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A Comparative Studies of Magnetocaloric Effect in Ni-Mn-Cu-Ga and Ni-Mn-Pb-Ga Alloys

K. Sielicki*, R. Wróblewski, M. Leonowicz
Faculty of Materials Science and Engineering, Warsaw University of Technology,
Wołoska 141, 02-507 Warszawa, Poland

Effect of Pb substitution for Cu on magnetocaloric properties of $Ni_2Mn_{1-x}Cu_xGa$ ($x = 0.25$, 0.27, 0.29) alloy was investigated experimentally. The magnetic measurements of Ni-Mn-Pb-Ga alloys conducted at low field of 4kA/m (50 Oe) showed that their Curie points are above the room temperature (RT). The analysis of isothermal magnetic curves allowed the estimation of magnetic entropy change (ΔS_M). The highest calculated value of $|\Delta S_M|$, ≈ 12 J/(kg K) and ≈ 1.8 J/(kg K), was registered for alloys containing 6.25 at.% of Cu and 6.75 at.% of Pb, respectively. The adiabatic temperature changes (ΔT) measured near RT are ≈ 0.4 K.

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1. Introduction

Magnetocaloric effect occurs in all ferromagnetic materials due to the interdependence of the thermal and magnetic effects. Such effects are commonly induced by application or removal of the magnetic field and expressed by the entropy change for the isothermal process [1]. The first who measured the field induced temperature change were Weiss and Piccard. In 1917 they reported the reversible temperature change of 0.7 K when applying a field of 1200 kA/m (1.5 T) to the nickel sample near the Curie temperature (354 °C) [2]. They also named the phenomenon – their publication title was "Le phénomène magnétocàlorique". What they observed was that the magnetocaloric effect [MCE] is reversible and reaches its maximum near the Curie temperature.

In recent years, discovery of a giant magnetocaloric effect [3] has stimulated basic and applied interest in the development of new materials, which can be useful for room-temperature magnetic refrigeration. A new interesting class of materials are ferromagnetic Heusler alloys based on the X_2YZ formula. Those alloys undergo a structural (martensitic) transition which involves a change in both structural and magnetic properties [4]. In 2000's it was discovered that these materials show also interesting magnetocaloric properties in the vicinity of the martensitic (T_M) and magnetic (T_C) transition. Optimum magnetocaloric properties are shown when both, the martensitic and ferromagnetic transitions, are close to each other [5]. Both temperatures, T_M and T_C, can be adjusted by tailoring the chemical composition. Replacing Mn with Cu in $Ni_2Mn_{1-x}Cu_xGa$, resulted in coincidence of the two transition temperatures ($T_M = T_C = T_{MC}$), for $x = 0.25$ [6].

*corresponding author; e-mail: ksielicki@inmat.pw.edu.pl

In this paper effect of Pb substitution for Cu on magnetocaloric properties of $Ni_2Mn_{1-x}Cu_xGa$ ($x = 0.25$, 0.27, 0.29) alloy was investigated.

2. Experimental

Two series of Ni-Mn-Cu-Ga and Ni-Mn-Pb-Ga alloys were prepared by induction melting of pure elements in argon atmosphere. After casting the ingots were homogenized at 1083 K for 48h and slowly cooled with the furnace.

Chemical composition of the specimens was checked using the energy dispersive spectroscopy (EDS) technique.

Magnetic properties and transformation temperatures was measured using the LakeShore 7410 vibrating sample magnetometer (VSM), equipped with a cryostat, at a magnetic field $H = 4$ kA/m (0.005 T) in the temperature range of 200–400 K. Heating and cooling rate of ≈ 2 K/min was applied.

The magnetic entropy changes (ΔS_M) were calculated using the experimental $M(T)$ curves and integrated Maxwell relation

$$\Delta S(TH) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \qquad (1)$$

The field induced temperature changes (ΔT) were recorded in direct measurement near room temperature (RT) at $H = 1600$ kA/m (2 T) using quasi-adiabatic regime.

3. Results and discussion

Two series of alloys having the following composition $Ni_{50}Mn_{25-a}X_aGa_{25}$ ($a = 6.25$, 6.75, 7.25), with X = Cu, Pb, were prepared. The study of the chemical composition showed that after metallurgical process the alloys composition slightly changed in comparison to the nominal values. The manganese content decreased by 1–2%

and gallium concentration increased by the same value. The nickel content was close to the nominal concentration in all the alloys.

The transformation temperatures T_M and T_C, recorded at $H = 4$ kA/m for the $Ni_{50}Mn_{25-a}Cu_aGa_{25}$ and $Ni_{50}Mn_{25-a}Pb_aGa_{25}$ alloys are shown in Fig. 1a and b, respectively.

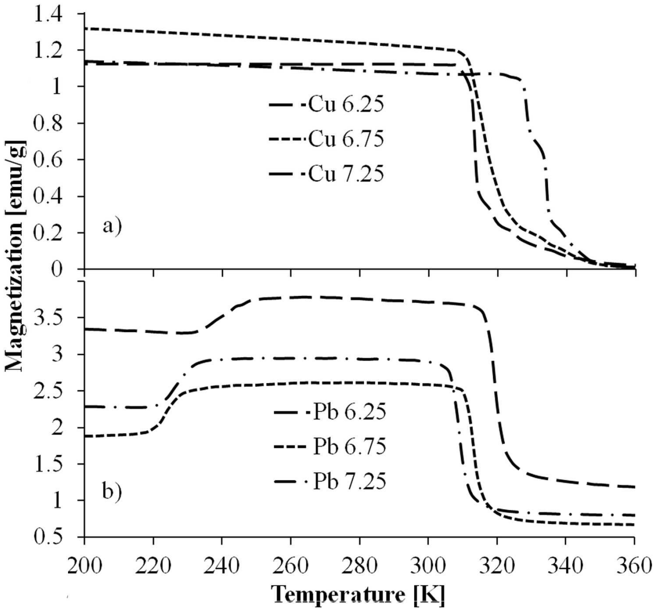

Fig. 1. Magnetization versus temperature for a) $Ni_{50}Mn_{25-a}Cu_aGa_{25}$, b) $Ni_{50}Mn_{25-a}Pb_aGa_{25}$ alloys, $H = 4$ kA/m.

One can see that the Pb substitution for Cu increased magnetization value for all alloys. Such behaviour is related with Mn atoms which are magnetic moment carriers in Heusler alloys [7]. Experimental studies show antiferromagnetic order in both $L2_1$ and B_2 Heusler alloys structure [8]. Antiferromagnetism is more favorable in alloys which have B_2-type crystal structure due to smaller interatomic Mn-Mn distances. Using nonmagnetic element, such as Cu or Pb, increases the Mn-Mn distance, providing ferromagnetic order and increasing of magnetization at the martensitic state. Using element with bigger atomic radius ($r_{Pb} > r_{Cu}$) provide increase distances between Mn atoms which results in increase of magnetization. The Pb substitution also slightly decreased the Curie points towards the room temperature, but dramatically decreased transformation temperature below RT.

The $|\Delta S_M|$ values calculated for Ni-Mn-Cu-Ga and Ni-Mn-Pb-Ga alloys are shown at Fig. 2. As we can see the values reach up to 10–12 J/(kg K) for alloy with Cu content (Fig. 2a–c), however the peaks are very narrow. This phenomenon is a result of overlapping both transition temperatures and gives a Curie transition (rapid loss of magnetization) the nature of first-order transition [6]. As we can see Pb substitution definitely decreased value of magnetic entropy changes. The Pb substitution leads to separating both transition temperatures (Fig. 2d–f) which results in significant decreases of magnetic entropy changes, down to ≈ 1.4 J/(kg K) for alloy with 6.25 at.% Pb content. This separation can be observed as two peaks of entropy changes corresponding to both transitions (Fig. 1b). The highest entropy change ≈ 1.8 J/(kg K), was recorded for alloy with 6.75 at.% of Pb at Curie temperature.

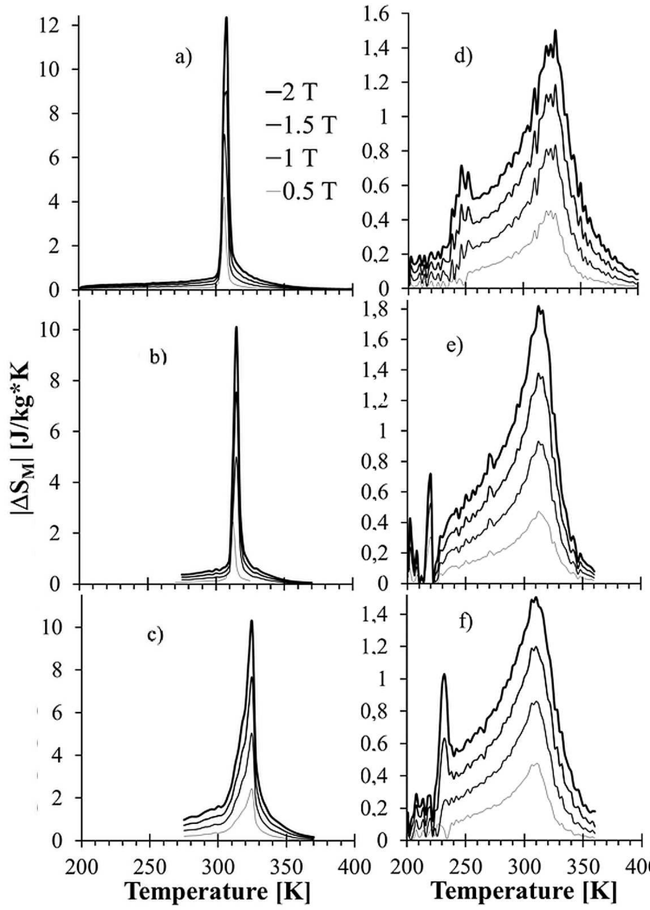

Fig. 2. Magnetic entropy changes calculated for $Ni_{50}Mn_{25-a}Cu_aGa_{25}$ a) 6.25, b) 6.75, c) 7.25 at.% and $Ni_{50}Mn_{25-a}Pb_aGa_{25}$ d) 6.25, e) 6.75, f) 7.25 at.% alloys.

Analysing obtained result shows that neither of prepared alloys has transformation temperatures in close vicinity of room temperature. The ΔT measurement at $H = 1200$ kA/m show that only two alloys — $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ and $Ni_{50}Mn_{18.75}Pb_{6.25}Ga_{25}$ — revealed a significant temperature change at RT (Fig. 3 a&b, respectively). Other samples exhibited very small temperature change just little over 0.1 K per cycle (magnetization-demagnetization). This phenomenon is corresponding with values of magnetic entropy change. Alloys with Cu content shows large ΔS_M but the peaks are above the RT. The $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy exhibits highest entropy change value at 308 K. Our experimental setup is not capable of measuring the ΔT above the RT however one could expect a peak value ≈ 1.5–2 K [6]. In the vicinity of RT copper containing alloys show very low values of $|\Delta S_{\mathrm{M}}| \approx 0.7$ J/(kg K) which still provide temperature change of ≈ 0.4 K.

The Pb substitution for Cu leads to decreasing of $|\Delta S_{\mathrm{M}}|$ values at Curie temperature but increasing around the RT. The highest ΔT value of ≈ 0.4 K was recorded for $Ni_{50}Mn_{18.75}Pb_{6.25}Ga_{25}$ alloy.

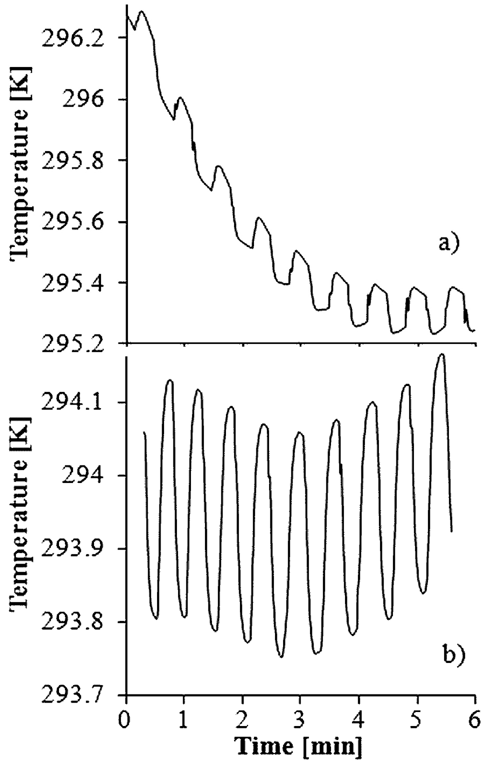

Fig. 3. The adiabatic temperature changes (ΔT) measured near RT in magnetic field 2T for a) $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ and b) $Ni_{50}Mn_{18.75}Pb_{6.25}Ga_{25}$ alloys.

4. Conclusions

The substitution of copper with lead, in the the $Ni_{50}Mn_{25-a}Cu_aGa_{25}$ alloys separates martensite-austenite and Curie transformation temperatures. The Curie point stays at the same temperature but the structural transformation temperature decreases dramatically.

The peak values of $|\Delta S_{\mathrm{M}}|$ and ΔT are:
(a) ≈ 12 J/(kg K); 0.4 K or (b) ≈ 1.8 J/(kg K); 0.3 K for alloys containing 6.25 at.% of Cu and Pb, respectively.

It also appears that magnetic field induced temperature change has the same magnitude at the Curie point regardless of the order of the transition in dopped Ni-Mn-Ga alloys.

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