ESOMAT 2009, 04001 (2009)
DOI:10.1051/esomat/200904001

Determining the liquidus and ordering temperatures of the ternary Ni-Mn-Ga and quaternary Ni-Mn-Ga-Fe/Cu alloys

I. Aaltio[1a], O. Söderberg[1], M. Friman[1], I. Glavatskyy[2], Y. Ge[1], N. Glavatska[2] and S-P. Hannula[1]

[1]Department of Materials Science and Engineering, Helsinki University of Technology, P.O. Box 6200, FI-02015 TKK, Espoo, Finland.
[2]Institute for Metal Physics, National Academy of Science of Ukraine, 36 Vernadsky blvd., UA-03680, Kiev, Ukraine.

Abstract. The high temperature transformations (e.g. liquidus, ordering temperature) of the alloys $Ni_{47.7}Mn_{31.2}Ga_{21.1}$, $Ni_{49.7}Mn_{28.7}Ga_{21.6}$, and $Ni_{49.6}Mn_{24.0}Ga_{26.6}$, $Ni_{47.3}Mn_{30.3}Ga_{20.3}Fe_{2.1}$, $Ni_{49.9}Mn_{28.3}Ga_{20.1}Fe_{1.7}$, $Ni_{51.3}Mn_{14.4}Ga_{26.3}Fe_{8.0}$, $Ni_{47.3}Mn_{25.5}Ga_{24.5}Cu_{2.7}$, $Ni_{48.3}Mn_{29.7}Ga_{21.1}Cu_{0.9}$, and $Ni_{49.4}Mn_{23.3}Ga_{25.6}Cu_{1.7}$ were studied for the practical melting and annealing purposes. At first the chemical compositions (SEM-EDS) and the martensitic and magnetic transition temperatures (DSC, ac magnetic susceptibility) of the alloys were determined. High temperature DSC measurements were made in argon with 10 K/min. Two first measurements were carried out in the solid state (301 - 1273 K) and in the third measurement the material was melted (max meas. temp. 1573 K). The ordering temperature was obtained from the measurements in the solid state. As the e/a ratio was above 7.53 the ordering temperature was in the range of 1019-1039 K, otherwise a clear change was observed. The variation in heating and cooling was less than 5 K with small quaternary additions, but alloying of 8% Fe increased this difference to 18 K. Alloys with close Ni/Mn/Ga-ratio showed only minor differences in solidus and liquidus temperatures, but if there was a clear change in the Ni/Mn-ratio even those alloys having close e/a ratios showed a clear difference in melting behavior. When Ni/Mn is 1.5-1.6 the liquidus was 1364±2 K, and with 1.7-1.8 it is 1384±5 K, while with higher values not clear region could be determined.

1. Introduction

Ni-Mn-Ga alloys have received interest because of their magnetic shape memory effect (MSME), as well as other functional properties such as giant magnetocalorimetry, conventional shape memory effect and superelasticity, magnetically assisted superelasticity, etc. [1]. It is well known that the crystal structures, properties and transformation temperatures of the martensites in the ternary alloys may vary considerably with their chemical composition [see, e.g., 2,3,4,5,6,7]. These properties can be influenced also by quaternary alloying [e.g., 8,9,10,11,12,13,14,15,16]. Fe-alloying has been shown to improve the ductility of the alloys and there are working MSM alloys, as well as polycrystalline high temperature shape memory alloys in this group [9]. Ni-Mn-Ga-Cu alloys are less studied and mainly for their magnetocaloric properties [17,18], but also as high temperature shape memory alloys [19]. In these alloys also MSME has been reported [20].

In order to obtain homogeneous crystal structure in these alloys, it is crucial that the annealing temperatures are selected based on the high temperature phase transition temperatures. Furthermore, for the alloy preparation also the melting and solidification temperatures are needed. According to [21,22,23], the critical transformations for the near-stoichiometric Ni-Mn-Ga alloys are the solidification to the disordered B2' structure and the solid state transition from B2' structure to the ordered, cubic $L2_1$ structure. The former one can be distinguished in the differential calorimeter measurement with a clear transformation peak, while the second one causes a small change of the slope or a minor peak, which can be detected only when the material is in a well-ordered state. So far, the high temperature behavior has been studied merely with the ternary alloys [21,22,23,24,25,26], and the detailed information concerning the quaternary alloys has not been available. Here, it is reported for alloys with a Fe- or Cu-addition. This data is compared with the respective information for the corresponding ternary alloys.

2. Experimental

[a]email: ilkka.aaltio@tkk.fi

Article available at http://www.esomat.org or http://dx.doi.org/10.1051/esomat/200904001

The studied alloys have different fabricating histories – alloys A1, A2, A3 and A8 were made with the modified Bridgman method at the Outokumpu Research Center in Finland; alloy A4 was fabricated at TKK using industrially pure ARMCO Fe and Ni-Mn-Ga master alloy by induction melting in argon [9], alloy A5 was fabricated at Adaptamat Ltd.; and alloys A6, A7 and A9 were prepared at IMP from the electrolytic pure Ni, Mn, Ga, and Fe or Cu [27]. Of these alloys the ternary alloy A2 and the quaternary alloys A5, A6 and A7 show the MSM effect [9,12,20]. All alloys were heat treated in vacuum quartz ampoules at 1273K for 48h and then at 1073K for 72h followed by air cooling.

Chemical analysis were performed by energy-dispersive spectrometer (EDS) attached to the scanning electron microscope (LEO-SEM) and by fluorescent spectroscopy. Temperatures of direct (M_S, M_F) and reverse (A_S, A_F) martensite transformation and the Curie points (T_C) were determined using the differential scanning calorimeter (Linkam-600) and the low-field ac magnetic susceptibility measurement. For the high temperature measurements in the temperature range of 301…1573 K, the Netzsch STA Jupiter 449C calorimeter was applied. Measurements were carried out in argon with 10 K/min. Two first measurements for each sample were made in the solid state up to 1273 K with a successive cooling to the ambient temperature, and the third measurement cycle was carried out up to 1573 K, i.e., above melting point, followed with cooling to the room temperature.

3. Results and discussion

The alloy compositions, valence electron concentrations, transformation temperatures of the martensitic and reverse reactions as well as the Curie points of the studied alloys are given in Table 1. The effect of the Fe- and Cu-alloying on the martensite transformation and the Curie temperature is discussed in detail elsewhere [9,12].

Table 1. Alloy compositions of the studied alloys, their phase transformation temperatures, the Curie points, valence electron concentrations both for the alloy in question and for its ternary Ni-Mn-Ga part.

Alloy Ni/Mn/Ga	Ni at%	Mn at%	Ga at%	X	X at%	e/a	M_s (K)	M_f (K)	A_s (K)	A_f (K)	T_c (K)
A1 2.26/1.48/1	47.7	31.2	21.1	-	-	7.587	305	303	313	314	371
A2 2.30/1.33/1	49.7	28.7	21.6	-	-	7.627	305	302	311	314	375
A3 1.86/0.90/1	49.6	24.0	26.6	-	-	7.438	205	195	257	262	367
A4 2.33/1.49/1	47.3	30.3	20.3	Fe	2.1	7.628	326	305	315	334	361
A5 2.48/1.41/1	49.9	28.3	20.1	Fe	1.7	7.710	323	319	325	333	386
A6 1.95/0.55/1	51.3	14.4	26.3	Fe	8.0	7.490	359	352	361	374	389
A7 1.93/1.04/1	47.3	25.5	24.5	Cu	2.7	7.547	329	328	336	340	357
A8 2.29/1.41/1	48.3	29.7	21.1	Cu	0.9	7.641	271	265	279	282	377
A9 1.93/0.91/1	49.4	23.3	25.6	Cu	1.7	7.526	339	333	333	340	352

The ordering temperature for the $L2_1$-B2' transformation [23] was established by observing the minor peaks or slope changes in the DSC curves of the first two measurements both during heating and cooling as well as during heating in the last measurement (insert of Figure 1). The obtained values are shown in Table 2. As the e/a ratio was above 7.53 the ordering temperature was in the range of 1019-1039 K, otherwise a clear change was observed. The variation in heating and cooling was less than 5 K with small quaternary additions, but 8% Fe-alloying increased this difference to 18 K. The highest value (1069 K) was obtained with the ternary A3 alloy exhibiting the lowest e/a value, 7.438, and the Ni/Mn ratio of 2. The lowest ordering temperature of 963 K is

connected to specimen A6 alloyed with 8.0 % Fe and having the e/a-ratio of 7.490 and Ni/Mn ratio of 3.6.

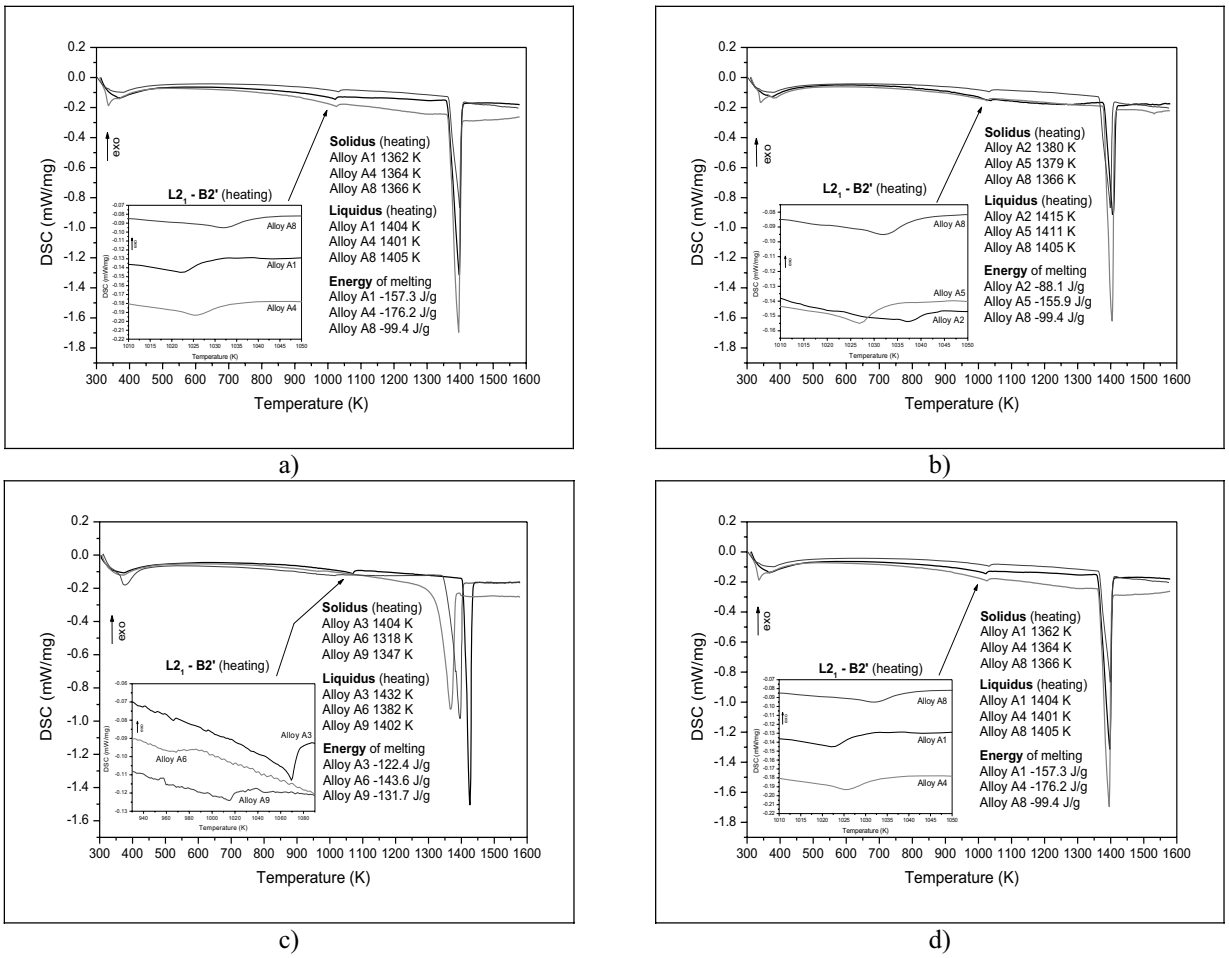

Fig. 1. Comparison of the heating curves during the melting cycle. (a) Alloys A1, A4 and A8, (b) Alloys A2, A5 and A8, (c) Alloys A3, A6 and A9, (d) Alloys A1, A7 and A9.

Table 2. The results of the high temperature DSC measurements. Subscripts: h = heating, c = cooling, sol = solidus, liq = liquidus.

	Alloy A1	**Alloy A2**	**Alloy A3**	**Alloy A4**	**Alloy A5**	**Alloy A6**	**Alloy A7**	**Alloy A8**	**Alloy A9**
$L2_1$-$B2'_h$ ± *deviation* (K)	1023 *± 0.5*	1039 *± 1.2*	1069 *±1.0*	1027 *± 0.8*	1027 *± 0.3*	963 *± 2.8*	1036 *± 1.5*	1033 *± 0.6*	1016 *± 0.3*
$B2'$-$L2_{1c}$ ± *deviation* (K)	1019 *± 1.4*	1034 *± 1.7*	1063 *±1.6*	1021 *± 0.7*	1021 *± 0.8*	945 *± 1.5*	1033 *± 4.4*	1029 *± 0.8*	1011 *± 0.2*
$Solidus_h$ - $T_{sol,h}$ (K)	1362	1380	1404	1364	1379	1318	1389	1366	1347
$Liquidus_h$ - $T_{liq,h}$ (K)	1404	1415	1432	1401	1411	1382	1423	1405	1402
Energy of melting (J/g)	-157.3	-88.1	-122.4	-176.2	-155.9	-143.6	-133.0	-99.4	-131.7
$Liquidus_c$ - $T_{liq,c}$ (K)	1359	1378	1400	1375	1372	1358	1395	1376	1362
$Solidus_h$ - $T_{sol,c}$ (K)	1344	1342	1384	1351	1355	1311	1375	1357	1345
Energy of solidification (J/g)	170.9	136.5	132.6	196.8	197.4	171.6	185.4	144.5	185
[$L2_1$-$B2'_h$]- [$B2'$-$L2_{1c}$] (K)	4	5	6	6	6	18	3	4	5
$T_{sol,h}$ - $T_{sol,c}$ (K)	18	38	20	13	24	7	14	9	2
$T_{liq,h}$ – $T_{liq,c}$ (K)	45	37	32	26	39	24	28	29	40
Difference energies (J/g)	13.6	48.4	10.2	20.6	41.5	28.0	52.4	45.1	53.3

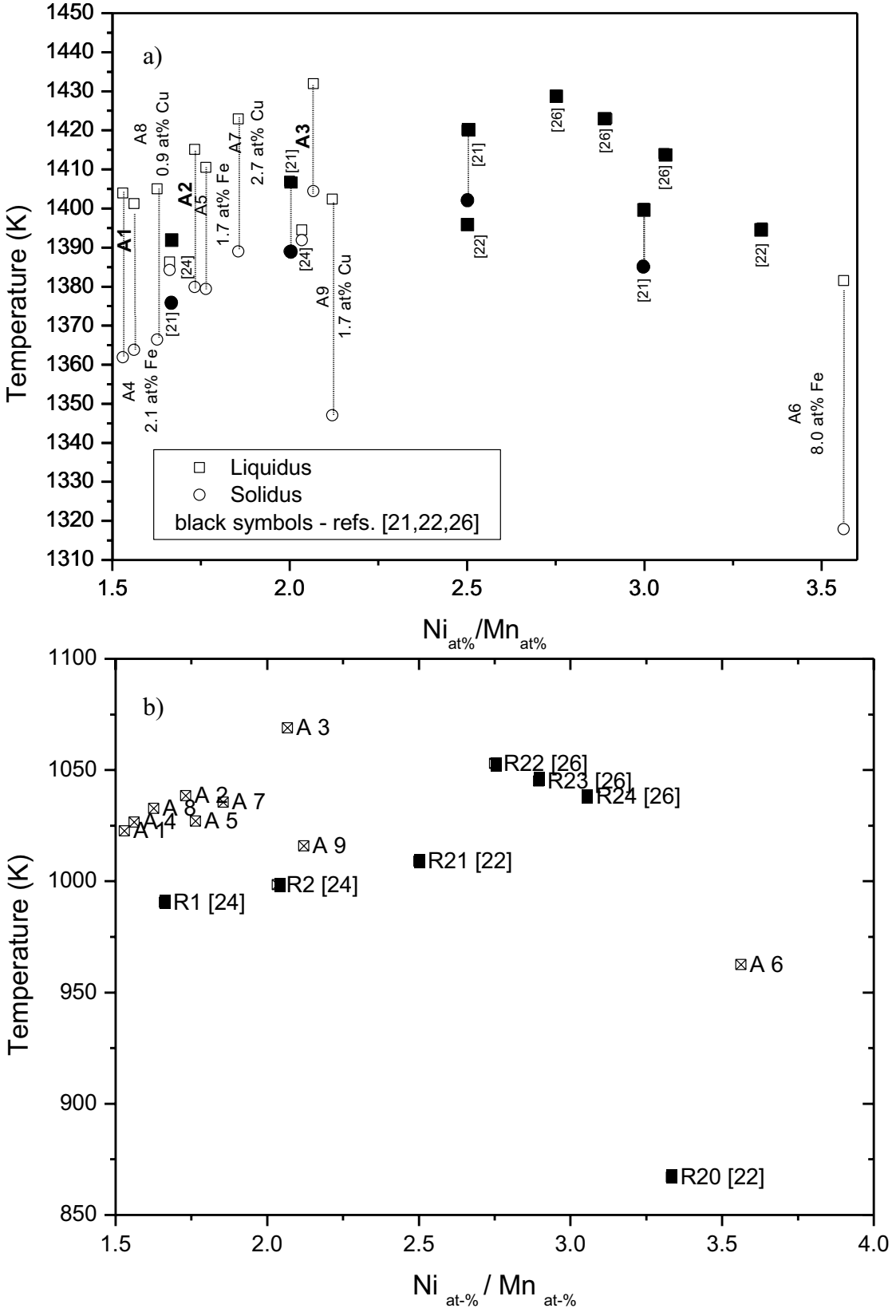

Fig. 2. (a) The liquidus and solidus temperatures and (b) the $L2_1$-B2' transition temperatures are plotted as a function of the $Ni_{at\%}/Mn_{at\%}$-ratio. □ = liquidus temperature during heating, ○= solidus temperature during heating, △ = $L2_1$-B2' temperature during heating. Note the break of x-axis in the figures. Closed symbols shows values reported in the literature.

Figures 1a-c show the DSC curves measured during the heating part of the melting cycle. These values are used for comparison of the materials since the original composition is expected to preserve as shown in [23,24]. After melting a clear shift of the transformation temperatures is observed during cooling (Table 2) due to the compositional change [23]. In Figures 1a and 1b alloys with quite similar ternary Ni-Mn-Ga part, i.e. close $(e/a)_t$, show only minor differences in the $T_{sol.h}$ and $T_{liq,h}$. When the ternary parts deviate from each other (Figs. 1c and 1d) more variation can be observed in the phase transformation temperatures, even though the e/a values of the alloys can be rather close to each other, for example alloys A1 and A9. When compared to the literature values shown in Figure 2a by closed symbols, the solidus-liquidus region in the present measurements is rather wide. For the quaternary alloys this is reasonable as alloying usually widens the transformation region. Some deviation for the $L2_1$-B2' temperatures shown in [24] is also observed now. Also, the variations in $L2_1$-B2' transition temperatures in the present study are to some extent larger even when the other phase transformations of the alloys are rather close to each other. However, the obtained results confirm that the generally applied homogenization temperature around 1273 K is quite appropriate and also the commonly used high temperature annealing at 1023 K is close to the $L2_1$-B2' transition temperature of the most of the here studied alloy, even though still on the B2' side.

4. Conclusions

The high temperature transformations and transitions temperatures for nine Ni-Mn-Ga-(X) alloys, where X is either Fe or Cu were determined. It is shown that with the small amounts of the quaternary element, the main factor influencing the transformation temperatures is the nickel/manganese-ratio of the material.

Acknowledgements

The Academy of Finland is acknowledged for the funding of the present work.

References

[1] O. Söderberg, I. Aaltio, Y. Ge, O. Heczko, S-P. Hannula, Mat. Sci. Eng. A **481-482**, 80 (2008).
[2] V.A. Chernenko, E. Cesari, V.V. Kokorin, I.N. Vitenko, Scr. Metall. Mater. **33**, 1239 (1995).
[3] N. Lanska, O. Söderberg, A. Sozinov, Y. Ge, K. Ullakko, V.K. Lindroos, J. Appl. Phys. **95**, 8074 (2004).
[4] P. Entel, V.D. Buchelnikov, V.V. Khovailo, A.T. Zayak, W.A. Adeagbo, M.E. Gruner, H.C. Herper and E.F. Wassermann, J. Phys. D: Appl. Phys. **39**, 865 (2006).
[5] Y.F. Wang, J.M. Wang, C.B. Jiang, H.B. Xu, Acta Metall. Sin. **19**, 171 (2006).
[6] C. Seguí, J. Pons, E. Cesari, Acta Mat. **55**, 1649 (2007).
[7] E. Cesari, J. Font, J. Muntasell, P. Ochin, J. Pons and R. Santamarta, Scripta Mat. **58**, 259 (2008).
[8] V.V. Khovailo, V.A. Chernenko, A.A. Cherechukin, T. Takagi, T. Abe, J. Magn. Magn. Mater. **272**, 2067 (2004).
[9] K. Koho, O. Söderberg, N. Lanska, Y. Ge, X. Liu, L. Straka, J. Vimpari, O. Heczko, V.K. Lindroos, Mat. Sci. Eng. A **378**, 384 (2004).
[10] H.B. Xu, Y. Li, C.B. Jiang, Mat. Sci. Eng. A **438-440**, 1065 (2006).
[11] I. Glavatskyy, N. Glavatska, O. Söderberg, S.-P. Hannula, J.-U. Hoffmann, Scripta Mat. **54**, 1891 (2006).
[12] R. Wroblewski, M. Leonowicz, Z. Zengqi, J. Liping: J. Magn. Magn. Mat. **316**, E595 (2007).
[13] H.B. Wang, C. Liu, Y.C. Lei, W. Cai, J. Alloys Compd. **465**, 458 (2008).
[14] D.E. Soto-Parra, F. Alvarado-Hernandez, O. Ayala, R.A. Ochoa-Gamboa, H. Flores-Zuniga, D. Rios-Jara, J. Alloys Compd. **464**, 288 (2008).
[15] B.R. Gautam, I. Dubenko, J.C. Mabon, S. Stadler, N. Ali, J. Alloys Compd. **472**, 35 (2009).

[16] C. Picornell, J. Pons, E. Cesari, J. Dutkiewicz, Intermet. **16**, 751 (2008).
[17] S. Stadler, M. Khan, J. Mitchell, A. Naushad, A.M. Gomes, I. Dubenko, A.Y. Takeuchi, A.P. Guimarães, Appl. Phys. Lett. **88**, 192511 (2006).
[18] A.M. Gomes, M. Khan, S. Stadler, N. Ali, I. Dubenko, A.Y. Takeuchi, A.P. Guimarães, J. Appl. Phys. **99**, 08Q106 (2006).
[19] Y.Q. Ma, S.Y. Yang, W.J. Jin, X.J. Liu, J. Alloys Compd. **471**, 570 (2009).
[20] I. Glavatskyy, N. Glavatska, J.-U. Hoffmann, O. Söderberg, S-P. Hannula, Scripta Mat. **56**, 565 (2007).
[21] D.L. Schlagel , Y.L. Wu, W. Zhang, T.A. Lograsso, J. Alloys Compd. **312**, 79 (2000).
[22] R.W. Overholser, M. Wuttig, D.A. Neuman, Scripta Mat. **40**, 1099 (1999).
[23] V.V. Khovailo, T. Takagi, A.N. Vasilev, H. Miki, M. Matsumoto, R. Kainuma, Phys. Stat. Sol. (a) **183**, R1 (2001).
[24] O. Söderberg, M. Friman, A. Sozinov, N. Lanska, Y. Ge, M. Hämäläinen, V. K. Lindroos, Z. Metallkd. **95**, 724 (2004).
[25] U. Gaitzsch, M. Pötschke, S. Roth, N. Mattern, B. Rellinghaus, L. Schultz, J. Alloys Compd. **443**, 99 (2007).
[26] B. Ingale, R. Gopalan, M. Rajasekhar, S. Ram, J.Alloys Compd. **475**, 276 (2009).
[27] N. Glavatska, A. Dobrinskiy, I.. Glavatskyy, I. Urubkov, O. Söderberg, S-.P. Hannula, Functional Mat. **13**, 331 (2006).