Journal of Alloys and Compounds 470 (2009) 233–236

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Phase equilibria in Zr–Ni–Sb ternary system at 870 K

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ARTICLE INFO

Article history:
Received 12 February 2008
Received in revised form 6 March 2008
Accepted 7 March 2008
Available online 29 April 2008

Keywords:
Intermetallics
Phase diagram
Crystal structure

ABSTRACT

The isothermal section of the phase diagram of the Zr–Ni–Sb ternary system at 870 K in the whole concentration range has been constructed by means of X-ray and metallographic analyses. Eight ternary intermetallic compounds Zr_6NiSb_2 (Zr_6CoAl_2-type), $Zr_5Ni_{0.5}Sb_{2.5}$ (W_5Si_3-type), $Zr_5Ni_{0.9}Sb_3$ (Hf_5CuSn_3-type), $ZrNi_2Sb$ ($ZrPt_2Al$-type), ZrNiSb (TiNiSi-type), $Zr_3Ni_3Sb_4$ ($Y_3Au_3Sb_4$-type), $Zr_2Ni_{0.7}Sb_{3.3}$ (Zr_2CuSb_3-type), and Zr_3NiSb_7 (own structure type) are formed in this system at 870 K.

1. Introduction

In the course of scientific and technological progress large attention is paid to the development of new functional materials based on intermetallic compounds. In search of new intermetallics having specific thermoelectric properties we focus on the investigation of the ternary systems with elements of IVb group, 3d-metals and Sn or Sb. The MeNiSn (Me = Ti, Zr, Hf) and TiCoSb compounds with MgAgAs structure type are semiconductors with narrow band [1–3]. It is very important to study an influence of 3d-metals and p-elements on the physical properties of intermetallics for optimization of their thermoelectric characteristics.

The contributions to the investigation of the Me–Me′–Sb ternary systems (Me–V, Ti, Zr, Hf; Me′–Mn, Fe, Co, Cu) have been made by our research team with the study of the phase equilibria in the V–Mn–Sb [4], Ti–Mn–Sb [5], Zr–Fe–Sb [6], Ti–Co–Sb [7] and {Ti, Zr, Hf}–Cu–Sb [8–10] systems.

In the present paper we report for the first time the phase equilibria constructed for the Zr–Ni–Sb ternary system at 870 K and the crystal structure data for ternary intermetallics formed in this system.

The phase diagram of Zr–Ni binary system as assessed by Massalski [11] and Villars and Calvert [12] has been used for our investigation. Six binary phases were observed at 870 K in the Zr–Ni system: $ZrNi_5$ ($AuBe_5$-type), Zr_2Ni_7 (Zr_2Ni_7-type), Zr_8Ni_{21} (Hf_8Ni_{21}-type), ZrNi (TlI-type), Zr_7Ni_{10} (Zr_7Ni_{10}-type) and Zr_2Ni (Cu_2Al-type). The high temperature phase Zr_9Ni_{11} (Zr_9Pt_{11}-type) exists above 1250 K and $ZrNi_3$ ($CdMg_3$-type) is characterized by narrow temperature range.

The phase diagram for Zr–Sb binary system is not completely studied up to now. According to version from Massalski compilation [11] there are four binary compounds: $ZrSb_2$ ($PbCl_2$-type), Zr_5Sb_3 (Mn_5Si_3-type), Zr_2Sb (La_2Sb-type) and Zr_3Sb (Ni_3P-type). The ZrSb compound (own structure type) was investigated in Ref. [13].

The data concerning the phase diagram and crystallographic characteristics of binaries of Ni–Sb system were assessed in Massalski compilation [11]. At 870 K four phases are observed: $NiSb_2$ (FeS_2-type), NiSb (NiAs-type), Ni_3Sb (Cu_3Ti-type) and $Ni_{2.64}Sb$ (BiF_3-type, ht modification, formed above 582 K).

2. Experimental details

The alloys were synthesized by arc-melting of the elemental components (zirconium, purity 99.96 wt.%; nickel-99.99 wt.% and antimony-99.99 wt.%) under high-purity argon gettered with Ti. A 5 wt.% excess of Sb was required to compensate the evaporative losses during arc-melting. The ingots were then sealed in evacuated fused-silica tubes and annealed at 870 K for 720 h. After the heat treatment, the ingots were quenched in cold water. The phase purity and final sample composition of the obtained alloys were controlled by X-ray powder diffraction and for some alloys were defined by energy-dispersive X-ray (EDX) analyses on a scanning electron microscope. The data for the crystal structure refinements were collected on Inel powder diffractometer (Cu Kα radiation, CPS 120 detector). The crystal structure calculation was performed by the Rietveld method using LHPM-Rietica program [14]. For the single crystal investigation intensity data were obtained on Bruker Platform/SMART 1000 CCD diffractometer with graphite-monochromated

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doi:10.1016/j.jallcom.2008.03.030

Table 1
Crystallographic characteristics of compounds in the Zr–Ni–Sb system

Compound	Structure type	Space group	Lattice parameters (nm)			V (nm^3)
			a	b	c	
Zr_6NiSb_2	Zr_6CoAl_2	$P\bar{6}\bar{2}m$	0.77255(7)	–	0.36850(8)	0.19047(4)
$Zr_5Ni_{0.5}Sb_{2.5}$	W_5Si_3	$I4/mcm$	1.11035(4)	–	0.55327(3)	0.68211(5)
$Zr_5Ni_{0.9}Sb_3$	Hf_5CuSn_3	$P6_3/mcm$	0.85881(5)	–	0.58049(3)	0.37078(4)
$ZrNi_2Sb$	$ZrPt_2Al$	$P6_3/mmc$	0.42106(2)	–	0.82991(4)	0.12742(1)
ZrNiSb	TiNiSi	$Pnma$	0.67408(3)	0.41627(2)	0.75251(3)	0.21116(2)
$Zr_3Ni_3Sb_4$	$Y_3Au_3Sb_4$	$I\text{-}43d$	0.90624(3)	–	–	0.74428(4)
$Zr_2Ni_{0.7}Sb_{3.3}$	Zr_2CuSb_3	$P\bar{4}m2$	0.39564(1)	–	0.87626(3)	0.13716(1)
Zr_3NiSb_7	Zr_3NiSb_7	$Pnma$	1.7516(1)	0.39266(4)	1.4396(1)	0.9901(1)

Mo Kα radiation. Calculations were carried out using SHELXTL package [15].

3. Results and discussion

The isothermal section of Zr–Ni–Sb ternary system was constructed at 870 K using X-ray and metallographic analyses of 77 ternary and binary alloys (Fig. 1).

During X-ray phase analysis of the Zr–Ni–Sb ternary samples the existence of the previously known Zr_6NiSb_2 [16], $Zr_5Ni_{1-x}Sb_{2+x}$ [17], Zr_5NiSb_3 [18], ZrNiSb [19] and $Zr_3Ni_3Sb_4$ [20] compounds has been confirmed and three new ternary compounds $Zr_2Ni_{0.7}Sb_{3.3}$, Zr_3NiSb_7 and $ZrNi_2Sb$ were found. Crystallographic data of the compounds in the Zr–Ni–Sb system, obtained in the present work, are listed in Table 1.

The structure of $Zr_2Ni_{0.7}Sb_{3.3}$ compound was determined using X-ray powder diffraction method. The powder pattern reflections were indexed on the basis of a tetragonal lattice with cell parameters $a = 0.39285(3)$, $c = 0.87329(8)$ nm. Futher analysis of the $h\,k\,l$ reflections and their intensities allowed determining the Zr_2CuSb_3 structure type (space group $P\bar{4}m2$) [21]. All relevant crystallographic data and experimental details are presented in Table 2. The final atomic parameters, refined to $R_p = 0.068$, $R_{wp} = 0.095$, $R_{Bragg} = 0.033$, are listed in Table 3. The observed, calculated and difference X-ray patterns of $Zr_2Ni_{0.7}Sb_{3.3}$ compound are shown in Fig. 2. The interatomic distances in the $Zr_2Ni_{0.7}Sb_{3.3}$ structure are close to the sum of the respective atomic radii of the components.

According to Ref. [22] $ZrNi_2Sb$ compound crystallizes in $MnCu_2Al$ structure type. During phase analysis of the samples near composition $\sim Zr_{25}Ni_{50}Sb_{25}$ the formation of compound with $MnCu_2Al$ structure at 870 K was not confirmed. The powder pattern reflections of $ZrNi_2Sb$ were indexed on the basis of a hexagonal lattice with cell parameters $a = 0.42106(2)$ nm, $c = 0.82991(4)$ nm corresponding to $ZrPt_2Al$ structure type (space

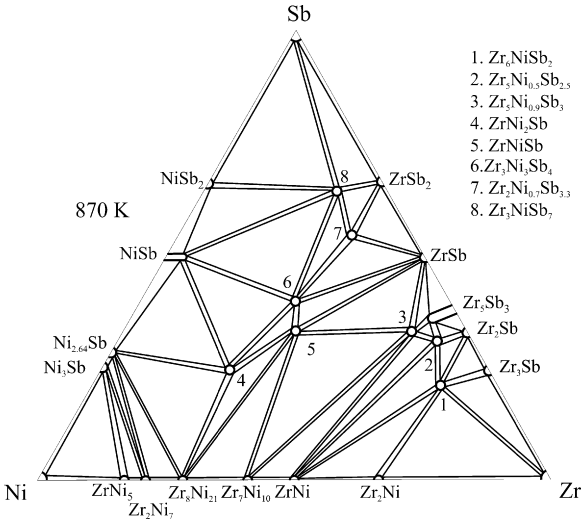

Fig. 1. Isothermal section of the Zr–Ni–Sb system at 870 K.

Table 2
Crystal data and structure refinement for $Zr_2Ni_{0.7}Sb_{3.3}$

Formula	$Zr_2Ni_{0.76(3)}Sb_{3.24(3)}$
Space group	$P\bar{4}m2$ (No. 115)
a (nm)	0.39566(1)
c (nm)	0.87631(3)
V (nm^3)	0.13718(1)
Z	1
ρ_{calc} (g cm^{-3})	7.545
2θ range	$15.0 \le (\text{Cu K}\alpha_1) \le 110.0^\circ$
No. of reflection	75
No. of variables	23
R_B, R_p, R_{wp}	0.033, 0.068, 0.095

Table 3
Atomic and thermal parameters for $Zr_2Ni_{0.7}Sb_{3.3}$ compound

Atom	Wyckoff position	x/a	y/b	z/c	$B_{iso} \times 10^2$ (nm^2)
Zr	2*g*	0	1/2	0.7315(4)	0.34(3)
M1[a]	1*a*	0	0	0	0.9(3)
M2[b]	1*b*	1/2	1/2	0	0.6(2)
Sb	2*g*	0	1/2	0.3825(3)	0.65(8)

[a] M1 = 0.12(3)Ni + 0.88(3)Sb.
[b] M2 = 0.64(3)Ni + 0.36(3)Sb.

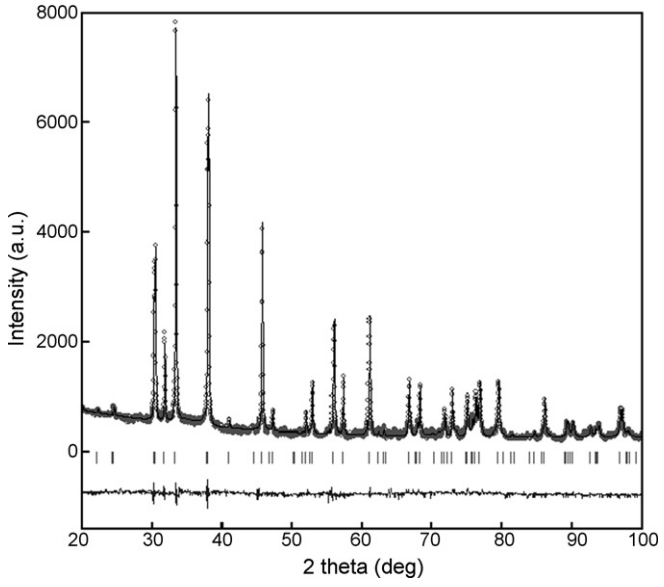

Fig. 2. The observed, calculated and difference X-ray patterns of $Zr_2Ni_{0.7}Sb_{3.3}$ compound.

Table 4
Crystal data and structure refinement for $ZrNi_2Sb$

	Single crystal method	Powder method
a (nm)	0.42131(3)	0.42106(2)
c (nm)	0.83092(10)	0.82991(4)
V (nm^3)	0.1277(2)	0.1274(1)
ρ_{calc} (g cm^{-3})	8.59	8.61
2θ range	$9.8^\circ \le$ (Mo Kα) $\le 66.1^\circ$	$15^\circ \le$ (Cu Kα_1) $\le 105^\circ$
No. of total reflections	1471 (R_{int} = 0.026)	
No. of unique reflections	119 (113 з $F^2 > 2\sigma(F^2)$)	43
No. of variables	9	19
Agreement factors	$R(F)$ = 0.017 $R_w(F^2)$ = 0.040	R_B = 0.085, R_p = 0.093, R_{wp} = 0.123

Formula: $ZrNi_2Sb$; space group, Z: $P6_3/mmc$ (No. 194), 2.

Table 5
Atomic and thermal parameters for $ZrNi_2Sb$ compound

Atom	Wyckoff position	x/a	y/b	z/c	$U_{eq}/B_{iso} \times 10^2$ (nm^2)
Single crystal method					
Zr	2c	1/3	2/3	1/4	0.0090(2)
Ni	4f	1/3	2/3	0.5955(1)	0.0106(2)
Sb	2a	0	0	0	0.0101(2)
Powder method					
Zr	2c	1/3	2/3	1/4	0.58(5)
Ni	4f	1/3	2/3	0.5963(3)	0.43(6)
Sb	2a	0	0	0	0.68(4)

group $P6_3/mmc$). All relevant crystallographic data and experimental details for powder and single crystal methods are presented in Table 4. The final atomic and thermal parameters are listed in Table 5. The observed, calculated and difference X-ray patterns of $ZrNi_2Sb$ compound are shown in Fig. 3. The interatomic distances in the $ZrNi_2Sb$ structure are close to the sum of the corresponding atomic radii of the components (the main distances are: Zr–Ni–0.27504(4) nm, 0.28707(9) nm; Zr–Sb–0.31987(2) nm; Ni–Ni–0.25677(17) nm; Ni–Sb–0.25586(3) nm).

During this work the crystal structures of $Zr_5Ni_{0.53}Sb_{2.47}$ and $Zr_5Ni_{0.9}Sb_3$ antimonides were refined by powder method. The crystal structure refinements of these compounds confirmed the structure of W_5Si_3 and Hf_5CuSn_3-types, respectively. All relevant crystallographic data and experimental details are presented in Tables 6 and 8, respectively. The refined atomic and thermal parameters are listed in Tables 7 and 9. The observed, calculated and

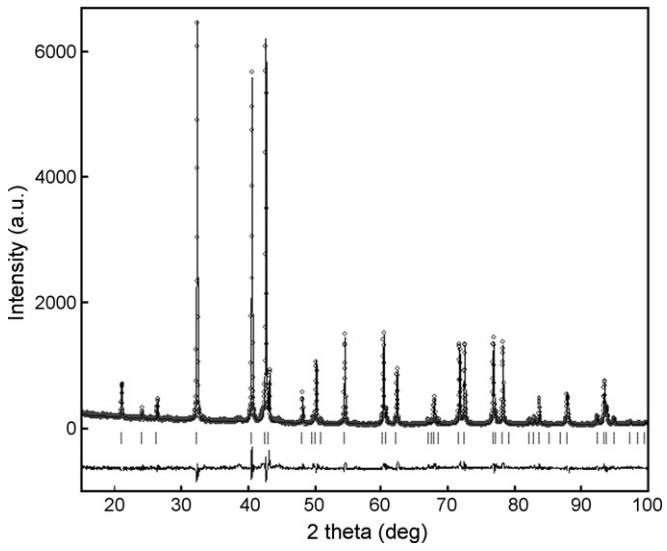

Fig. 3. The observed, calculated and difference X-ray patterns of $ZrNi_2Sb$ compound.

Table 6
Crystal data and structure refinement for $Zr_5Ni_{0.5}Sb_{2.5}$

Formula	$Zr_5Ni_{0.53(4)}Sb_{2.47(4)}$
Space group	$I4/mcm$ (No. 140)
a (nm)	1.11035(4)
c (nm)	0.55327(3)
V (nm^3)	0.68211(5)
Z	4
ρ_{calc} (g cm^{-3})	7.669
2θ range	$15^\circ \le$ (Cu Kα_1) $\le 100^\circ$
No. of reflection	111
No. of variables	23
R_B, R_p, R_{wp}	0.025, 0.074, 0.102

Table 7
Atomic parameters for $Zr_5Ni_{0.5}Sb_{2.5}$ compound

Atom	Wyckoff position	x/a	y/b	z/c	$B_{iso} \times 10^2$ (nm^2)
Zr1	16k	0.0790(4)	0.2181(4)	0	1.19(9)
Zr2	4b	0	1/2	1/4	0.5(1)
M[a]	4a	0	0	1/4	0.8(2)
Sb	8h	0.1646(3)	x + 1/2	0	0.33(9)

[a] M = 0.53(4)Ni + 0.47(4)Sb.

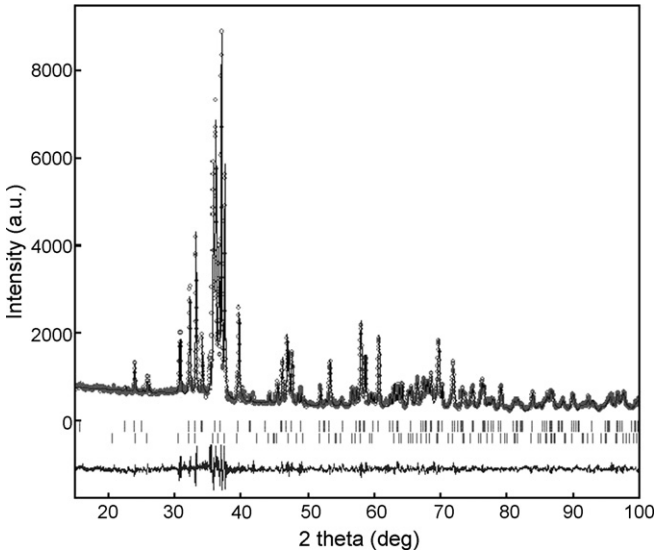

Fig. 4. The observed, calculated and difference X-ray patterns of $Zr_5Ni_{0.5}Sb_{2.5}$ compound.

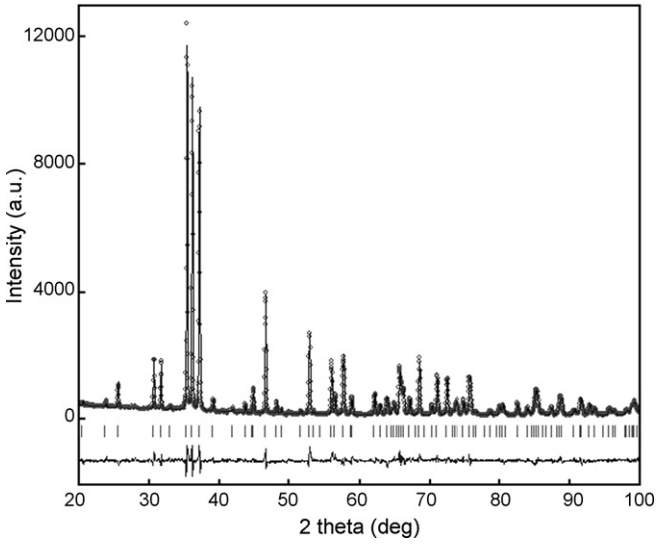

Fig. 5. The observed, calculated and difference X-ray patterns of $Zr_5Ni_{0.9}Sb_3$ compound.

Table 8
Crystal data and structure refinement for $Zr_5Ni_{0.9}Sb_3$

Formula	$Zr_5Ni_{0.91(2)}Sb_3$
Space group	$P6_3/mcm$ (No. 193)
a (nm)	0.85881(5)
c (nm)	0.58049(3)
V (nm^3)	0.37078(4)
Z	2
ρ_{calc} (g cm^{-3})	7.831
2θ range	$20^\circ \le (\text{Cu K}\alpha_1) \le 100^\circ$
No. of reflection	85
No. of variables	22
R_B, R_p, R_{wp}	0.049, 0.097, 0.125

Table 9
Atomic and thermal parameters for $Zr_5Ni_{0.9}Sb_3$ compound

Atom	Wyckoff position	x/a	y/b	z/c	$B_{iso} \times 10^2$ (nm^2)
Zr1	6g	0.2611(3)	0	1/4	0.73(7)
Zr2	4d	1/3	2/3	0	0.59(7)
Ni[a]	2b	0	0	0	0.17(2)
Sb	6g	0.6121(2)	0	1/4	0.50(6)

[a] Occupation 0.91(2).

Table 10
Atomic and thermal parameters for Zr_3NiSb_7 compound

Atom	Wyckoff position	x/a	y/b	z/c	$B_{iso} \times 10^2$ (nm^2)
Zr1	4c	0.34664(4)	1/4	0.19076(5)	0.00788(14)
Zr2	4c	0.37045(4)	1/4	0.47072(5)	0.00721(13)
Zr3	4c	0.39237(4)	1/4	0.90990(5)	0.00782(14)
Ni	4c	0.43680(5)	1/4	0.68908(6)	0.00903(18)
Sb1	4c	0.02147(3)	1/4	0.29766(3)	0.00871(11)
Sb2	4c	0.03748(2)	1/4	0.07626(3)	0.00790(10)
Sb3	4c	0.07123(3)	1/4	0.56057(3)	0.00977(11)
Sb4	4c	0.09131(3)	1/4	0.82504(3)	0.00823(10)
Sb5	4c	0.22833(3)	1/4	0.35390(3)	0.00918(11)
Sb6	4c	0.24792(2)	1/4	0.02153(3)	0.00875(11)
Sb7	4c	0.28995(3)	1/4	0.68532(4)	0.01218(11)

difference X-ray patterns of $Zr_5Ni_{0.53}Sb_{2.47}$ and $Zr_5Ni_{0.9}Sb_3$ compounds are shown in Figs. 4 and 5, respectively.

The new antimony-rich compound at composition ~$Zr_{30}Ni_{10}Sb_{60}$ was found and its crystal structure was solved by single crystal method. Single crystal used for structure refinement was isolated from a crushed ingot of the annealed $Zr_{27}Ni_9Sb_{64}$ sample. Zr_3NiSb_7 antimonide crystallizes in the orthorhombic space group $Pnma$ ($Z = 4$, $a = 1.75165(19)$ nm, $b = 0.39266(4)$ nm, $c = 1.43968(15)$ nm), and represents a new structure type. The refined atomic and thermal parameters are listed in Table 10. The detailed description and analysis of crystal structure investigation of Zr_3NiSb_7 compound will be published in our next manuscript.

X-ray analysis shows the formation of $Zr_xNi_{1-x}Sb$ substitutional solid solution based on NiSb binary compound (NiAs-type) up to about 5 at.% of Zr. The cell parameters change from $a = 0.3934$ nm, $c = 0.5138$ nm (for NiSb) to $a = 0.3959(1)$ nm, $c = 0.5141(2)$ nm (for $Zr_5Ni_{45}Sb_{50}$ composition).

For examination the process of solid solution formation between Zr_5NiSb_3 (Hf_5CuSn_3 structure type) and Zr_5Sb_3 (Mn_5Si_3-type) or Zr_5Sb_4 (Ti_5Ga_4-type) additional alloys in the Zr_5Sb_3–Zr_5NiSb_3–Zr_5Sb_4 region were prepared. X-ray phase analysis of obtained samples showed the existence of solid solution formed by the nickel insertion into the Zr_5Sb_3 binary to the final composition $Zr_{59}Ni_6Sb_{35}$ ($a = 0.8429(5)$ nm, $c = 0.5759(5)$ nm).

Compared with the previously studied Zr–Fe–Sb (four intermediate compounds) and Zr–Cu–Sb (three intermediate compounds) systems, the Zr–Ni–Sb system presents a higher number of compounds. The isostructural compounds only with W_5Si_3-type appear in all three systems. On the other hand it worth to note the close analogy between the crystal structure, stoichiometries of the ternary phases in the Zr–Fe–Sb and Zr–Ni–Sb systems, especially in the Zr-rich region.

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