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THE MAGNETIC ENTROPY CHANGES IN Pb DOPED Ni-Mn-Cu-Ga ALLOYS

Effect of Pb addition on magnetocaloric properties of $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ (a = 1, 2, 3, 4, 5) alloys was investigated experimentally. The magnetic measurements conducted at low field of 4 kA/m showed that addition of Pb led to separation of the both transformation temperatures and significantly shifted the structural transition effect towards lower temperatures as well as increased the Curie temperature. The analysis of isothermal magnetic curves allowed for the calculation of magnetic entropy change (ΔS_M). Although the peak values of $|\Delta S_M|$ for alloys containing 4 and 5 at.% Pb, ~3 J/(kg*K) and ~1.5 J/(kg*K) respectively, are low they stretch over the structural transformation and Curie temperature, and are at least 30 K wide at half maximum height.

Keywords: magnetocaloric effect; magnetic entropy change; Curie temperature; Heusler alloys

1. Introduction

The magnetocaloric effect [MCE] can be induced by application and removal of the external magnetic field and is expressed by magnetic entropy changes for the isothermal process [1]. Such effect occurs in all ferromagnetic materials due to the interdependence of the thermal and magnetic effects. The most intensive effect occurs at temperatures close to the magnetic transition and strongly depends on the type of the transition [2,3]. In 1917, Weiss and Piccard measured the field induced temperature change in ferromagnets and were first who reported the reversible temperature change of 0.7 K when applying the external magnetic field of 1200 kA/m (1.5 T) for the nickel sample, close to the Curie point (354°C) [4]. They named the discovered phenomenon "Le phenomene magnetocalorique". They also observed that the magnetocaloric effect is reversible and reaches its maximum close the Curie point. The interest on the magnetocaloric properties of new materials have renewed attention in recent years, since discovery of a giant magnetocaloric effect [5], which can successfully be applied at room-temperature for magnetic refrigeration. An interesting group of materials present ferromagnetic Heusler alloys based on the X_2YZ formula. Those alloys undergo a structural (martensitic) transition which involves a change of both structural and magnetic properties [6]. It was discovered that these materials show also interesting magnetocaloric properties in the vicinity of the structural (T_M) and magnetic (T_C) transition points. The optimal magnetocaloric properties are shown when both, the martensitic and ferromagnetic transitions, are close to each other [7]. The transformation temperatures T_M and T_C can be adjusted by tailoring the chemical composition. In $Ni_2Mn1\text{-}xCuxGa$ alloys replacing Cu for Mn leads to coincidence of both transition temperatures ($T+ = T_C = T_{MC}$), for $x = 0.25$ [7]. Substitution of Pb for Cu in NiMnCuGa alloy resulted in slight decrease of the Curie temperature and a significant shift of the structural transition towards lower temperatures, leading to separation of the both transformations [8]. Thus, by a proper combination of Cu and Pb addition in Ni_2MnGa alloys, it is possible to control the position and magnitude of the magnetocaloric effect. The main problem with the application of Heusler alloys is narrow operating temperature range. To broaden it, the stacked plates of alloys with similar chemical composition and slightly different magnetostructural transition temperatures, are considered [9].

In this paper the effect of Pb addition on the magnetocaloric properties of $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ (a = 1, 2, 3, 4, 5) alloys was investigated.

2. Experimental

The Ni-Mn-Cu-Ga alloys, doped with Pb, were prepared by induction melting of pure elements in argon atmosphere. The series of alloys having the following composition $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ (a = 1, 2, 3, 4, 5) were prepared.

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After casting the ingots were homogenized at 1083 K for 48 h 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 were 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 change (ΔS_M) was calculated using the experimental $M(T)$ curves and integrated Maxwell relation

$$\Delta S\left(T,H\right)=\mu_0\int_0^H\left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1)$$

where: S_M – magnetic entropy, μ_0 – magnetic permeability of vacuum, M – magnetization, T – temperature and H – magnetic field.

3. Results and discussion

The transformation temperatures T_M and T_C, recorded at H = 4 kA/m for the $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ alloys with 1 to 5 at%. Pb content are shown in Fig. 1 and Table 1.

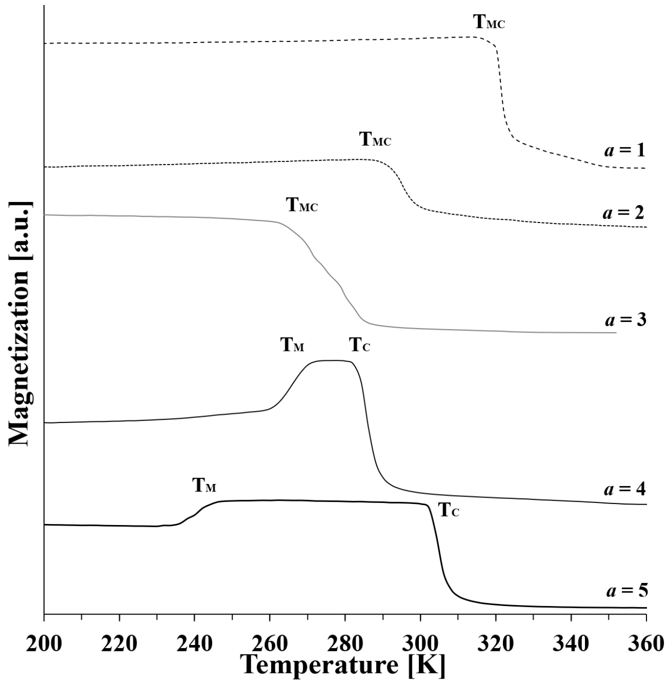

Fig. 1. Magnetization versus temperature for $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ (a = 1, 2, 3, 4, 5 at. %) alloys, H = 4 kA/m

One can see that with increasing value of the Pb addition (up to 3 at.%) the Curie temperature decreases from ~330 K to 280 K. Further addition of Pb leads to separation of both transformation temperatures and significant shift the structural transition toward lower temperatures and increase of the Curie temperature. These results are consistent with the previous measurements of the transformation temperatures for $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ and $Ni_{50}Mn_{18.75}Pb_{6.25}Ga_{25}$ alloys [8].

TABLE 1

Transformation temperatures for $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ alloys, H = 4 kA/m

	T_M [K]	T_C [K]
1	320	320
2	295	295
3	270	270
4	270	285
5	245	308

As one can see the values reach up to 12 J/(kg*K) for the alloy with 1 at.% of Pb addition (Fig. 2a) and up to 6 J/(kg*K) for 2 at.% of Pb (Fig. 2b), however the peaks are very narrow and much lower than for the quaternary $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy [8]. This results from overlapping of both transition temperatures which gives the Curie transition nature of structural transition (rapid loss of magnetization) [7]. The Pb addition significantly decreases the value of the magnetic entropy changes, down to ~1.1 J/(kg*K) for the alloy with 3 at.% of Pb content (Fig. 2c), and shifts the transition temperature below the RT. Further addition of Pb leads to separation of the transition temperatures (Fig. 2d, e) and separates them by shifting the structural transition to lower and Curie to higher temperatures. As a result two peaks of entropy changes, corresponding to both transitions (Fig. 2d, e), are observed which is consistent with behavior reported for $Ni_{50}Mn_{18.75}Pb_{6.25}Ga_{25}$ alloy [8]. The maximal entropy change ~3 J/(kg*K) was observed for 4 at.% of Pb at structural transformation temperature and ~1.5 J/(kg*K) for 5 at.% of Pb at Curie temperature.

Analysis of the obtained results shows that addition of Pb in $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ has significant influence on transformation temperatures. The Pb addition decreases the magnetic entropy change values. Despite the large decrease of entropy change values $|\Delta S_M|$, the alloys with Pb addition show similar value of the adiabatic temperature changes □T in close vicinity to the room temperature as NiMnCuGa alloys as it was reported in [8,9]. Based on that proper combination of Pb and Cu content, in NiMnGa alloys, can be useful for developing of the magnetocaloric stacked alloys with wide operating temperature range.

4. Conclusion

The increasing addition of Pb in $Ni_{50}Mn_{18,75}Cu_{6,25\text{-}a}Pb_aGa_{25}$ alloys separates structural and Curie transformation temperatures and shift them towards opposite directions – structural transition to lower and Curie to higher temperature. The highest entropy changes ~3 J/(kg*K) was recorded for 4 at.% of Pb at structural transformation temperature and ~1.5 J/(kg*K) for 5 at.% of Pb at Curie temperature. Despite the low entropy change values $|\Delta S_M|$ the Pb content can be useful for developing of magnetocaloric stacked alloys with wide operating temperature range.

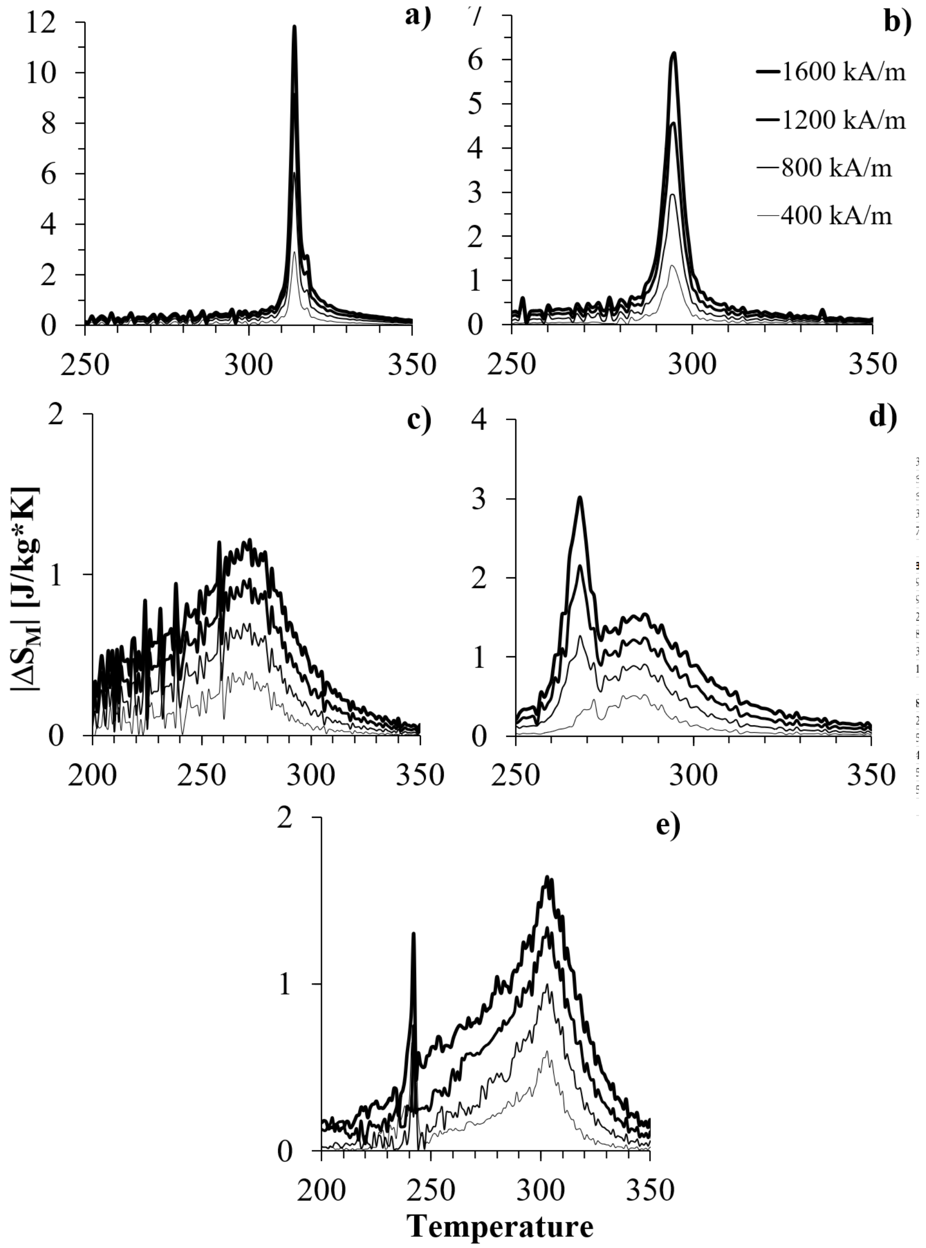

Fig. 2. Magnetic entropy changes calculated for $Ni_{50}Mn_{18,75}Cu_{6,25-a}Pb_aGa_{25}$; a) 1, b) 2, c) 3, d) 4, e) 5 at.% alloys

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