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THE STRUCTURE AND MAGNETOCALORIC EFFECT OF MnCoGe ALLOY MODIFIED BY Nb

The aim of this work was to investigate the effect of partial substitution of Mn by Nb on structure and thermomagnetic properties in the (Mn, Nb)-Co-Ge alloy. The master alloys were prepared by arc-melting in an arc furnace with high purity of constituent elements under a low pressure of Ar. The prepared specimens were studied in as-cast state. The X-ray was performed by BRUKER D8 Advance diffractrometer with Cu Kα radiation. The analysis of the XRD pattern revealed coexistence of two orthorhombic phases with different lattice constants. The analysis of the temperature dependence of magnetizaton confirmed the XRD results and showed that produced material manifested two magnetic phase transitions corresponding to detected phases. The values of the Curie temperature were 275 and 325 K. The values of magnetic entropy change ΔS_M equaled 3.30 and 2.13 J/(kg K), respectively for recognized phases. Biphase structure of produced material allowed to reach relatively high refigeration capacity 307 J/(kg). Moreover, the analysis of field dependences of magnetic entropy change ($\Delta S_M = CB^n$) allowed to construct temperature dependence of exponent n. The analysis of elaborated n vs. T curve confirmed biphasic structure of produced material.

Keywords: magnetocaloric effect; Heusler alloys; X-ray diffraction; magnetic measurement

1. Introduction

The magnetocaloric effect (MCE) is observed in all ferromagnetic materials, which are exposed on changes of the external magnetic field [1]. The effect has been known for many years as adiabatic demagnetization. It was used to obtain temperatures below 1K, but it is not the only possibility of using this effect in magnetic systems [2].

A natural magnetocaloric material is pure Gd. The most popular magnetocaloric materials include pure Gd and its alloys [3], La (Fe, Si) 13 alloys [4,5] and manganites [6]. Recently, the research has focused on full Heusler [7] and semi Heusler [8] alloys. In recent years, research has been conducted on Heusler alloys such as: $(MnNiGe)_{1-x}$-$(FeCoGe)_x$ [9], $Co_{1-x}Cu_xMnSb$ [10], NiFeSb [11], $CoV_{1-x}MnSb$, $NiTi_{1-x}Mn_xSb$ [12], Co(Mn,Nb)Sb [13], $(Zr_{0.5}Hf_{0.5})Co(Sb_{0.85}Sn_{0.15})$ [14], $MnFeP_{1-x}Ax_x$ [15], MnCoGe [16]. The Heusler alloys are a group of chemical compounds and alloys, which are intesively studied due to their enormous magnetocaloric properties. Two different grades of Heusler alloys are known, half and full Heusler alloys. The general formula of full Heusler is described as: X_2YZ (where: X and Y – atoms from the minor group, Z – atoms from the main group) [17]. The full Heusler is characterized by: 2: 1: 1 stoichiometry, a Cu_2MnAl type structure and the $Fm\bar{3}m$ space group (No. 225, L21). The L21 structure contains four interpenetrating cubic wall-centered (fcc) subnets. The X atoms are in the 4a position (0,0,0), the Y atoms are in the 4b position (0.5,0.5,0.5) and the Z atoms are in the 8c position (0.25,0.25,0.25), these alloys are mostly metals. This structure is shown in Fig. 1. [18,19].

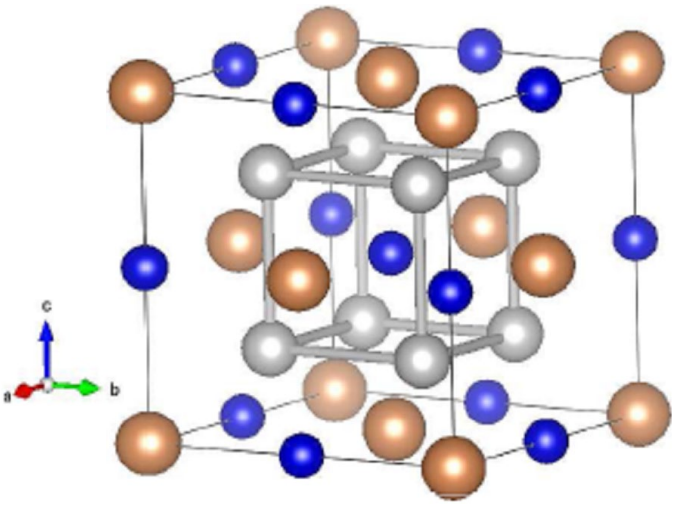

Fig. 1. Structure of the full Heusler phase [19]

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The formula describing a half-Heusler is written: XYZ. This type of Heusler alloys is characterized by: 1: 1: 1 stoichiometry, MgAgAs type structure and F$\bar{4}$3 m space group (No. 216, $C1_b$). The structure of $C1_b$ is obtained by removing one X location from the structure $L2_1$. The X atoms are in the 4a position (0,0,0), the Y atoms are in the 4b position (0.5,0.5,0.5), the Z atoms are in the 4c position (0.25,0.25,0.25), these alloys are semiconductors. This structure is shown in Fig. 2 [18,20].

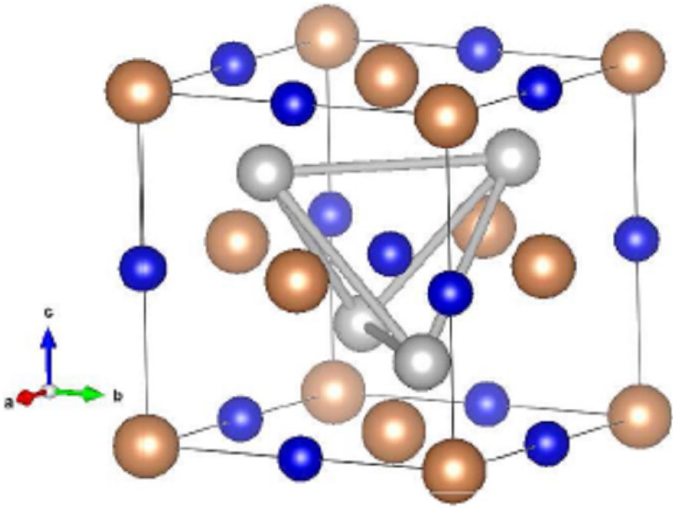

Fig. 2. Structure of the semi Heusler phase [20]

All of the tested alloys show a magnetocaloric effect and work at a temperature close to the room temperature. The results of the tested compounds show their potential application as an active magnetic regenerators in magnetic refrigerators. A literature review shows investigation based on substitution on Mn by Cr, Zr, Pd and others [21-23]. However, an effect of Nb alloying has not already been studied. According to that, the aim of this study was to investigate the effect of the partial substitution of Mn by Nb in the MnCoGe alloy and its influence of thermomagnetic properties.

2. Sample preparation and experimental details

The sample with a nominal composition of $Mn_{0.9}Nb_{0.1}CoGe$ was prepared by the arc melting of high purity elements in a protective atmosphere of Ar gas. The sample was remelted several times to ensure in its homogeneity. The XRD studies were performed using a Bruker D8 Advance diffractometer with CuKα radiation and the LynxEye semiconductor detector. The X-ray pattern was analyzed with the Bruker EVA software and supported by the Rietveld analysis using PowderCell 2.4 package [24]. The Magnetic measurements (the Curie temperature and magnetocaloric effect) were performed using a Quantum Design Physical Properties Measuring System (PPMS) model 6000, equipped to work with a wide range of magnetic fields and temperatures.

3. Results and discussion

Fig. 3 shows the XRD characteristics of the tested alloy. The analysis showed the coexistence of two orthorhombic phases with different crystal lattice parameters. The presence of orthorhombic phases suggests that the tested material is in a paramagnetic state.

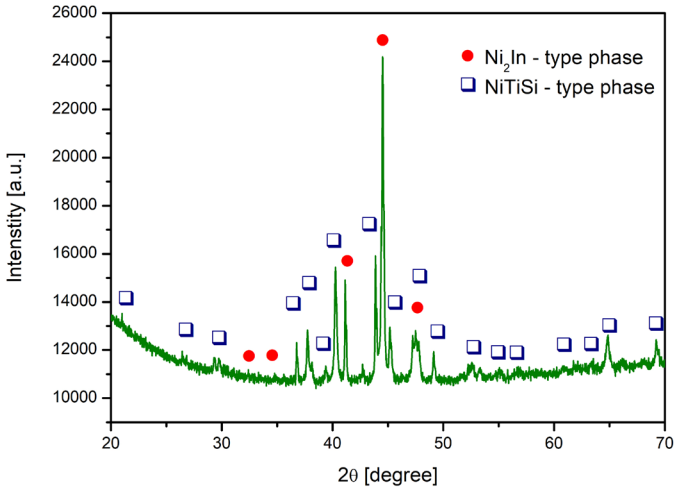

Fig. 3. XRD pattern of the tested alloy

Two different orthorhombic phases (Ni_2In, NiTiSi) both are from the Pnma space group, show a random distribution of elements in the structure. It is impossible to correctly identify which phase consists of niobium (Nb). The dependence of the magnetization on temperature should reveal two Curie temperatures in this material, which suggests the existence of two different phases with different lattice constant. The lattice constants of recognized phases were collected in TABLE 1. The curve $M = f(T)$ is presented in Fig. 4. and its first derivative.

TABLE 1

Lattice parameters (a, b, c) of phases detected in the investigated alloy

Phase	Lattice parameter		
	***a* [Å]**	***b* [Å]**	***c* [Å]**
Ni_2In	5.877	3.524	6.981
NiTiSi	5.463	3.989	6.994

The analysis of the dependence of magnetization on temperature revealed two Curie temperatures which are 275 and 325 K. The determination of the Curie temperature value confirmed the earlier assumptions that the material is in a paramagnetic state.

The dependence of magnetization on magnetic field collected over a wide temperature range was measured to determine the magnetocaloric effect (MCE). Based on the $M = f(T;H)$ curves, the change in magnetic entropy ΔS_M was calculated using the thermomagnetic Maxwell equation [25]:

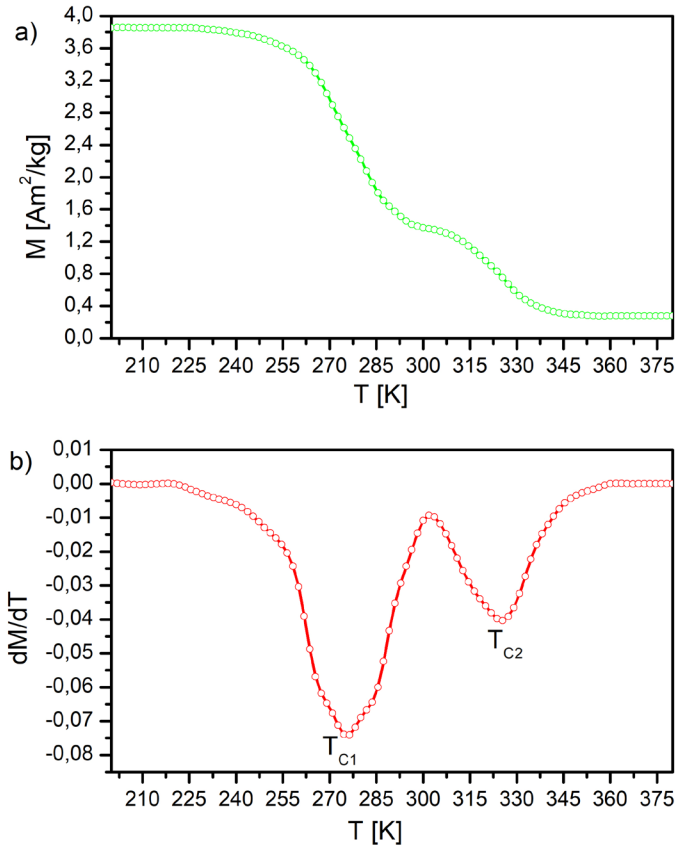

Fig. 4. The temperature dependence of the magnetization (a) and its first derivative of magnetization (b) for studied sample

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

Where: ΔS_M – the magnetic entropy change, M – magnetization, T – temperature, H – the magnetic field, μ_0 – the magnetic permeability of the vacuum. The ΔS_M values have been collected in TABLE 2. Fig. 5 shows the temperature dependences of the magnetic entropy change.

TABLE 2

The values of T_C (Curie temperature), ΔS_M (the magnetic entropy change) and RC (refrigeration capacity) revealed for all investigated samples

$Mn_{0.9}Nb_{0.1}CoGe$			
$\Delta(\mu_0 H)$	T_{C1} = 275 [K]	T_{C2} = 325 [K]	RC
[T]	ΔS_{M1} [J (kg K)$^{-1}$]	ΔS_{M2} [J (kg K)$^{-1}$]	[J kg^{-1}]
1	0.77	0.24	36
2	1.58	0.62	100
3	2.26	0.99	173
4	2.84	1.59	232
5	3.30	2.13	307

The parameter that we also use to characterize the magnetocaloric material is its refrigeration capacity (RC) described by the Wood-Potter relations [26]:

$$RC\left(\delta T,H_{\max}\right)=\int_{T_{cold}}^{T_{hot}}\Delta S_M\left(T,H_{\max}\right)dT \tag{2}$$

Where: RC is refrigeration capacity, $dT = T_{hot} - T_{cold}$ is the temperature range of the thermodynamic cycle (dT corresponds to fullwidth at half maximum of magnetic entropy change peak) and $H_{\max}$ is maximum value of external magnetic field. The RC values have been collected in TABLE 2.

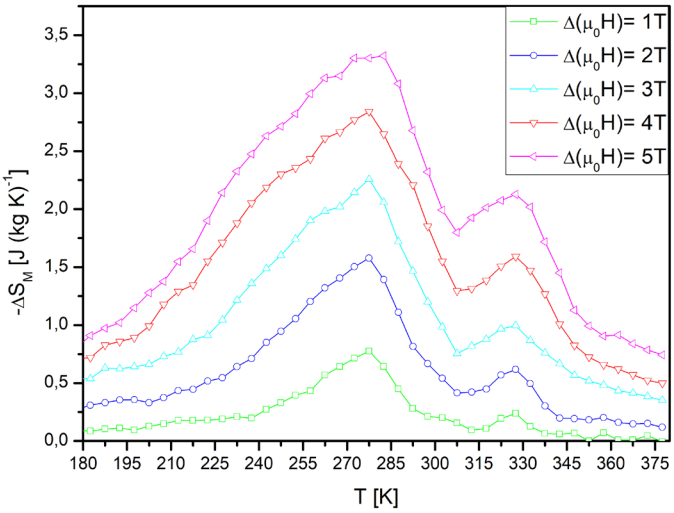

Fig. 5. The ΔS_M vs. T curve measured in various external magnetic fields

Two peaks are clearly seen in Fig. 5. The first peak is visible at around 275 K and the second peak at 325 K. These values correspond well with the Curie points revealed by the curve $M = f(T)$. The maximum value of ΔS_M reaches about 3.3 J/(kgK) due to the change of the external 5 T magnetic field. The obtained low value of the maximum magnetic entropy change is probably due to the second order phase transition. This shape of the curve $M = f(T)$ is expected due to the potential practical use of the produced alloy as an active element in magnetic refrigerator.

Fig. 6 shows the dependence of the field exponent (ΔS_M) n on temperature $n(T)$. Franco et al. in [27-29] showed that the maximum dependence of the magnetic field induction on the change in magnetic entropy can be described as the relationship [30]:

$$\Delta S_M = CB_{\max}^n \tag{3}$$

Where: C – depends on temperature, n – exponent depends on the magnetic state of the sample, $B_{\max}$ – maximum change of the external magnetic field induction, which corresponds to the maximum value of ΔS_M. As shown in articles [27-29]. The exponent n can be easily obtained by reconstructing the Eq. (3) as proposed in [31]:

$$\ln\Delta S_M = \ln C + n\ln B_{\max} \tag{4}$$

The exponent n is strongly dependent on the magnetic state of the sample. If the sample is in a ferromagnetic state then the value of the exponent n is equal to 1. When the sample

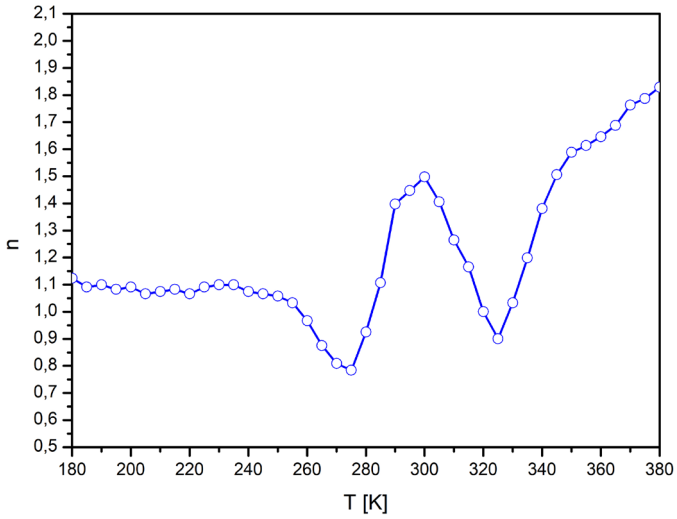

Fig. 6. Temperature dependence *n* calculated for the mean-field model

is above the Curie temperature, the value of the exponent n is equal to 2. At the Curie point, the exponent n is described by the formula [30]:

$$n = 1 + 1/\delta(1 - 1/\beta) \tag{5}$$

Where: δ and β – critical exponent. The condition is compliance with the Curie-Weiss law. The above conditions were formulated for materials with a second-order phase change. At low temperatures below T_C, the value of the exponent n is below 1. At $T = T_C$, the value of n has the minimum value. This may indicate that the magnetization curve depends on the temperature at the tested temperatures, and is not dependent on the field. In the peaks corresponding to the T_C, the value of the exponent n is less than 1. It can be seen in the graph that with the temperature increase above the Curie temperature, the value of the exponent n increases. It can be seen that the exponent n is strongly dependent on the temperature and changes with increasing magnetic field of the material [32]. The values of n for the temperature corresponding to the Curie temperature, as well as ΔS_M are 0.78 (T_C = 275 K, ΔS_M = 3.30 J(kg K)$^{-1}$) and 0.90 (T_C = 325 K, ΔS_M = 2.13 J(kg K)$^{-1}$). Above the first T_C the maximum value of n is 1.5, and above the second T_C the maximum value of n is 1.8.

In the works [32,33] studies were carried out on the compounds $MnCo_{0.98}Nb_{0.02}Ge$ [32] and $Mn_{0.96}Nb_{0.04}CoGe$ [33], the T_C value was 259.3K ($MnCo_{0.98}Nb_{0.02}Ge$) and 269 K ($Mn_{0.96}Nb_{0.04}CoGe$). The value of ΔS_M was respectively: 3 J(kg K)$^{-1}$ at $\Delta H = 5T$ ($MnCo_{0.98}Nb_{0.02}Ge$) and 2.95 J(kg K)$^{-1}$ at $\Delta H = 5T$ ($Mn_{0.96}Nb_{0.04}CoGe$). It can be seen that the T_C value in the $Mn_{0.9}Nb_{0.1}CoGe$ alloy is higher than in the mentioned alloys, and also in the case of the alloy tested in this article, there are two Curie temperatures, which the alloys did not show in the articles [32, 33]. The value of magnetic entropy determined in this article has a higher value than in the above-mentioned alloys.

4. Conclusions

This article examines the structure and thermomagnetic properties of the $Mn_{0.9}Nb_{0.1}CoGe$ alloy. The XRD studies of the material in as cast state revealed the existence of two orthorhombic structures at room temperature. The analysis of temperature dependence of magnetization and its first derivative showed two Curie points corresponding to the identified phases. Two overlapping peaks, corresponding to the two detected Curie points, were also measured depending on the temperature of the change in magnetic entropy. The maximum value of magnetic entropy change and refrigeration capacity reached 3.3 J(kg K)$^{-1}$ and 307 Jkg^{-1}, respectively. Produced material could be applied as an active magnetic regenerator in magnetic refrigerator.

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