Co_xMn_{32}Al_{18}$ (x = 3, 4, 5, 6, 7, and 8) alloys were prepared by arc-melting the appropriate amounts of high-purity Ni, Co, Mn, and Al in the argon atmosphere. These samples were remelted three times to ensure composition homogeneity. After that, the samples were sealed in evacuated quartz tubes and annealed at 1373 K for 72 h followed by quenched into ice water. X-ray diffraction (XRD) experiments using Cu $K\alpha$ radiation were conducted at room temperature. The magnetization was measured by a superconducting quantum interference device (SQUID, Quantum Design) at heating and cooling rates of 2 K/min in the magnetic field range of 0–60 kOe.

3. Results and discussion

The temperature dependence of magnetization (M–T) in a magnetic field of 1 kOe is measured to characterize the magnetic transition in $Ni_{50-x}Co_xMn_{32}Al_{18}$ alloys. Fig. 1 shows the M–T curves for $Ni_{50-x}Co_xMn_{32}Al_{18}$ (x = 3, 4, 5, 6, 7, and 8) alloys in a magnetic field of 1 kOe on heating and cooling. All these alloys show similar thermo-magnetic behaviors. With decreasing temperature, a sharp increase of magnetization is observed, corresponding to a paramagnetic–ferromagnetic transition at the Curie temperature of austenite. Further decreasing temperature causes a sudden drop of magnetization, which corresponds to the MT. Upon heating, the reverse MT from martensite to austenite has been confirmed according to the jump of magnetization. Between the cooling and the heating processes, there is an obvious thermal hysteresis around the MT temperatures, which is a signature of the first-order transition. As shown in Fig. 1, the character temperatures of MT are martensitic start temperature (M_s), martensitic finish temperature (M_f), austenitic start temperature (A_s), austenitic finish temperature (A_f), Curie temperature of martensitic phase (T_C^M), and of austenitic phase (T_C^A). Obviously, the content of Co has the significant

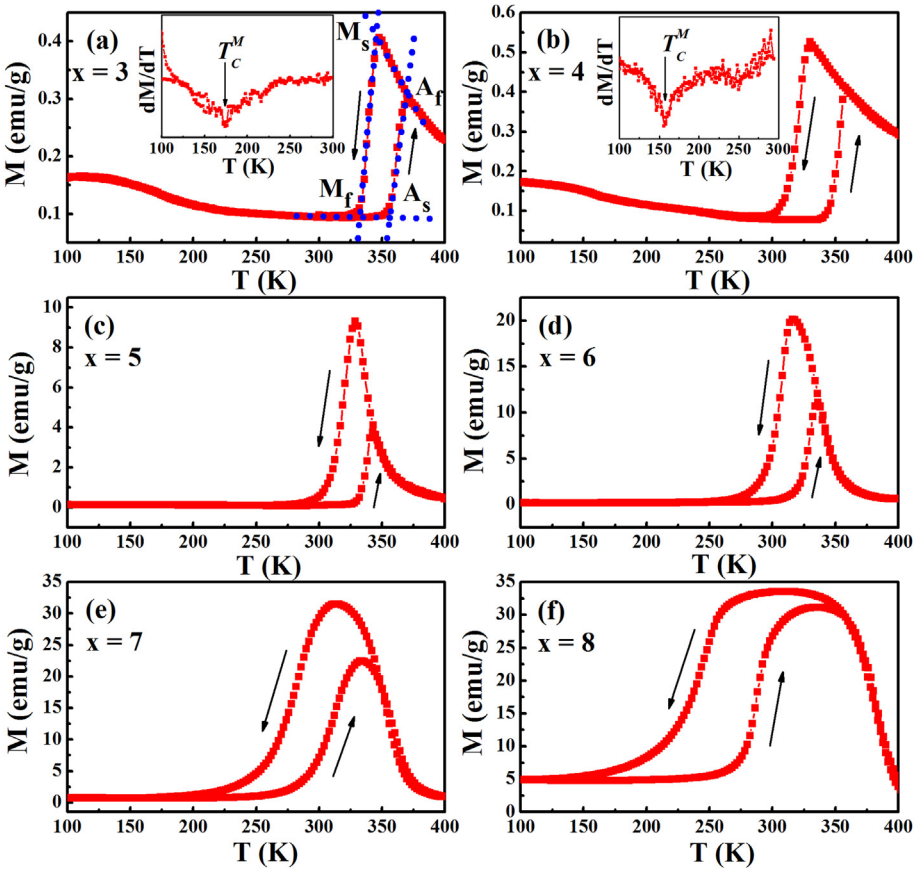

Fig. 1. Temperature dependence of magnetization under a magnetic field of 1 kOe on heating and cooling for $Ni_{50-x}Co_xMn_{32}Al_{18}$ alloys with (a) x = 3, Inset: partially enlarged dM/dT versus T curve; (b) x = 4, Inset: partially enlarged dM/dT versus T curve; (c) x = 5; (d) x = 6; (e) x = 7; (f) x = 8.