MAGNETOCALORIC EFFECT AROUND CURIE TEMPERATURE IN Ni$_{50-x}$ Cu$_x$Mn$_{38}$Sn$_{12}$B$_3$ SHAPE MEMORY RIBBONS

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Abstract. The magnetocaloric effect in Ni$_{50-x}$Cu$_x$Mn$_{38}$Sn$_{12}$B$_3$ ribbons depending on the Cu substitution ($x=0, 1, 3$) was investigated around the Curie temperature. The purpose of the present study was to analyze the magnetocaloric effect around a second order phase transition (around the Curie temperature) which has a smaller thermal hysteresis compared to a first order phase transition (Martensitic transition). The Curie temperature of the ribbons shifted to higher temperatures with increasing Cu content. A conventional magnetocaloric effect (MCE) was observed around the Curie temperature when the ribbons are subjected to a magnetic field change of 5 T. The magnetic entropy changes were calculated based on the isothermal magnetization $M(H)$ data using thermodynamic Maxwell equation. The highest magnetic entropy change and the refrigerant capacity was obtained for the $x=1$ ribbon.

1. Introduction

Ni-Mn-X (X = Sn, In and Sb) metamagnetic shape memory alloys (MSMAs) are of great interests due to their potential applications such as magnetic refrigeration materials, magnetic shape memory effect, magneto-resistance, magneto-thermal conductivity, elasta-caloric effect [1-11]. These alloys are one step ahead in practical applications when considering the cost-performance relationship [12]. They have also a large refrigeration capacity ($RC$) around martensitic-austenite phase transition [13] which is comparable to the compounds containing rare-earth element [14,15]. Strong conventional magnetocaloric effect (MCE) is caused by a magnetic transition since the magnetization strongly varies in a very narrow temperature range around transition temperature. The MCE can be tuned [16,17] by substituting or doping ferromagnetic [18-20] or non-ferromagnetic elements [21-23].
The total adiabatic entropy change of a magnetic material is the sum of magnetic $\Delta S_M$, lattice $\Delta S_L$, and electronic $\Delta S_E$ entropy given by $\Delta S_T = \Delta S_M + \Delta S_L + \Delta S_E$. The lattice and electronic entropy are independent of external magnetic field. The total entropy is constant if the process is adiabatic and reversible. When a magnetic field is applied on the material, the magnetic moments of the material are aligned along the magnetic field direction which implies a decrease in magnetic entropy. For the conservation of total entropy change, the decrease in the magnetic entropy is compensated by an increase in the lattice entropy. The increase in lattice entropy causes an increase of the material temperature.

This study investigates the effect of Cu substitution on magnetocaloric effect in the vicinity of Curie temperature ($T_c$) in Ni$_{50-x}$Cu$_x$Mn$_{38}$Sn$_{12}$B$_3$ (x = 0, 1, 3) shape memory ribbons. The Curie temperatures for x = 0, 1, 3 were found to be 315, 321 and 319 K, respectively, which are very close to room temperature. This makes the investigation of the MCE around the Curie temperature important. On the other hand, the transition around the Curie temperature is a second order phase transition and this will be discussed below. Such a transition provides a large usable temperature range (compared to a first order transition [24] observed in this compound at low temperature) as the transition temperature of the ribbon has to span the entire working region of the cooling device. The MCE and the effective refrigerant capacity $RC_{eff}$ were calculated depending on the Cu substitution. The magnetic entropy change $\Delta S_M$ was determined on the basis of magnetization data $M(H)$. The highest $RC$ value (96.44 J/kg) was found for the x=3.

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2. EXPERIMENTAL

The appropriate amount of Ni, Mn, Sn, B and Cu powders were mixed to fabricate $\text{Ni}_{50-x}\text{Cu}_x\text{Mn}_{38}\text{Sn}_{12}\text{B}_3$ ($x = 0, 1, 3$) shape memory ribbons and the mixture was melted in an arc-melter in an argon atmosphere. Thus, the ingots of the polycrystalline $\text{Ni}_{50-x}\text{Cu}_x\text{Mn}_{38}\text{Sn}_{12}\text{B}_3$ were produced. In order to make the ingots more homogeneous, the melting process was repeated several times. The obtained ingots were used to produce the ribbons by melt-spinning technique. The dimensions of the produced ribbons were about 5-6 mm in width, 20-25 mm in length and 15-20 $\mu$m in thickness, respectively. The ribbons were also heat treated in vacuumed quartz ampoules at 1173 K for 2 h and then quenched in ice-water.

Magnetic measurements were performed with Quantum Design Physical Property Measurement System (PPMS) - 9T. The system is able to resolve the magnetization changes of less than $10^{-6}$ emu at a data rate of 1 Hz. The sweep rate, which means how fast the magnetic field change between the field set points, was set to 100 Oe/sec for all the measurement.

3. RESULTS AND DISCUSSION

Figure 1 shows the magnetization-temperature (M-T) curves of the ribbons under a magnetic field of 1T. A magnetic transition (MT) from a ferromagnetic state to a paramagnetic state was observed. Curie temperatures $T_c$ were obtained to be 315, 320 and 317 K for $x= 0, 1$ and 3, respectively. $T_c$ values were determined by taking the first derivative of $M(T)$ curves. The increase of the Curie temperature is attributed to the enhancement of ferromagnetic coupling.

Figure 2a shows the isothermal $M$-$H$ curves of the $x= 0$ parent ribbon at the temperatures from 300 to 360 K in an interval of 5 K. The measurements were performed at the temperatures in the vicinity of the Curie temperature. A similar $M(H)$ characteristic was also observed for the $x=1$ and 3 ribbons.
Figure 1. The magnetization curve of the samples as a function of temperature at the magnetic field of 1 T.

The Arrott plot technique was used to determine the nature of magnetic phase transition. Figure 2b shows $M^2$ versus $H/M$ curves obtained from $M(H)$ data (figure 2a) at the temperatures around the Curie temperature. According to Banerjee’s criterion [25], if the slope is positive, the material undergoes a second order phase transition (SOPT). Figure 2b clearly indicates that the ribbons used in this study undergo a second order phase transition around the Curie temperature. For the $x=1$ and 3 Cu substituted ribbons, a similar Arrott plot characteristic was observed. As the transition around the Curie temperature is a second order phase transition, there exists a small thermal hysteresis. A large thermal hysteresis generally accompanies to the first order magnetic phase transition and this strongly influences the refrigerant efficiency of the MCE. It should be emphasized that the thermal hysteresis increases the temperature range of refrigeration cycle, causing a reduce in the refrigerant efficiency [26]. On this purpose, in this study the MCE properties of Ni$_{50-x}$Cu$_x$Mn$_{38}$Sn$_{12}$B$_3$ ribbons were investigated around the Curie temperature. The magnetocaloric efficiency around a transition with small thermal hysteresis is much higher and the corresponding MCE can be more effectively used in the magnetic refrigeration technology. It is worth to note that the MCE was generally investigated
in the literature around the martensitic transition which has very large thermal hysteresis. For the Ni_{50-x}Cu_xMn_{38}Sn_{12}B_3 ribbons there is no study reported in the literature on the investigation of the MCE around the Curie temperature.

**Figure 2.** a) the $M$-$H$ curves of the ribbon (x=0) up to 5T, at different temperatures between 300 K and 360K in an interval of 5K, b) Arrott ($M^2$ vs $H/M$) plots.

Magnetic entropy change can be calculated by using the following thermodynamic Maxwell equation:

$$\Delta S_M = \int_{H_0}^{H_F} \left( \frac{\partial M}{\partial T} \right)_H \ dH$$  \hspace{1cm} \text{Eq. 1}$$

where $H_0 = 0$, if the field is changed from 0 to $H$. $\frac{\partial M}{\partial T}$ can be calculated numerically with a simple formula given below, Eq. 2. The integral was numerically solved using the trapezoidal integration.
\[
\frac{\partial M}{\partial T} = \sum_{i=1}^{i_{\text{max}}} \frac{M(T_{i+1}) - M(T_i)}{T_{i+1} - T_i}
\]

Eq. 2

If the number of experimental \( M(H) \) curves is \( N \) (an integer number), the resulting \( \Delta S_M - T \) data will have \( N-1 \) points. The reason for this loss is the numerical method used for the calculation of the derivative, see eq.2.

![Graph showing temperature dependence of the isothermal magnetic entropy change change \( \Delta S_M \) at different Cu substitution levels under a magnetic field change of 5 T.](image)

**Figure 3.** Temperature dependence of the isothermal magnetic entropy change change \( \Delta S_M \) at different Cu substitution levels under a magnetic field change of 5 T.

Figure 3 shows \( \Delta S_M \) as a function of temperature calculated by using Eq. 1 at different substitution levels \( (x = 0, 1 \text{ and } 3) \). The measurements were performed at the temperatures below and above Curie temperature \( (T_c) \) with the temperature steps of \( \Delta T = 5 \text{ K} \). The \( \Delta S_{M,\text{max}} \) values were calculated to be 2.34, 2.71 and 2.60 J/kgK for
the x=0, 1 and 3 ribbons, respectively, indicating an increase in $\Delta S_{M}^{\text{max}}$ of 15.8% for the x=1 ribbon compared to the x=0 ribbon.

The magnetization difference, $\Delta M$, between two phases is responsible for magnetic entropy change [27]. If one wants to improve $\Delta S_{M}$, the magnetization difference $\Delta M$ should be tuned. In the present study, the magnetization was increased by substituting Cu for Ni, see figure 1. Magnetic properties of Heusler alloys are very sensitive to the structural disorder and strongly depends on the exchange interaction between Mn-Mn atoms [28] because the contribution of the magnetic moments of Ni atoms to the total magnetic moment in Ni-Mn-X (X=Sn, Sb, In) alloys is quite low [29,30]. The exchange interaction determines whether the magnetic order is ferromagnetic or antiferromagnetic. The substitution of Cu for Ni causes a change of the distances between Mn-Mn atoms. These new interatomic distances are more favorable for the ferromagnetic order. Therefore, the Cu substitution leads to a strong ferromagnetic coupling. Figure 1 supports this idea and an increase in the magnetization difference $\Delta M$ was observed in the x=1 and 3 ribbons. The $\Delta M$ value is decreased in the x=3 ribbon compared to the x=1 ribbon but it was still bigger than the $\Delta M$ value of the x=0 parent ribbon.

A large refrigerant capacity value $RC$ as well as large entropy change is also crucial parameter for the magnetic refrigeration applications. The area under $\Delta S_{M} - T$ curve in Figure 3 gives the refrigerant capacity \( \left( RC = \int_{T_1}^{T_2} \Delta S_{M} \, dT \right) \), which is a measurement of heat transport between hot and cold reservoirs in an ideal refrigerator. $T_1$ and $T_2$ are the temperatures which correspond to half maximum value ($\Delta T_{\text{FWHM}}$) in both side of $\Delta S_{M}$ peak. The area was calculated by trapezoidal integration method and the corresponding RC versus x is given in Figure 4. The highest $RC$ value was found to be 88.89 J/kg for the x=1 which indicates an increase of $RC$ by 13.7%. The maximum $RC$ obtained in this study is comparable with the other Heusler alloys [26,31-34].

Hysteresis loss (HL) must be taken into account for evaluating effective refrigerant capacity $RC_{\text{eff}}$ during a thermodynamic cycle. The area between magnetization and demagnetization curves gives HL. The $RC_{\text{eff}}$ can be calculated by subtracting hysteresis loss from $RC$, $RC_{\text{eff}} = RC - HL$ [27]. The calculated hysteresis areas at 335 K for the x=0, 1 and 3 were very small and found to be 0.59, 0.66 and 1.05 J/kg for the x=0,1 and 3, respectively. Then, the calculated $RC_{\text{eff}}$ values are 77.58, 88.24 and 82.2 J/kg for the x= 0, 1 and 3, respectively. The obtained $RC_{\text{eff}}$ values are comparable with the other Ni-Mn-Sn systems, see figure 8 in ref [27] and a promising value for the magnetocaloric applications in the future.
In this study, the effect of Cu substitution on the magnetocaloric effect and Curie temperature was investigated. The Cu substitution helped to tune not only the magnetocaloric effect also the Curie temperature. An increase of 6 K was observed in the Curie temperature of the x=1 ribbon. However, a decrease in the Curie temperature of the x=3 ribbon was observed, but it was still above the Curie temperature of the x=0 parent ribbon. For the x=1 ribbon, a significant magnetic entropy change ($\Delta S_M^{max}$ = 2.71 J/kgK) was obtained under a magnetic field change of 5 T. The highest $RC_{eff}$ value, which is a better criterion to evaluate the cooling efficiency, was obtained to be 88.89 J/kg for the x=1.
REFERENCES


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