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Influence of atomic ordering on elastocaloric and magnetocaloric effects of a Ni–Cu–Mn–Ga ferromagnetic shape memory alloy

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ABSTRACT

The coexisting elastocaloric and magnetocaloric effects in ferromagnetic shape memory alloys have attracted much attention for the potential application in solid state refrigeration. Previous studies show that the $L2_1$ atomic ordering of Heusler ferromagnetic shape memory alloys plays important role on their magnetocaloric effect. However, no research work investigates the effect of atomic ordering on their elastocaloric effect yet. In this study, we investigated the influence of atomic ordering on the elastocaloric and magnetocaloric effects of a $Ni_{51}Cu_4Mn_{20}Ga_{25}$ ferromagnetic shape memory alloy. The alloy exhibits normal elastocaloric effect and normal magnetocaloric effect near room temperature. Moreover, we found that the enhancement of atomic order in this alloy can greatly increase the entropy change and refrigeration capacity of its elastocaloric and magnetocaloric effects. This is attributed to that the atomic ordering modifies the magnetic and martensitic transitions of the system.

1. Introduction

Caloric effects are inherent properties of materials, which refer to the isothermal entropy changes upon application of external fields [1–3]. They have attracted increasing interests, because the solid state refrigeration based on caloric effects is considered to be more environments friendly and energetically efficient compared with the conventional gas refrigeration [3,4]. Depending on the species of the external field, the caloric effect is called magnetocaloric [4–7], electrocaloric [8,9], elastocaloric [1,2,10–14] and barocaloric effect [15–17] when it responses to the electric field, magnetic flied, uniaxial stress and hydrostatic pressure, respectively. In the last several decades, the investigation of caloric effects is mainly focus on the magnetocaloric effect. Until recently, more attentions have been paid on the electrocaloric and mechanic–caloric effect (including elastocaloric and barocaloric effect), because they provide alternative solutions for solid state refrigeration besides magnetic refrigeration [3].

The materials with strong interplay between magnetic and structural degree of freedom usually exhibit a magnetic transition and a first order structure transition. The magnetocaloric effects and mechanic–caloric effect (elastocaloric and barocaloric effect) are expected to coexist in these materials [3]. The magnetocaloric effect can be classified into two types: normal and inverse magnetocaloric effect. The normal magnetocaloric effect shows negative magnetic entropy change while the inverse one shows positive magnetic entropy change upon applying field [4,7]. It has been shown that the former exists in the materials with paramagnetic to ferromagnetic transition and the later exists in those with a ferromagnetic to paramagnetic (or antiferromagentic) transition upon cooling. Similarly, there are also two kinds of mechanic–caloric effect. The normal barocaloric or elastocaloric effect possesses a negative mechanical entropy change, which is originated from the structure transition with decreasing volume or length upon cooling, and the corresponding inverse ones are defined for the opposite situation [3]. So far, the combination of different kinds of magnetocaloric effect and mechanic–caloric effect has been reported in a number of material systems such as La–Fe–Si, $Gd_5Si_2Ge_2$, Ni–Mn–X (In, Ga) based Heusler ferromagnetic shape memory alloys (FSMAs) [10–12,15–17]. Among these refrigeration materials, the Ni–Mn–X based Heusler FSMAs are considered to be competitive candidates for their tunable magnetic and martensitic (structural) transition and strong coupling between magnetism and structure [7].

The parent phase of Ni–Mn–X based Heusler FSMAs undergo a B2 to $L2_1$ transition with next-nearest neighbor atomic ordering

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upon cooling from very high temperature (950–1050 K) [18–20]. The degree of $L2_1$ atomic order is low as the alloy is fast quenched from high temperature. However, high degree of atomic order can be achieved by annealing the alloy at a proper temperature, which is below the B2–$L2_1$ transition temperature but sufficient high to allow the migration of atoms [18,19]. It has been shown that the transforming behaviors such as martensitic and magnetic transition temperatures of Ni–Mn–X based FSMAs are closely related with the $L2_1$ atomic ordering, since it varies the electronic structure and associated phase stability of the system [18–22]. More interestingly, it was reported that the magnetocaloric effect of these materials is also greatly affected by atomic ordering [22,23]. However, there is no research work investigating the effect of atomic ordering on elastocaloric effect so far.

In this work, we studied the elastocaloric and magnetocaloric effect of a $Ni_{51}Cu_4Mn_{20}Ga_{25}$ FSMA and the influence of atomic order on these two functional properties. Our results show that the $Ni_{51}Cu_4Mn_{20}Ga_{25}$ FSMA exhibits both normal magnetocaloric and normal elastocaloric effects, which possess negative entropy changes upon application of their conjugated fields. Moreover, we found that the entropy change and refrigeration capacity of its magnetocaloric and elastocaloric effects can be greatly increased by increasing atomic order, which can be understood from the modification of magnetic and martensitic transitions by atomic ordering. The multi-caloric effect of our sample is expected to be improved by either mechanical or magnetic filed [2] and may lead to novel applications.

2. Experimental procedure

The ingot with the nominal composition of $Ni_{51}Cu_4Mn_{20}Ga_{25}$ was fabricated by arc melting appropriate quantities of nickel (99.99%), copper (99.99%), manganese (99.9%) and gallium (99.99%) under an argon atmosphere. The as-cast samples were annealed at 1173 K for 24 h in evacuated quartz tubes and quenched into room temperature water subsequently. To investigate the effect of atomic ordering on elastocaloric and magnetocaloric effects, the as-quenched samples were further annealed at 773 K for 10 h and then cooled to room temperature in furnace. Similar heat treatment process has been widely performed to improve atomic order in Heusler FSMAs [20,21]. To characterize the B2–$L2_1$ transition and martensitic transition of the sample, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) was performed respectively at a temperature sweeping rate of 10 K/min. The magnetic transition was characterized by measuring magnetization vs. temperature (M–T) curve under the magnetic field of 0.1 T. To detect the structure of the samples, the X-ray diffraction (XRD) analysis was performed on their powder form, which ensures the accuracy of the peak intensity of XRD profile. The elastocaloric entropy change (ΔS_E) was characterized through the measurement of length elongation vs. temperature (ΔL–T) curves under different uniaxial tensile stresses, which was performed in a dynamic mechanical analyzer (DMA). The tensile sample is 15 mm (length) × 1.3 mm (width) × 0.65 mm (thickness) in size and was gripped in a tensile clamp. The length elongation of the tensile sample was monitored by the sensor in DMA. Moreover, the magnetocaloric entropy change (ΔS_M) was identified through measuring magnetization vs. magnetic field (M–H) curves at a series of temperatures.

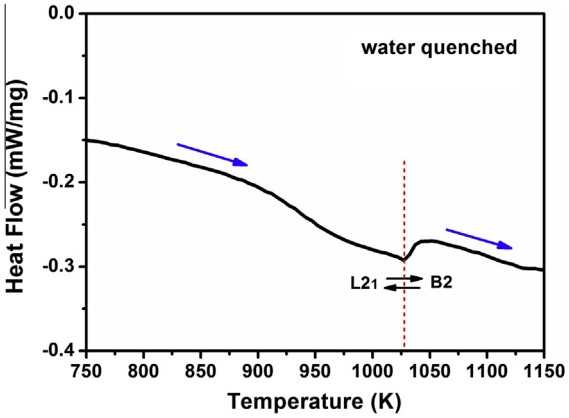

Fig. 1. TGA measurement (on heating) of water quenched $Ni_{51}Cu_4Mn_{20}Ga_{25}$ sample, which shows the B2–$L2_1$ atomic ordering transition occurs around 1026 K.

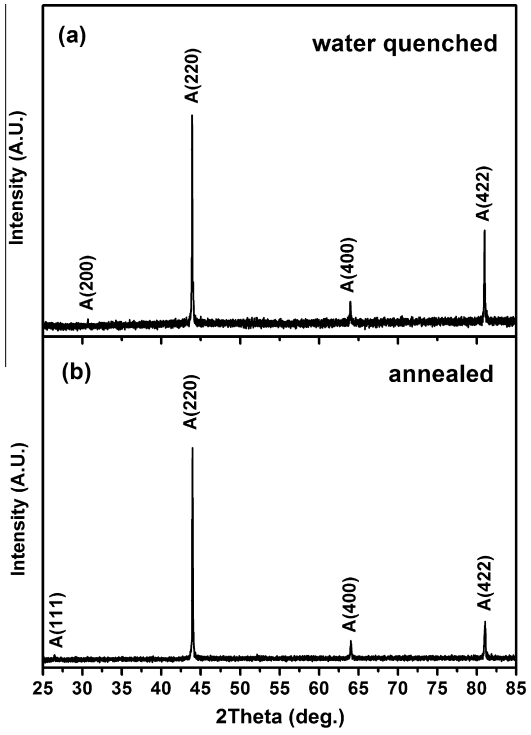

Fig. 2. The XRD curves of (a) water quenched and (b) annealed $Ni_{51}Cu_4Mn_{20}Ga_{25}$ samples, which show that the $L2_1$ atomic order increases after annealing treatment at 773 K for 10 h.

3. Results and discussion

Fig. 1 shows the DTA curve of the water quenched sample. It reveals a small peak around 1026 K, which corresponds to the B2–$L2_1$ transition, being consistent with previous observation in Ni–Mn–Ga based alloy [20]. The $L2_1$ structure for the parent phase of water quenched sample is identified by the XRD measurement, as shown in Fig. 2(a). To explore the effect of annealing on the $L2_1$ atomic order, the XRD profile of annealed sample was also determined in Fig. 2(b). In comparison with those of the water quenched sample, the superlattice diffraction peak $(111)_A$ of the annealed sample enhances and its superlattice diffraction peak $(200)_A$ fades away obviously, demonstrating $L2_1$ atomic order is increased after annealing [22].

The existence of martensitic and ferromagnetic transitions in water quenched and annealed samples are revealed by the DSC and magnetic measurements in Fig. 3. The martensitic transition temperature T_M of water quenched sample is 288 K as determined by its DSC curve of cooling process (Fig. 3(a)) and its Curie temperature T_C is 298 K as determined from its M–T curve (Fig. 3(b)). The T_M and T_C of the annealed sample are slightly increased, which are determined to be 304 K and 310 K from Fig. 3(c) and (d) respectively. Moreover, the martensitic transition latent heat of annealed sample is 1.20 K W/g obtained by integrating corresponding DSC peak in Fig. 3(c), which is larger than the transition latent heat (0.93 K W/g) of water quenched one as calculated from Fig. 3(a). All the above results demonstrate that the martensitic and magnetic transitions are promoted by the increase of atomic disorder.

To investigate the influence of atomic ordering on elastocaloric effect, the length elongation vs. temperature (ΔL–T) curves of water quenched and annealed samples are measured under different testing tensile stresses (σ), as shown in Fig. 4(a) and (b)