

## ISOTHERMAL SECTION OF THE Ni–Mn–Sb TERNARY SYSTEM AT 773K

W.-Q. Ao <sup>a,b</sup>, H.-Z. Yu <sup>b</sup>, F.-L. Liu <sup>b</sup>, F.-S. Liu <sup>b,#</sup>, J.-Q. Li <sup>b</sup>, Y. Du <sup>a,\*</sup>, S.-H Liu <sup>a</sup>, C.-Y. Shi <sup>a</sup>

<sup>a</sup> State Key Laboratory of Powder Metallurgy, Central South University, Changsha, China

<sup>b</sup> College of Materials Science and Engineering, Shenzhen University, Guangdong Research Center for Interfacial Engineering of Functional Materials and Shenzhen Key Laboratory of Special Functional Materials, Shenzhen, China

(Received 04 November 2018; accepted 27 March 2019)

### Abstract

The isothermal section of the Ni–Mn–Sb ternary system at 773 K was measured by means of 117 alloys which were analyzed by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), and electron probe microanalysis (EPMA) techniques. The existence of 7 binary compounds, namely NiMn, Mn<sub>2</sub>Sb, MnSb, NiSb<sub>2</sub>, NiSb, Ni<sub>3</sub>Sb<sub>2</sub>, Ni<sub>3</sub>Sb and 2 ternary compounds, namely Ni<sub>2</sub>MnSb and NiMnSb were confirmed for this isothermal section. The four binary compounds Ni<sub>3</sub>Sb (Cu<sub>3</sub>Ti structure, Pmmn space group), Ni<sub>3</sub>Sb<sub>2</sub> (Ni<sub>3</sub>Sb<sub>2</sub>-type structure, C2 space group), NiSb<sub>2</sub> (FeS<sub>2</sub>-type structure, Pnm space group) and Mn<sub>2</sub>Sb (Cu<sub>2</sub>Sb-type structure, P4/nmm space group) in the binary systems Ni–Sb and Mn–Sb were stoichiometric compounds, the homogeneity ranges of which were negligible. However the five single phases in the Ni–Mn system and the two binary compounds MnSb and NiSb showed more or less homogeneity ranges formed by substitution of Mn and Sb for Ni atom. The Heusler compound  $\mu$  (Ni<sub>2</sub>MnSb) has L21-type ordered structure with space group Fm-3m,  $a = 0.6017$  nm. And the crystal structure for the Half-Heusler compound  $\kappa$  (NiMnSb) is C1b-type (F-43m) with  $a = 0.5961$  nm. The approximate homogeneity ranges of the two ternary compounds  $\mu$  and  $\kappa$  at 773 K were investigated.

**Keywords:** Ni–Mn–Sb; Ternary system; Phase diagram; Metals and alloys

### 1. Introduction

The magnetocaloric effect (MCE) is an intrinsic property of magnetic material, which has attracted much attention for its potential application in magnetic refrigeration. A large MCE usually occurs as the result of first-order magnetic transition in materials, such as Gd–Si–Ge [1], La–Fe–Si [2], and Fe–Mn–P–As [3, 4]. To date, the large inverse MCE have been reported in Ni–Mn based Heusler alloys, such as Ni–Mn–Sn [5], Ni–Mn–In [6, 7], and Ni–Mn–Sb [8], which undergoes a first order structure transition (martensitic transition) from a high-symmetry austenitic phase to a low-symmetry martensitic phase with an abrupt drop of magnetization. The large MCE has been studied in compounds doping with Si, Ga, Ge and Co in Sb site in Ni–Mn–Sb system [9–13]. Understanding the phase relationships of Ni–Mn–Sb system is helpful for the development of relative materials. Up to now, no phase diagram containing the whole range of the Ni–Mn–Sb system has been

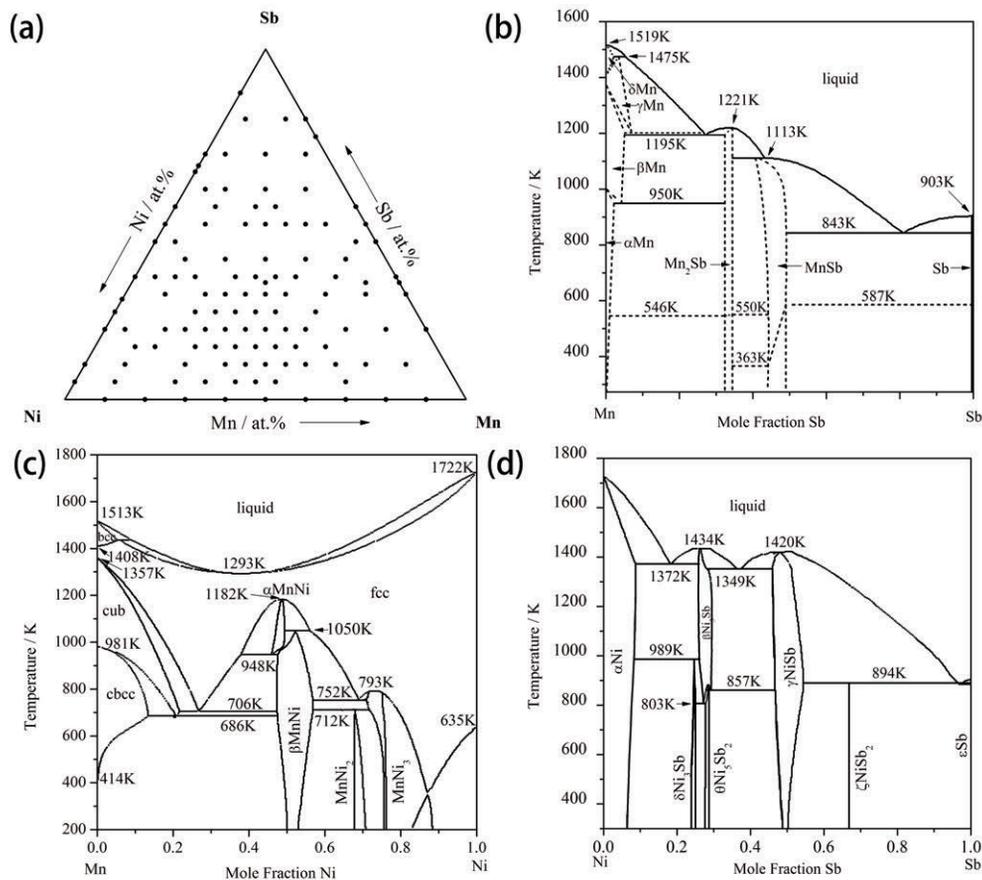
constructed. In this work, we investigated the phase equilibria in the Ni–Mn–Sb ternary system at 773 K.

In the ternary Ni–Mn–Sb system, the phase diagrams in all three sub-binary systems Ni–Mn [14–17], Mn–Sb [18] and Ni–Sb [19, 20] have been well investigated. All three sub-binary systems were shown in Fig.1.

The binary diagram of the Ni–Mn system has been researched by many groups. Tsiuplakis and Kneller [14] investigated the Ni–Mn binary system in which eight compounds NiMn<sub>3</sub>, NiMn<sub>2</sub>, NiMn ( $\eta$ ), NiMn ( $\eta'$ ), NiMn ( $\eta''$ ), Ni<sub>2</sub>Mn ( $\xi$ ), Ni<sub>2</sub>Mn ( $\xi'$ ), and Ni<sub>3</sub>Mn were found. After that, Coles [15] reinvestigated the Ni<sub>50</sub>Mn<sub>50</sub> region and showed that not so many phases existed at the equiatomic composition between 753 and 903 K, as stated by Tsiuplakis and Kneller. In Coles's and Ding's papers [15–16], actually only one compound existed in the equiatomic region between 773 K and 923 K. According to C. Guo's paper [17], there were four intermetallic compounds in Ni–Mn system:  $\alpha$ NiMn (B2 type structure),  $\beta$ NiMn (L1<sub>0</sub> type

\*Corresponding author: \* yong-du@csu.edu.cn; # fsliu@szu.edu.cn





**Figure 1.** The nominal alloy compositions in the Ni-Mn-Sb ternary system prepared in this work and the three binary phase diagrams Ni-Mn [17], Mn-Sb [18] and Ni-Sb [20]

structure),  $\text{Ni}_2\text{Mn}$  and  $\text{Ni}_3\text{Mn}$ , in which only  $\beta\text{NiMn}$  existed stably at 773 K. We also confirmed that only  $\beta\text{NiMn}$  compound was stable at 773 K in Ref. [21].

For the Mn-Sb binary system [18], there were two compounds –  $\text{MnSb}$ , and  $\text{Mn}_2\text{Sb}$  with some solid solution ranges at 773 K. The Ni-Sb binary system was reported by Cha [19] in 1990 and lately revised by Zhang [20] in 2008. The main difference between them was that the chemical formulation for the compounds in the region of 20-30 at.% Sb was different. In Ref. [19], there were five intermetallics, and the nominal compositions were  $\text{Ni}_3\text{Sb}$ ,  $\text{Ni}_5\text{Sb}_2$  (HT),  $\text{Ni}_7\text{Sb}_3$  (LT),  $\text{NiSb}$ , and  $\text{NiSb}_2$ . Zhang revised this binary system by combining lots of experimental information, namely the five intermetallics as  $\delta\text{Ni}_3\text{Sb}$ ,  $\beta\text{Ni}_3\text{Sb}$  (HT),  $\theta\text{Ni}_3\text{Sb}_2$  (LT),  $\gamma\text{NiSb}$  and  $\zeta\text{NiSb}_2$ , respectively [20]. According to Zhang's assessment, four intermetallics, except for the  $\beta\text{Ni}_3\text{Sb}$  (HT) phase, existed at 773 K in Ni-Sb binary system. Two ternary compounds  $\text{Ni}_2\text{MnSb}$  and  $\text{NiMnSb}$  in the Ni-Mn-Sb ternary system have been reported [22, 23]. Crystallographic data for all the intermetallic compounds related to this paper were taken from Ref. [24] and showed in Table 1.

## 2. Experimental

All the Ni-Mn-Sb alloys were prepared by melting in pure argon atmosphere, using a water-cooled copper tray and a non-consumable W electrode. The Mn, Ni, and Sb metals were used as raw materials, the purity is higher than 99.9%. Ti was used as an oxygen getter during the preparing process. The samples were melted three times to ensure complete melt and homogeneous composition. 117 alloy ingots were prepared. As Sb and Mn evaporate, additional 2 - 3% Sb and Mn were added to compensate losses during arc-melting, especially at high Sb and Mn content. The weight loss of the ingots was less than 1 wt.%. The melted ingots were sealed in vacuum quartz tubes and then put in a muffle furnace for homogenizing heating at different temperatures to reach fine homogenization. The heat-treating temperature for the alloys was selected by the phase diagrams of the Mn-Ni, Ni-Sb and Mn-Sb systems and the differential thermal analysis (DTA) result for some key alloys. The homogenization heating was performed at 873 K for 20 days for the Sb-rich alloys

**Table 1.** Crystallographic data for the compounds in the Ni-Mn-Sb system

Compounds	Space group	Structure type	Lattice parameters (Å)			Reference
			a	b	c	
$\beta$ NiMn	I4/mmm	AuCu	3.723		3.52	[24]
MnSb	P6 <sub>3</sub> /mmc	NiAs	4.14		5.789	[24]
Mn <sub>2</sub> Sb	P4/nmm	Cu <sub>2</sub> Sb	4.08		6.56	[24]
NiSb <sub>2</sub>	Pnmm	FeS <sub>2</sub>	5.182	6.316	3.84	[24]
NiSb	P6 <sub>3</sub> /mmc	NiAs	3.935		5.136	[24]
Ni <sub>5</sub> Sb <sub>2</sub>	C2	Ni <sub>5</sub> Sb <sub>2</sub>	1.294	5.427	11.456	[24]
Ni <sub>3</sub> Sb	Pmmn	Cu <sub>3</sub> Ti	5.32	4.28	4.514	[24]
Ni <sub>2</sub> MnSb	Fm $\bar{3}$ m	L2 <sub>1</sub>	5.982			[24]
NiMnSb	F $\bar{4}$ 3m	C1 <sub>b</sub>	5.913			[24]

with more than 40 at.% Sb, and 1173 K for 15 days for the the rest of the specimens. Then all of the ingots were cooled to 773 K at the rate of 10 K/min, and held at 773 K for 30 days. All ingots were quenched in liquid nitrogen after heat-treating process. Most ingots were cut into two parts for XRD analysis and morphology observation.

The alloys were ground in an agate mortar into micrometer powder for X-ray diffraction. The phases in each sample were confirmed through XRD analysis using a Bruker diffractometer, the type of D8 Advance SS/18kW and with Cu-K $\alpha$  radiation at 40 kV, 200 mA. The data were obtained in the range of 2 $\theta$  from 20° to 80° at a step length of 0.02°. The phase analysis and structure refinement were carried out using the JADE 6.0 and Topas 3.0 softwares. After standard metallographic specimen preparation, the micro-morphology and the compositions of each phase were measured by EPMA (JXA-8530F, JEOL, Japan). Pure elements Mn, Ni and Sb were used as standards and the EPMA measurements were performed at 20.0 kV. The microstructures and energy dispersive (EDS) spectroscopy analyses were carried out using a Hitachi S-4700N VP-SEM scanning electron microscopy (SEM).

### 3. Results and discussion

#### 3.1 Phase analysis and identification

Phase identification was performed based on the Rietveld refinement results and equilibrium phase composition determined by EPMA and EDS techniques. In this work the XRD analysis of the ingots in the boundary binary systems confirmed the existence of seven binary compounds,  $\beta$ NiMn in the Ni-Mn system, Mn<sub>2</sub>Sb and MnSb in the Mn-Sb system, NiSb<sub>2</sub>, NiSb, Ni<sub>5</sub>Sb<sub>2</sub> and Ni<sub>3</sub>Sb in the Ni-Sb system at 773 K, in a fine agreement with those reported in this system [17-20]. Two ternary compounds Ni<sub>2</sub>MnSb and NiMnSb existed in the 773

K isothermal section in this system. The PDF files for the compounds above-mentioned can be found on JCPDS PDF cards (2004).

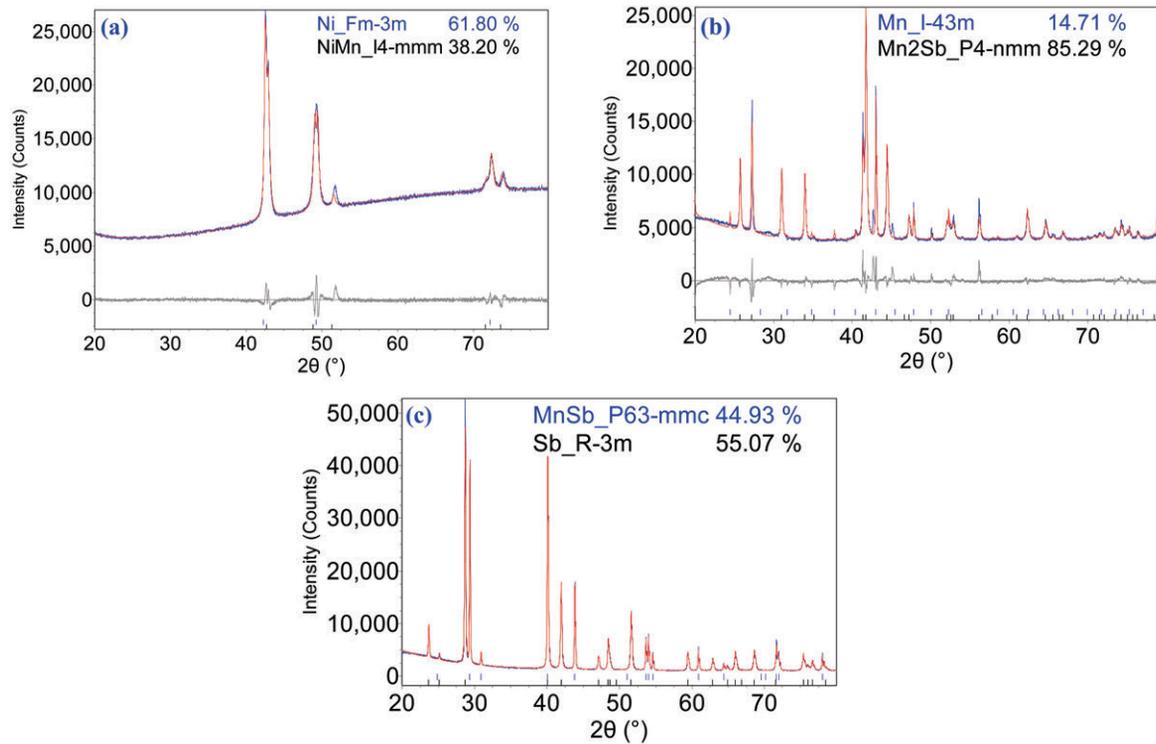
Three representative XRD patterns for the alloys on the Ni-Mn and Mn-Sb boundary were presented in Fig.2. It can be seen that the three alloys Mn<sub>0.6</sub>Ni<sub>0.4</sub>, Mn<sub>0.8</sub>Sb<sub>0.2</sub>, Mn<sub>0.25</sub>Sb<sub>0.75</sub> were located in the two-phase regions of  $\alpha$ Ni +  $\beta$ NiMn,  $\alpha$ Mn + Mn<sub>2</sub>Sb and MnSb +  $\epsilon$ Sb, respectively, from which, the three binary compounds  $\beta$ NiMn, Mn<sub>2</sub>Sb and MnSb were confirmed.

For the Ni-Sb binary system, 4 binary compounds NiSb<sub>2</sub>, NiSb, Ni<sub>5</sub>Sb<sub>2</sub> and Ni<sub>3</sub>Sb were confirmed at 773 K. In earlier time, P. Nash found a low-temperature phase  $\theta$ Ni<sub>7</sub>Sb<sub>3</sub> [19] in Ni-Sb system, but the later research of Y.B. Zhang [20] and C.H. Li [25] showed that this low-temperature phase's real equilibrium composition should be Ni<sub>5</sub>Sb<sub>2</sub>. The Ni<sub>5</sub>Sb<sub>2</sub> phase was confirmed in this work, which was well agreed with the later research results.

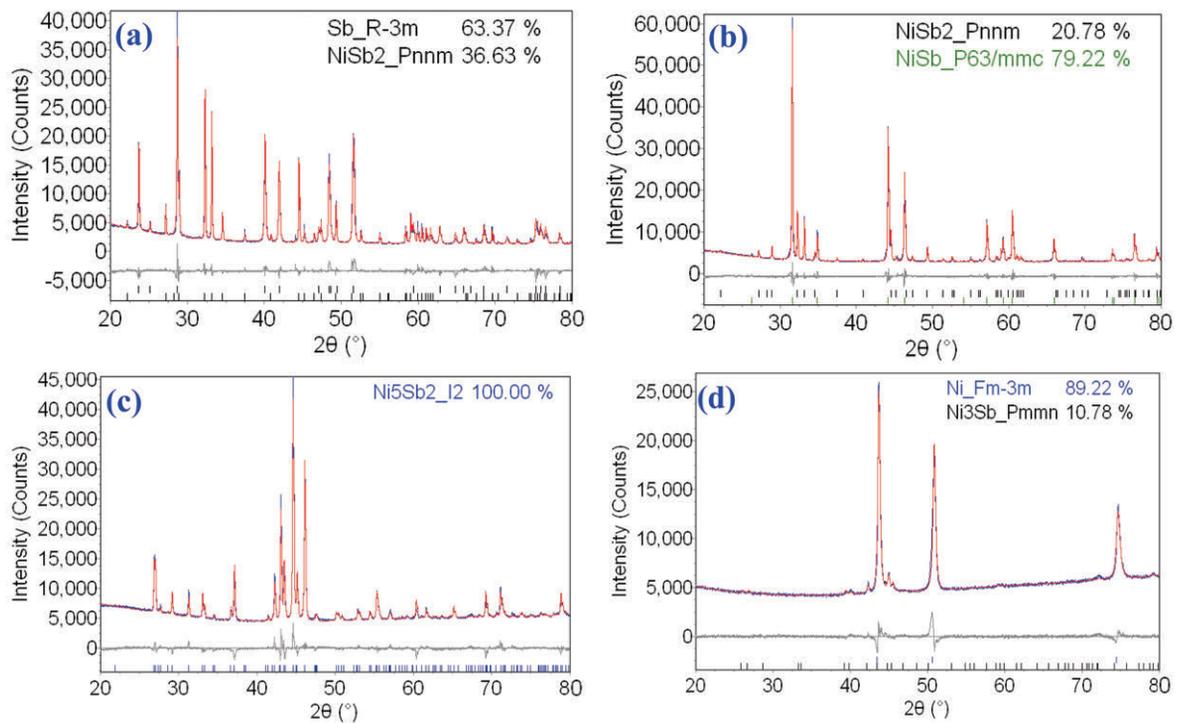
Several representative Rietveld structure refinement results for the compounds on Ni-Sb binary system were shown in Fig.3. According to the patterns above, we can see that the Ni<sub>0.12</sub>Sb<sub>0.88</sub>, Ni<sub>0.45</sub>Sb<sub>0.55</sub>, Ni<sub>0.72</sub>Sb<sub>0.28</sub>, and Ni<sub>0.9</sub>Sb<sub>0.1</sub> alloys were located in the phase regions of Sb+NiSb<sub>2</sub>, NiSb+NiSb<sub>2</sub>, Ni<sub>5</sub>Sb<sub>2</sub> and  $\gamma$ Ni+Ni<sub>3</sub>Sb, respectively, from which, the four binary compounds NiSb<sub>2</sub>, NiSb, Ni<sub>5</sub>Sb<sub>2</sub> and Ni<sub>3</sub>Sb were confirmed in the Ni-Sb binary boundary at 773 K.

Two ternary compounds, Ni<sub>2</sub>MnSb and NiMnSb, were verified in the Ni-Mn-Sb ternary system at 773 K. The Heusler alloy Ni<sub>2</sub>MnSb has L2<sub>1</sub>-type totally ordered structure [22] (S.G. Fm-3m, a = 0.6011 nm), in which, Ni atoms located at all the apex angle positions of the 8 little cubes while 4 Mn atoms and 4 Sb atoms occupied the 8 cubic center positions alternately and orderly (Fig.4(a)). The Half-Heusler alloy NiMnSb has C1<sub>b</sub>-type ordered structure [23] (S.G. F-43m, a = 0.5932 nm), in which, half of the Ni atoms which were located in the middle of the large

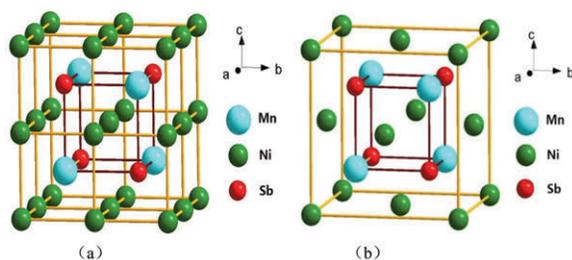




**Figure 2.** Representative XRD patterns of the compounds (a)  $Mn_{0.6}Ni_{0.4}$  alloy; (b)  $Mn_{0.8}Sb_{0.2}$  alloy; (c)  $Mn_{0.25}Sb_{0.75}$  alloy, in the binary regions of  $\alpha Ni + \beta NiMn$ ,  $\alpha Mn + Mn_2Sb$  and  $MnSb + \epsilon Sb$ , respectively



**Figure 3.** Rietveld structure refinement results for the XRD patterns of the compounds (a)  $Ni_{0.12}Sb_{0.88}$  alloy; (b)  $Ni_{0.45}Sb_{0.55}$  alloy; (c)  $Ni_{0.72}Sb_{0.28}$  alloy; (d)  $Ni_{0.9}Sb_{0.1}$  alloy



**Figure 4.** The crystal structure of (a) the Heusler alloy  $Ni_2MnSb$  ( $L_{21}$ -type structure) and (b) the Half-Heusler alloy  $NiMnSb$  ( $C1_b$ -type structure)

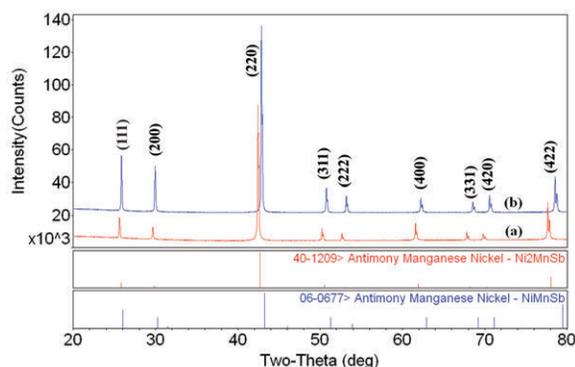
cube and at the middle of the 12 edges of the cube (Fig.4(b)), contrasting with the compound  $Ni_2MnSb$  were missing.

The XRD patterns of the compounds  $Ni_2MnSb$  and  $NiMnSb$  were shown in Fig.5. The biggest difference between them was the relative diffraction peak intensity of the first and second peak. In  $Ni_2MnSb$  phase the intensity of the (111) lattice plane was almost twice of the (200) plane, while in  $NiMnSb$  phase, they were nearly the same. The space group and structure type for  $Ni_2MnSb$  was S.G.Fm-3m,  $L_{21}$ -type. And those for  $NiMnSb$  was S.G.F-43m,  $C1_b$ -type. Table.2 showed the Rietveld refinement data result of their XRD patterns. From the tab.2 we can see that the Rietveld refinement factors were so small and the Rietveld result was reliable.

### 3.2 Determination of the phase regions and homogeneity ranges

By comparing the XRD patterns analysis and the EPMA or EDS compositional results, the phase compositions in each alloy were identified and the phase homogeneity regions in this system were determined. The XRD patterns of typical alloys in this isothermal section were shown in Fig.6. We can see that the two alloys of sample 6#- $Ni_{0.15}Mn_{0.15}Sb_{0.7}$  and 47#- $Ni_{0.1}Mn_{0.7}Sb_{0.2}$  (labeled with A and B in Fig.9) were located in the ternary regions of Sb + MnSb +  $NiSb_2$ ,  $NiMnSb + Mn_2Sb + \alpha Mn$ , respectively.

Fig.7 showed the typical Rietveld structure refinement results and the SE (Secondary electron) images for 59# -  $Ni_{0.3}Mn_{0.3}Sb_{0.4}$  and 60# -



**Figure 5.** XRD patterns for the samples with composition of (a)  $Ni_{0.50}Mn_{0.25}Sb_{0.25}$  and (b)  $Ni_{0.33}Mn_{0.34}Sb_{0.33}$

$Ni_{0.2}Mn_{0.4}Sb_{0.4}$  (labeled with capital letter C and D in Fig.9) compounds, from which we can see that this two alloys were located in the phase regions of  $NiMnSb + NiSb + MnSb$  and  $NiMnSb + MnSb$ , and the XRD results were in good agreement with the EDS results.

Fig.8 was the typical Rietveld structure refinement results for the XRD patterns and BSE images for EPMA results of the 70#- $Ni_{0.6}Mn_{0.25}Sb_{0.15}$ , 79# -  $Ni_{0.45}Mn_{0.25}Sb_{0.3}$ , 58#-  $Ni_{0.4}Mn_{0.2}Sb_{0.4}$  and 40#-  $Ni_{0.2}Mn_{0.7}Sb_{0.1}$  compounds (labeled with capital letter E to H in Fig.9), from which we can see that the four alloys were located in the phase region of  $Ni_2MnSb + \gamma Ni$ ,  $Ni_2MnSb + NiSb$ ,  $NiMnSb + NiSb$ , and  $NiMnSb + \beta Mn$ , respectively. The EPMA images, presented in Fig. 8(b), indicated that the dark region was recognized as  $\gamma Ni$  phase and the grey region as  $Ni_2MnSb$  phase. The EPMA images in Fig. 8(d) showed that the major phase was  $Ni_2MnSb$  (dark matrix) and the minor phase was  $NiSb$  (white slice). In the same way, it was verified that the dark region was  $NiMnSb$  and the grey region was  $NiSb$  in Fig. 8(f), while the dark matrix was  $\beta Mn$  and the grey region was  $NiMnSb$  in Fig. 8(h). The XRD analysis was in good agreement with the EPMA results. From Figs. 8b and 8d, as well as Figs. 8f and 8h, we can see that the contrast of the  $Ni_2MnSb$  and  $NiMnSb$  phases is drastically changing. This is because the signal intensity in EPMA picture is proportional with the average atomic number Z. The average Z values of

**Table 2.** Rietveld refinement result for the XRD patterns for  $Ni_2MnSb$  and  $NiMnSb$  compounds

Phase	$R_{exp}$	$R_{wp}$	$R_B$	Gof	a (nm)	Atom	Site	x	y	z	Occ.
$Ni_2MnSb$	1.43%	5.44%	5.25%	3.81	0.6011(3)	Mn1	4a	0	0	0	1
						Ni1	8c	1/4	1/4	1/4	1
						Sb1	4b	1/2	1/2	1/2	1
$NiMnSb$	1.89%	7.25%	5.55%	3.83	0.5932(3)	Mn1	4c	1/4	1/4	1/4	1
						Ni1	4a	0	0	0	1
						Sb1	4d	3/4	3/4	3/4	1



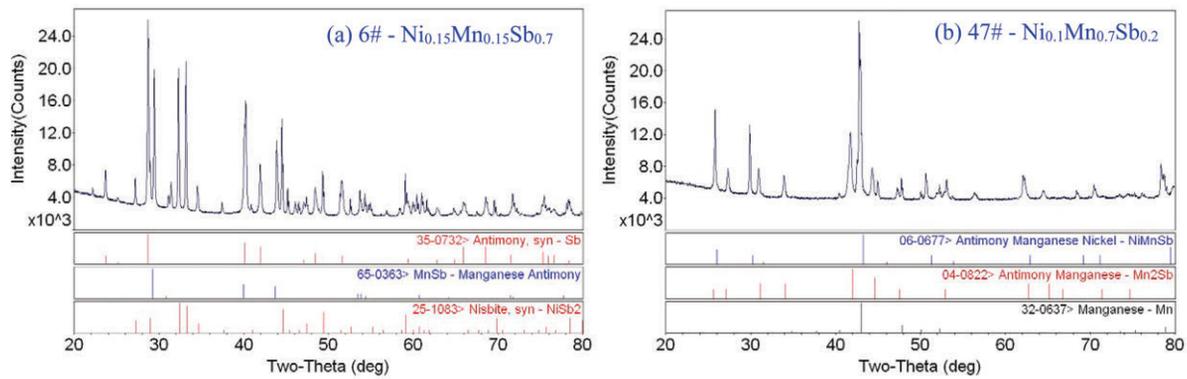


Figure 6. Typical XRD patterns of the compounds (a) 6#- $Ni_{0.15}Mn_{0.15}Sb_{0.7}$ ; (b) 47#- $Ni_{0.1}Mn_{0.7}Sb_{0.2}$ , labeled with A and B in Fig.9

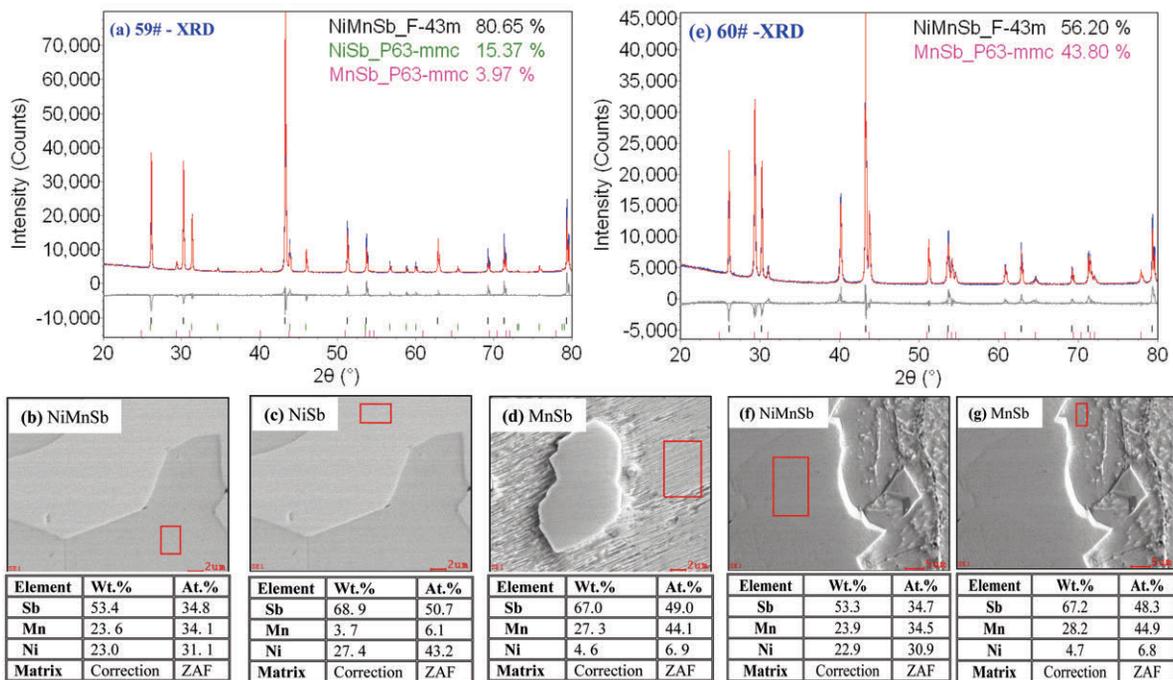


Figure 7. Typical Rietveld structure refinement results for the XRD patterns and SE results of the 59#- $Ni_{0.3}Mn_{0.3}Sb_{0.4}$  (a-d) and 60#- $Ni_{0.2}Mn_{0.4}Sb_{0.4}$  (e-g) compounds labeled with C and D in Fig.9

$Ni_2MnSb$  and  $NiMnSb$  are smaller than that of  $NiSb$ , but bigger than  $Mn$  or  $Ni$ . In this way, the  $Ni_2MnSb$  and  $NiMnSb$  phases showed as dark regions in Figs. 8d and 8f, as well as white regions in Figs. 8b and 8h.

### 3.3 773K Isothermal section of the Ni-Mn-Sb ternary system

By comparing and analyzing the XRD patterns, EDS and EPMA compositional results of the 117 samples and confirming the phases presented in each sample, the phase equilibrium in the Ni-Mn-Sb ternary system at 773 K was investigated and the isothermal section was constructed, as presented in

Fig. 9. It consisted of fourteen single-phase regions, twenty-seven two-phase and fourteen three-phase regions. The 14 single-phase regions were  $\gamma Ni^1$  (less Mn,  $\alpha$ ),  $\gamma Ni^2$  (more Mn,  $\alpha$ ),  $\beta NiMn$  ( $\beta$ ),  $\alpha Mn$  ( $\Omega$ ),  $\beta Mn$  ( $\psi$ ),  $Mn_2Sb$  ( $\eta$ ),  $MnSb$  ( $\lambda$ ),  $Sb$  ( $\sigma$ ),  $NiSb_2$  ( $\omega$ ),  $NiSb$  ( $\theta$ ),  $Ni_5Sb_2$  ( $\xi$ ),  $Ni_3Sb$  ( $\phi$ ),  $Ni_2MnSb$  ( $\mu$ ), and  $NiMnSb$  ( $\kappa$ ). And the 14 three-phase regions were  $\sigma + \omega + \lambda$ ,  $\theta + \omega + \lambda$ ,  $\theta + \kappa + \lambda$ ,  $\eta + \kappa + \lambda$ ,  $\eta + \kappa + \Omega$ ,  $\psi + \kappa + \Omega$ ,  $\psi + \kappa + \alpha$ ,  $\beta + \kappa + \alpha$ ,  $\beta + \kappa + \mu$ ,  $\beta + \alpha + \mu$ ,  $\phi + \alpha + \mu$ ,  $\phi + \xi + \mu$ ,  $\theta + \xi + \mu$ , and  $\theta + \kappa + \mu$ .

The solid solution ranges for each single phase in the 773K isothermal section of Ni-Mn-Sb ternary system were confirmed and summarized in Tab.3. The four binary compounds  $Ni_3Sb$ ,  $Ni_5Sb_2$ ,  $NiSb_2$  and  $Mn_2Sb$  in

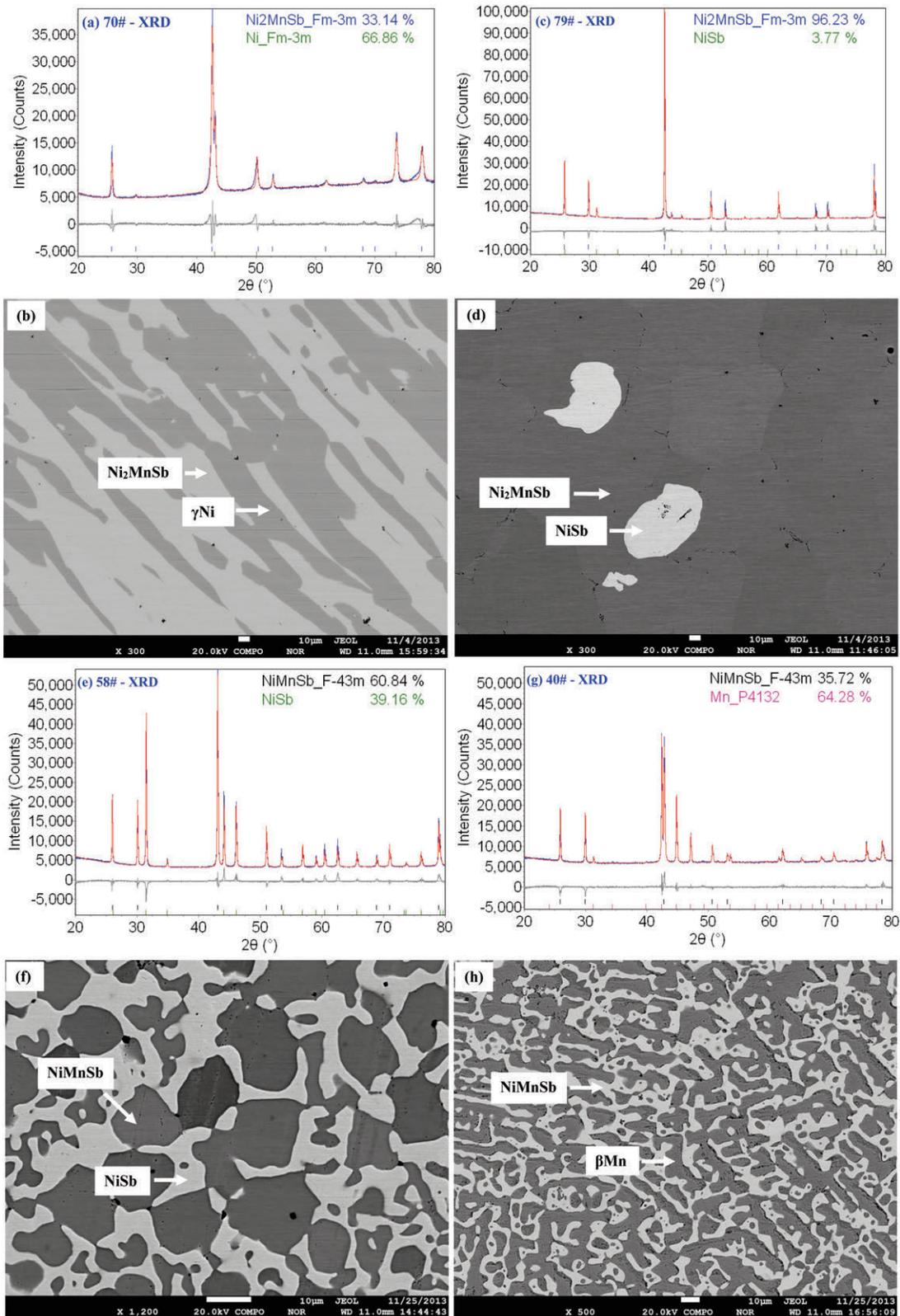


Figure 8. Typical Rietveld structure refinement results for the XRD patterns and EPMA results of the 70# - Ni<sub>0.6</sub>Mn<sub>0.25</sub>Sb<sub>0.15</sub> (a, b), 79# - Ni<sub>0.45</sub>Mn<sub>0.25</sub>Sb<sub>0.3</sub> (c, d), 58#- Ni<sub>0.4</sub>Mn<sub>0.2</sub>Sb<sub>0.4</sub> (e, f) and 40#- Ni<sub>0.2</sub>Mn<sub>0.7</sub>Sb<sub>0.1</sub> (g, h) compounds, labeled with E to H in Fig.9



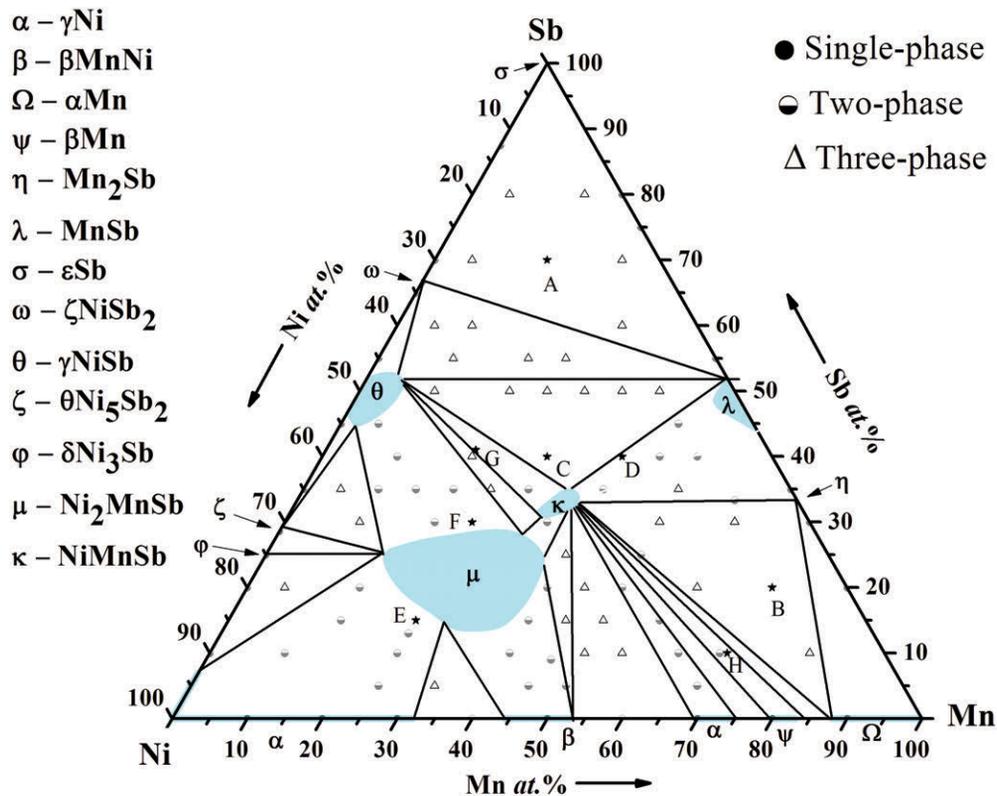


Figure 9. The 773K Isothermal section of the phase diagram of the Ni-Mn-Sb system

the Ni-Sb and Mn-Sb binary boundary were stoichiometric compounds as reported in Ref. [18, 20], the homogeneity ranges of which were negligible, as shown in Fig. 9. The other nine single phases,  $\gamma\text{Ni}^1$ ,  $\gamma\text{Ni}^2$ ,  $\beta\text{NiMn}$ ,  $\alpha\text{Mn}$ ,  $\beta\text{Mn}$ ,  $\text{MnSb}$ ,  $\text{NiSb}$ ,  $\text{Ni}_2\text{MnSb}$ , and  $\text{NiMnSb}$ , showed more or less homogeneity ranges. Two  $\gamma\text{Ni}$  single-phase regions  $\gamma\text{Ni}^1$  (less Mn) and  $\gamma\text{Ni}^2$  (more Mn) existed in the Ni-Mn-Sb isothermal section at 773 K. The homogeneity ranges of the five single phase regions along the Ni - Mn boundary were consistent with the results in Ref. [21]. The homogeneity range of  $\gamma\text{Ni}^1$  was about 32 at.% Mn and  $\gamma\text{Ni}^2$  about from 70 at.% to 75 at.% Mn. The homogeneity ranges of  $\alpha\text{Mn}$  and  $\beta\text{Mn}$  were about 17-

20 at.% Ni and 0-12 at.% Ni. The compound  $\beta\text{NiMn}$  showed a solid solubility of  $\text{Ni}_{47-56}\text{Mn}_{44-53}$  by replacement of Mn for Ni atoms but no for Sb atoms. This is in accordance with the Hume-Rothery 15 % empirical rule [26]: the solid solubility of two kinds of atoms in the alloy could be very small if the difference of their radius is over 15 %, as we know that  $R_{\text{Mn}} = 0.179\text{nm}$ ,  $R_{\text{Ni}} = 0.162\text{nm}$ ,  $R_{\text{Sb}} = 0.153\text{nm}$ . The Heusler alloy  $\text{Ni}_2\text{MnSb}$  with  $L2_1$ -type structure formed a solid solution by the way of substitution of Ni and Sb atoms for Mn atoms, and showed a relative large solid solution region, in which the content of Ni atoms varied between 37.8 - 59.7 at.%, 15.3 - 38.6 at.% for Mn atoms and 13.2 - 29.0 at.% for Sb atoms. In

Table 3 The approximate homogeneity ranges for the nine single phases in the 773K isothermal section of Ni-Mn-Sb ternary system

Phase	Solid solution atoms		
	Ni / at.%	Mn / at.%	Sb / at.%
$\gamma\text{Ni}^1$	68-100	0-32	0-7
$\gamma\text{Ni}^2$	25-30	70-75	0
$\beta\text{NiMn}$	47-56	44-53	0
$\alpha\text{Mn}$	17-20	80-83	0
$\beta\text{Mn}$	0-12	88-100	0
$\text{MnSb}$	0-6.8	44.1-56.5	43.5-49.4
$\text{NiSb}$	43.2-53.5	0-6.1	44.1-53.2
$\text{Ni}_2\text{MnSb}$	37.8-59.7	15.3-38.6	13.2-29.0
$\text{NiMnSb}$	28.3-36.2	32.9-37.6	30.3-35.1

contrast, the solid solubility of NiMnSb compound at 773 K was  $\text{Ni}_{28.3-36.2}\text{Mn}_{32.9-37.6}\text{Sb}_{30.3-35.1}$ , much smaller than that of  $\text{Ni}_2\text{MnSb}$ .

### Conclusions

The 773K isothermal section of the Ni-Mn-Sb ternary system was investigated. It consisted of 14 single-phase regions, 27 two-phase regions as well as 14 three-phase regions. Seven binary compounds NiMn,  $\text{Mn}_2\text{Sb}$ , MnSb,  $\text{NiSb}_2$ , NiSb,  $\text{Ni}_5\text{Sb}_2$  and  $\text{Ni}_3\text{Sb}$  were confirmed. The fourteen single-phase regions were  $\gamma\text{Ni}^1$  (less Mn,  $\alpha$ ),  $\gamma\text{Ni}^2$  (more Mn,  $\alpha$ ),  $\beta\text{NiMn}$  ( $\beta$ ),  $\alpha\text{Mn}$  ( $\Omega$ ),  $\beta\text{Mn}$  ( $\psi$ ),  $\text{Mn}_2\text{Sb}$  ( $\eta$ ), MnSb ( $\lambda$ ), Sb ( $\sigma$ ),  $\text{NiSb}_2$  ( $\omega$ ), NiSb ( $\theta$ ),  $\text{Ni}_5\text{Sb}_2$  ( $\xi$ ),  $\text{Ni}_3\text{Sb}$  ( $\phi$ ),  $\text{Ni}_2\text{MnSb}$  ( $\mu$ ), and NiMnSb ( $\kappa$ ). And the fourteen three-phase regions were  $\sigma + \omega + \lambda$ ,  $\theta + \omega + \lambda$ ,  $\theta + \kappa + \lambda$ ,  $\eta + \kappa + \lambda$ ,  $\eta + \kappa + \Omega$ ,  $\psi + \kappa + \Omega$ ,  $\psi + \kappa + \alpha$ ,  $\beta + \kappa + \alpha$ ,  $\beta + \kappa + \mu$ ,  $\beta + \alpha + \mu$ ,  $\phi + \alpha + \mu$ ,  $\phi + \xi + \mu$ ,  $\theta + \xi + \mu$ , and  $\theta + \kappa + \mu$ . The four binary compounds  $\text{Ni}_3\text{Sb}$ ,  $\text{Ni}_5\text{Sb}_2$ ,  $\text{NiSb}_2$ , and  $\text{Mn}_2\text{Sb}$  were stoichiometric, the homogeneity ranges of which were negligible. The solid solution ranges for the nine single phases in the 773K isothermal section of Ni-Mn-Sb ternary system were determined. The compositions of the binary compounds NiSb and MnSb were determined to be  $\text{Ni}_{43.2-53.5}\text{Mn}_{0-6.1}\text{In}_{44.1-53.2}$  and  $\text{Ni}_{0-6.8}\text{Mn}_{44.1-56.5}\text{Sb}_{43.5-49.4}$ , respectively.

Two ternary compounds,  $\text{Ni}_2\text{MnSb}$  and NiMnSb, were verified and no other ternary compounds were found in the Ni-Mn-Sb ternary system at 773 K section. The Heusler alloy  $\text{Ni}_2\text{MnSb}$  ( $\text{Fm}\bar{3}m$ ,  $a = 0.6011$  nm) showed a large solid solution region with  $\text{Ni}_{37.8-59.7}\text{Mn}_{15.3-38.6}\text{Sb}_{13.2-29.0}$ , while the Half-Heusler alloy NiMnSb ( $\text{F}43m$ ,  $a = 0.5932$  nm) showed a small solid solution region with  $\text{Ni}_{28.3-36.2}\text{Mn}_{32.9-37.6}\text{Sb}_{30.3-35.1}$ .

### Acknowledgement

The work was subsidized by the National Natural Science Found (Grant Nos: 51101103 and 51571144), the Science and Technology Innovation Commission of Shenzhen (Grant Nos. JCYJ20150827155136104, JCYJ20150324141711684 and JCYJ20150069)

### References

- [1] V.K. Pecharsky, K.A. Gschneidner Jr, J. Magn. Magn. Mater., 167 (3) (1997) 179-184.
- [2] X. Chen, Y. Chen, Y. Tang, D. Xiao, J. Magn. Magn. Mater., 368 (2014) 155-168.
- [3] S. Fujieda, K. Fukamichi, S. Suzuki, J. Alloys Compd., 566(2013)196-200.
- [4] G. Billon, B. Ouddane, P. Recourt, A. Boughriet, Estuari. Coast. Shelf S., 55 (2) (2002) 167-181.
- [5] Z. Zhong, S. Ma, D. Wang, Y. Du, J. Mater. Sci.

Technol., 28(3) (2012) 193-199.

- [6] J.I. Pérez-Landazábal, V. Recarte, J. Torrens-Serra, E. Cesari, Acta Mater., 71(2014) 117-125.
- [7] F.S. Liu, Q.B. Wang, W.Q. Ao, Y.J. Yu, L.C. Pan, J.Q. Li, J. Magn. Magn. Mater., 324 (4) (2012) 514-518.
- [8] V. Sánchez-Alarcos, J.I. Pérez-Landazábal, V. Recarte, I. Lucia, J. Vélez, J.A. Rodríguez-Velamazán, Acta Mater., 61 (12) (2013) 4676-4682.
- [9] R. Sahoo, A.K. Nayak, K.G. Suresh, A.K. Nigam, J. Magn. Magn. Mater., 324(7) (2012) 1267-1271.
- [10] W. Wang, J. Yu, Q. Zhai, Z. Luo, H. Zheng, Intermetallics, 42(3) (2013) 126-129.
- [11] B. Tian, F. Chen, Y. Tong, L. Li, J. Alloys Compd., 604 (2014) 137-141.
- [12] H.C. Xuan, P.D. Han, D.H. Wang, Y.W. Du, J. Alloys Compd., 582(12) (2014) 369-373.
- [13] S. Singh, I. Glavatsky, C. Biswas, J. Alloys Compd., 601(8) (2014) 108-111.
- [14] K.E. Tsioplakis, E. Kneller, Z. Metallkd., 60, (1969) 433-438.
- [15] B.R. Coles, J. Phase Equilib., 16(2) (1995) 108-109.
- [16] L. Ding, P.F. Ladwig, X. Yan, Y.A. Chang, Appl. Phys. Lett., 80(7) (2002) 1186-1188.
- [17] C. Guo, Z. Du, Intermetallics, 13(5) (2005) 525-534.
- [18] V.G. Vanyarkho, N.A. Moshchalkova, V.M. Gunchenko, N.V. Fadeeva, Inorg. Mater., 24(2) (1988) 762-765.
- [19] G.H. Cha, S.Y. Lee, P. Nash, Binary alloy phase diagrams, ASM International, Ohio, 1990, p. 2853-2855.
- [20] Y.B. Zhang, C.R. Li, Z.M. Du, C.P. Guo, Calphad, 32(2) (2008) 378-388.
- [21] W.Q. Ao, F.S. Liu, J.Q. Li, Y. Du, F.L. Liu, J. Alloys Compd., 622 (2015) 149-154.
- [22] A. Szytula, Phys. Stat. Sol., 10(57) (1972) 57-65.
- [23] R.A.M.v.W. M J Otto, P J van der Valk, J Wijngaard, C F van Bruggen, C Haasl and K H J Buschow, J. Phys.: Condens. Matter., 1 (1989) 2341-2350.
- [24] P. Villars, Pearson's Handbook: Desk edition: Crystallographic Data for Intermetallic Phases, ASM International, Ohio, 1997, p. 2360-2532.
- [25] C.H. Li, J. Hu, Q. Peng, X. Wang, Mater. Chem. Phys., 110(1) (2008) 106-109.
- [26] W. Hume-Rothery, Acta Metall. Mater., 14(1) (1966) 17-20.



## IZOTERMALNI PRESEK Ni–Mn–Sb TROJNOG SISTEMA NA TEMPERATURI OD 773K

W.-Q. Ao <sup>a,b</sup>, H.-Z. Yu <sup>b</sup>, F.-L. Liu <sup>b</sup>, F.-S. Liu <sup>b,#</sup>, J.-Q. Li <sup>b</sup>, Y. Du <sup>a,\*</sup>, S.-H. Liu <sup>a</sup>, C.-Y. Shi <sup>a</sup>

<sup>a</sup> Glavna državna laboratorija za metalurgiju praha, Centralno - južni univerzitet, Čangša, Kina

<sup>b</sup> Fakultet za inženjerstvo i nauku o materijalima, Univerzitet u Šenzenu, Istraživački centar za međupovršinsko inženjerstvo funkcionalnih materijala u Guandongu i Glavna laboratorija za specijalne funkcionalne materijale u Šenzenu, Šenzen, Kina

### Apstrakt

Izotermalni presek Ni-Mn-Sb trojnog sistema na temperature od 773 K određen je uz pomoć 117 legura koje su analizirane korišćenjem rendgenske difrakcije (XRD), skenirajućeg elektronskog mikroskopa (SEM), i tehnikama energetsko-disperzivne spektroskopije i mikroanalize elektronskom sondom (EPMA). Postojanje 7 binarnih jedinjenja, tj. NiMn, Mn<sub>2</sub>Sb, MnSb, NiSb<sub>2</sub>, NiSb, Ni<sub>3</sub>Sb<sub>2</sub>, Ni<sub>2</sub>Sb, kao i 2 trojna jedinjenja - Ni<sub>2</sub>MnSb i NiMnSb potvrđeno je za ovaj izotermalni presek. Četiri binarna jedinjenja Ni<sub>3</sub>Sb (Cu<sub>3</sub>Ti struktura, Pmmn prostorna grupa), Ni<sub>3</sub>Sb<sub>2</sub> (Ni<sub>3</sub>Sb<sub>2</sub>-tip strukture, C2 prostorna grupa), NiSb<sub>2</sub> (FeS<sub>2</sub>-tip strukture, Pnnm prostorna grupa) i Mn<sub>2</sub>Sb (Cu<sub>2</sub>Sb-tip strukture, P4/nmm prostorna grupa) u binarnim sistemima Ni-Sb i Mn-Sb bila su stehiometrijska jedinjenja, čiji je raspon homogenosti bio zanemarljiv. Pa ipak, pet pojedinačnih faza u Ni-Mn sistemu i dva binarna jedinjenja MnSb i NiSb su manje ili više pokazala interval homogenosti stvoren zamenom Mn i Sb atomom Ni. Heuslerovo jedinjenje  $\mu$  (Ni<sub>2</sub>MnSb) ima L2<sub>1</sub>-tip raspoređene strukture sa prostornom grupom Fm-3m,  $a = 0.6017$  nm. Kristalna struktura za Half-Heuslerovo jedinjenje  $\kappa$  (NiMnSb) je C1<sub>b</sub>-tip (F-43m) sa  $a = 0.5961$  nm. Istraživan je približni raspon homogenosti dva trojna jedinjenja  $\mu$  i  $\kappa$  na temperaturi od 773 K.

**Ključne reči:** Ni-Mn-Sb; Trojni sistem; Fazni dijagram; Metali i legure

