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Combination of conventional elastocaloric and magnetocaloric effects in a $Co_{37}Ni_{35}Al_{28}$ ferromagnetic shape memory alloy

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ABSTRACT

The elastocaloric and magnetocaloric effects in a polycrystalline ferromagnetic shape memory alloy $Co_{37}Ni_{35}Al_{28}$ are investigated. The alloy shows conventional elastocaloric effect with entropy change of -5.05 J kg^{-1} K^{-1} under 350 MPa. The temperature change of its elastocaloric effect is over 1 K within a working temperature range of 80 K covering ambient temperature. Moreover, the alloy also shows conventional magnetocaloric effect. The conventional elastocaloric and magnetocaloric effects of the alloy possess the same sign of entropy change and temperature change, the simultaneous use of multiple caloric effects can be achieved by applying stress and magnetic field, which improves its overall refrigeration capability.

The solid state refrigeration has gained more and more attention as the promising alternative to replace the vapor compression cooling, because it has advantages in energy efficiency, environmental protection and potential applications for microcooling [1–3]. There are different types of materials including magnetocaloric [4–8], electrocaloric [9], barocaloric [10–11] and elastocaloric [3,12–21] materials can be used for solid state refrigeration, which exhibit entropy or temperature change by application of the magnetic field, electric field, hydrostatic pressure and uniaxial stress respectively. Developing advanced refrigerant materials has becomes important research field of materials science, since it plays crucial role in improving the energy conversion and transportation of solid state refrigerators.

Among the refrigerant materials, the magnetic shape memory alloys are considered as very promising candidates, because they exhibit both magnetocaloric and elastocaloric effect and provide multiple solutions for solid state refrigeration. Magnetic shape memory alloys possess large magnetocaloric effect as their magnetic transition accompanies large magnetization change [22]. Moreover, many magnetic shape memory alloys also exhibit large elastocaloric effect, when their martensitic transformations satisfy two conditions: 1) the transition possesses large transforming lattice strain and 2) the transition temperature is very sensitive to the uniaxial stress [22]. Depending on the category of magnetic transition they undergo, magnetic shape memory alloys may show two kinds of magnetocaloric effect. The first type originates from the magnetic transition from high temperature paramagnetic (PM) state to the low temperature ferromagnetic (FM) state on cooling, i.e., the conventional ferromagnetic transition. It is named conventional magnetocaloric effect and characterized by a negative magnetic entropy change induced by applying magnetic field. On the contrary, the second type is called inverse magnetocaloric effect, which is characterized by positive magnetic entropy change upon applying magnetic field and stems from FM-PM transition on cooling (also named metamagnetic transition) [5,23]. Similarly, there also exist conventional and inverse elastocaloric effects [24,25]. The entropy change of conventional elastocaloric effect is negative, which originates from the decrease of sample length during the martensitic transformation upon cooling. However, the entropy change of the inverse one is positive, caused by the opposite situation.

It is a good strategy to utilize the multiple caloric effects of magnetic shape memory alloys for solid state refrigeration [26]. However, many magnetic shape memory alloys (eg. Ni-Mn-In-Co, Ni-Mn-Sn) show conventional elastocaloric effect and inverse magnetocaloric effect [5,18,23,27]. Since these two caloric effects have opposite sign of entropy change, they partially cancel out each other and lead to the reduction of the total entropy change. Thus, in order to improve the caloric response of materials, it is important to develop the system whose entropy change of magnetocaloric effect (ΔS_E) and entropy change of magnetocaloric effect (ΔS_M) possess the same sign. The combination of them may enhance the overall refrigeration capability. However, few materials were reported to show the same sign of ΔS_E and ΔS_M. This may due to two possible reasons. Firstly, few materials systems can show both

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conventional elastocaloric and magnetocaloric effects, which requires the material undergoes martensitic transformation and conventional ferromagnetic transition simultaneously upon cooling. Secondly, the systems with structure transition and conventional ferromagnetic transition such as $Mn_{1-x}Fe_xNiGe$ based hexagonal compounds [28] are usually very brittle and it is very difficult to measure their elastocaloric effect.

In this work, we show that the $Co_{37}Ni_{35}Al_{28}$ ferromagnetic shape memory alloy possesses both conventional elastocaloric and magnetocaloric effects. It exhibits the same sign of ΔS_E and ΔS_M and the same sign of ΔT_E (temperature change of elastocaloric effect) and ΔT_M (temperature change of magnetocaloric effect) within the room temperature range. Especially, its ΔT_E is more than 1 K over a wide temperature range (302 K ~ 382 K) spanning room temperature. Its conventional elastocaloric and magnetocaloric effects stem from the coexistence of martensitic transformation and conventional ferromagnetic transition on cooling. The combination of these two caloric effects provides a route to increase the overall refrigeration capacity of the refrigerant materials.

A polycrystalline alloy sample with a nominal composition of $Co_{37}Ni_{35}Al_{28}$ was prepared by arc melting under an argon atmosphere. The as-casted ingot was annealed in evacuated quartz tubes at 1300 °C for 24 h and then quenched into room temperature water. The martensitic transformation of the heat treated sample was detected by the differential scanning calorimetric (DSC) measurement, which was performed at a temperature sweeping rate of 10 K/min. Its magnetic transition was characterized by measuring the magnetization vs. temperature (M-T) curve under the magnetic field of 500 Oe.

The heat treated ingot was cut into the small square pillars with the size of 2.8 mm × 3 mm × 9 mm for stress-strain test and elastocaloric measurement, which were conducted in a testing machine (Autograph AG-I 50kN Model M1, Shimadzu) with a compressive deformation mode. The stress-strain curve (compressive deformation) was measured at a strain rate of $0.01\%\ s^{-1}$ for both loading and unloading processes. The entropy change of elastocaloric effect ΔS_E was characterized by the strain vs. temperature curves under different stresses. Since it is generally accepted that the temperature change of elastocaloric effect ΔT_E provides more reliable and straightforward information to evaluate the elastocaloric performance of materials, the ΔT_E of the sample was detected directly by a T-type thermocouple welded on its surface. In order to approximate the near adiabatic condition during ΔT_E measurement, a high strain rate of $0.50\%\ s^{-1}$ was loaded to the sample until reaching to its target stress of 350 MPa, and then held for 30s to ensure the sample temperature returned to its initial value. Subsequently, the stress was unloaded with the same strain rate of $0.50\%\ s^{-1}$.

The entropy change of magnetocaloric effect ΔS_M was identified through measuring magnetization vs. magnetic field (M-H) curves at a series of temperatures. The temperature change of magnetocaloric effect ΔT_M was also detected by a T-type thermocouple welded on the sample surface. To approximate the near adiabatic condition during ΔT_M measurement, the sample was rapidly put into a chamber with magnetic field of 5 T in 2 s, and the held for 50 s to wait the sample recovering to its initial temperature. After that, the sample was quickly moved out from the chamber in 2 s for withdrawing the magnetic field to 0 T.

The transforming properties of $Co_{37}Ni_{35}Al_{28}$ alloy are revealed by the DSC and magnetic measurements in Fig. 1(a). The sample shows obvious latent heat peaks in its DSC curve (top of Fig. 1(a)) upon heating/cooling cycle, which demonstrates it undergoes martensitic transformation. The transformation enthalpy ΔH_h and ΔH_c for heating and cooling processes are determined to be −1.26 J/g and −1.56 J/g, respectively. The martensitic transformation starting temperature M_S and finishing temperature M_f is determined to be 307 K and 282 K from the exothermic peak of the cooling process. The corresponding reverse transformation starting temperature A_S and finishing temperature A_f is determined to be 305 K and 322 K from the endothermic peak of the heating process. The ideal entropy change ΔS_{ideal} of sample induced by the complete spontaneous martensitic transformation can be calculated by $\Delta S_{ideal} = \Delta H_{ideal}/T_0$ [3,29]. The ΔH_{ideal} is the ideal transformation enthalpy, which is −1.41 J/g estimated by the relationship $\Delta H_{ideal} = (\Delta H_h + \Delta H_c)/2$; the T_0 is the equilibrium temperature defined as $T_0 = (M_S + A_f)/2$ [3,29]. Thus, the ΔS_{ideal} is calculated to be $-4.48\ J\ kg^{-1}\ K^{-1}$ for spontaneous martensitic transformation.

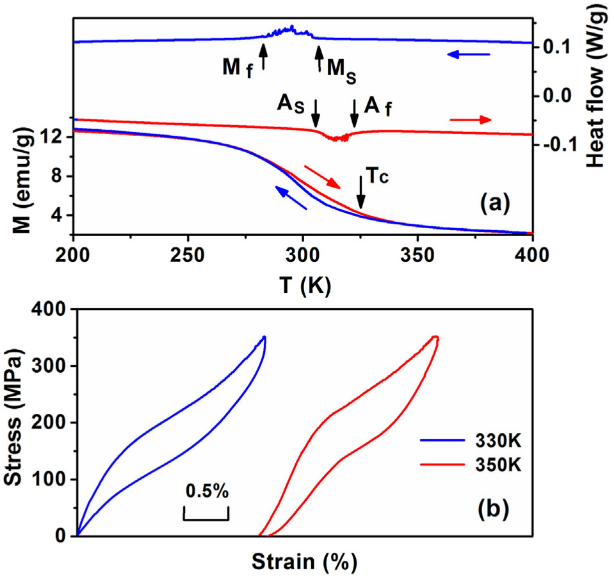

Fig. 1. (a) The DSC curves (top) and magnetization vs. temperature curves (bottom) of $Co_{37}Ni_{35}Al_{28}$, which are measured during both cooling and heating processes. A magnetic field of 500 Oe was applied for the measurement of magnetization vs. temperature curves. (b) The stress-strain curves of $Co_{37}Ni_{35}Al_{28}$, which are measured with the maximum compressive stress of 350 MPa at 330 K and 350 K.

The M-T curves measured under a magnetic field of 500 Oe for both cooling and heating processes are displayed in the bottom of Fig. 1(a). It shows that the magnetization increases at low temperature, demonstrating the alloy undergoes a conventional ferromagnetic transition on cooling. The ferromagnetic transition temperature T_C is 325 K. Comparing with the cooling process, the ferromagnetic transition temperature is closer to the martensitic transformation temperature during the heating process (Fig. 1(a)). This indicates that the elastocalric and magentocalric effects of the sample may appear in closing temperature ranges upon heating.

Since the elastocaloric effect is associated with the stress-induced martensitic transformation, the stress-strain curves of the $Co_{37}Ni_{35}Al_{28}$ were measure at 330 K and 350 K to show the typical features of its deformation behavior above A_f. As displayed in Fig. 1(b), a complete superelastic behavior can be observed at these two testing temperatures upon loading up to 350 MPa, demonstrating a complete stress-induced martensitic transformation can be achieved under 350 MPa.

The entropy change of elastocaloric effect ΔS_E is an important parameter for characterizing the elastocaloric effect. To obtain the ΔS_E of $Co_{37}Ni_{35}Al_{28}$, the compressive strain (ε) as a function of temperature (T) was measured under different uniaxial stresses (σ) on heating, as displayed in Fig. 2(a). There is a rapid change of strain during martensitic transformation, which moves to higher temperature with increasing stress, because the stress enhances the martensitic transformation temperature. Notably, the martensitic transformation temperature is greatly enhanced to beyond our testing temperature range (272 K ~ 352 K) by loading large stress of 350 MPa. The sample keeps staying in the martensitic state and does not undergo transformation under this high stress level. However, it still shows obvious strain change (~0.5%) within testing temperature range, which is caused by the orientation of the martensitic variants with temperature change.