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Phase Relations in the Nb–Ni–Sb System

Ya. F. Lomnytska and V. V. Berezovets

Franko National University, ul. Kirila i Mefodiya 6, Lviv, 79005 Ukraine

e-mail: yalomnytska@yahoo.com

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Abstract—Phase relations in the Nb–Ni–Sb system at 1070 K are studied by x-ray diffraction. The results confirm the existence of the ternary compound $Nb_{28}Ni_{33.5}Sb_{12.5}$ (new structure type), which is shown to have a narrow homogeneity range. The system contains no solid solutions based on binary compounds, as evidenced by structural analysis data for NiSb and $NbSb_2$ in three-phase Nb–Ni–Sb samples.

INTRODUCTION

The Nb–Ni–Sb system was reported earlier to contain a compound of composition $Nb_{28}Ni_{33.5}Sb_{12.5}$ (new structure type) [1]. Phase equilibria in this system have not been investigated. The purpose of this work was to study the 1070-K phase relations in the Nb–Ni–Sb system, construct its phase diagram, identify new ternary compounds, and find out whether the system contains solid solutions based on binary compounds.

EXPERIMENTAL

Phase relations in the Nb–Ni–Sb system were studied over the entire composition range using 55 samples prepared from high-purity (99.9+%) metal powders by arc melting. At low Sb concentrations, the samples were sintered in evacuated silica ampules during heating to 1070 K. At Sb contents above 67 mol %, the temperature was raised to 870 K. After 100 h of sintering, the samples were ground, pressed, and sintered again. Next, the samples were homogenized by annealing at 1070 (≤67 mol % Sb) or 870 K (>67 mol % Sb) for 600–800 h, followed by quenching in cold water without breaking the vacuum. In our studies, we used only those samples which differed in weight from the starting mixture by no more than 2%.

The phase composition of the samples was determined by powder x-ray diffraction (XRD) using a Debye–Scherrer camera (CrK radiation) and DRON-3M diffractometer (CuK_α radiation). Intensity data were collected in the 2θ range 10°–85° (DRON-3M, CuK_α radiation, step size of 0.05°, counting time of 10 s per data point). Single-crystal XRD measurements were performed on a Nonius Kappa x-ray diffractometer (95-mm CCD chamber, horizontal graphite monochromator, $5.82° \le 2\theta \le 84.22°$, Mo$K_\alpha$ radiation). In solving the structure of crystals and refining their lattice parameters, we used the CSD software package [2].

EXPERIMENTAL RESULTS

Phase relations in the Nb–Ni–Sb system. We reinvestigated the constituent binary systems. In the Nb–Ni binary [3], we obtained the compounds $NbNi_3$ ($TiAl_3$ structure type) and Nb_6Ni_7 (W_6Fe_7) [4], both with narrow homogeneity ranges. In the Ni–Sb system at 1070 K, we obtained $Ni_{1.12–0.94}Sb_{0.88–1.06}$ (NiAs) and Ni_5Sb_2 (Ni_5Sb_2) [3, 4]. In the composition range $Ni_{0.70}Sb_{0.30}$–$Ni_{0.80}Sb_{0.20}$, the samples, both unannealed and annealed at 870 K, contained, in addition to Ni_5Sb_2, the high-temperature phase of Ni_3Sb (BiF_3) and trace levels of the low-temperature phase of Ni_3Sb (Cu_3Ti) [4]. $NiSb_2$ ($FeSb_2$) was found in Sb-rich (>67 mol % Sb) Nb–Ni–Sb samples at 870 K. In the Nb–Sb system at 1070 K, we obtained Nb_3Sb (Cr_3Si), $NbSb_2$ ($OsGe_2$), and Nb_5Sb_4 (Ti_5Te_4) [4]. NbSb (NiAs) [4], which was reported to form peritectically [3], was not obtained in our preparations at 1070 K. At the same time, the XRD patterns of Nb–Ni–Sb samples quenched from 870 K and containing more than 50 mol % Sb indicated the presence of trace levels of that phase. It seems likely that NbSb forms below 870 K. Nb_3Sb_2 and Nb_4Sb_3, phases with unidentified structures [4], were not obtained at 1070 or 870 K. We suppose that Nb_3Sb_2 and Nb_5Sb_4 (Ti_5Te_4) are the same phase. The crystal data for all of the phases in the Nb–Ni–Sb system are presented in Table 1.

The 1070-K section of the Nb–Ni–Sb phase diagram inferred from the present XRD results is shown in Fig. 1. The only ternary compound in the system is $Nb_{28}Ni_{33.5}Sb_{12.5}$ (new structure type) [1]. To determine the composition region of this phase, we prepared samples with constant Nb and Sb contents, differing in composition from the ternary compound by 2 mol %.

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Table 1. Crystal data for phases of the Nb–Ni–Sb system

Phase	Structure type	Sp. gr.	*a*, Å	*b*, Å	*c*, Å	Source
Sb	α-As	$R\bar{3}m$	4.3007		11.222	[5]
			4.309(2)		11.286(8)	This work
Nb	α-Fe	*Im*3*m*	3.3014			[5]
			3.311(3)			This work
$Nb_{0.96}Ni_{0.02}Sb_{0.02}$	α-Fe	*Im*3*m*	3.307(3)			This work
NbNi	W_6Fe_7	$R\bar{3}m$	5.072(4)		27.65(1)	[4]
$Nb_{1.12–1.06}Ni_{0.88–0.94}$			5.064(2)–5.109(6)		28.25(1)–27.33(2)	This work
$NbNi_3$	$TiAl_3$	*I*4/*mmm*	3.62		7.41	[4]
			3.556(1)		7.422(2)	This work
Ni	Cu	*Fm*3*m*	3.5239			[5]
$Ni_{0.94}Nb_{0.06}$	Cu	*Fm*3*m*	3.563			[4]
			3.573(1)			This work
$Ni_{0.93}Nb_{0.05}Sb_{0.02}$	Cu	*Fm*3*m*	3.5961(6)			This work
$Ni_{0.93}Nb_{0.02}Sb_{0.05}$	Cu	*Fm*3*m*	3.5582(5)			This work
$Ni_{0.9}Sb_{0.1}$	Cu	*Fm*3*m*	3.588			[4]
			3.574(1)			This work
Ni_5Sb_2	New	*C*2	12.9456	5.4271 (β = 151.71°)	11.457	[4]
$Ni_{5.0–5.1}Sb_{2.0–1.9}$			12.872(2)–12.76(5)	5.4266(6)–5.424(2) (β = 151.59(1)°–151.51(1)°)	11.425(7)–11.34(5)	This work
NiSb			3.934		5.131	[4]
$Ni_{1.12–0.94}Sb_{0.88–1.06}$	NiAs	$P6_3/mmc$	4.033–3.914		5.202–5.135	[4]
			4.032(2)–3.936(1)		5.200(1)–5.126(1)	This work
Nb_3Sb			5.2643			[4]
$Nb_{3.0–3.1}Sb_{1.0–0.9}$	Cr_3Si	*Pm*3*n*	5.261(1)–5.311(3)			This work
Nb_5Sb_4	Ti_5Te_4	*I*4/*m*	10.314		3.5566	[4]
			10.321(1)		3.5549(6)	This work
$NbSb_2$	$OsGe_2$	*C*2/*m*	10.218	3.630 (β = 120.03°)	8.315	[4]
			10.2395(2)	3.6318(1) (β = 120.035(1)°)	8.3322(2)	This work
$Nb_{28}Ni_{33.5}Sb_{12.5}$	New	*Pnnm*	13.2334	16.5065	5.0337	[1]
			13.278(4)–13.206(6)	16.532(5)–16.480(9)	5.049(2)–5.036(2)	This work

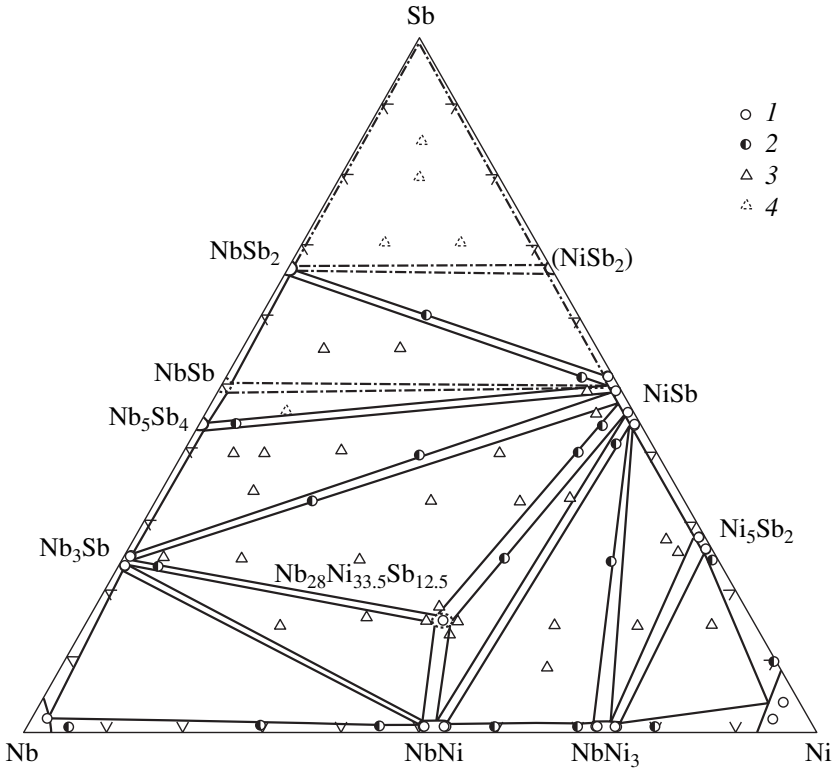

Fig. 1. 1070-K section of the Nb–Ni–Sb phase diagram in the region 0–67 mol % Sb: (*1*) single-, (*2*) two-, and (*3*) three-phase samples; (*4*) samples annealed at 870 K; the dash–dot lines represent 870-K phase equilibria.

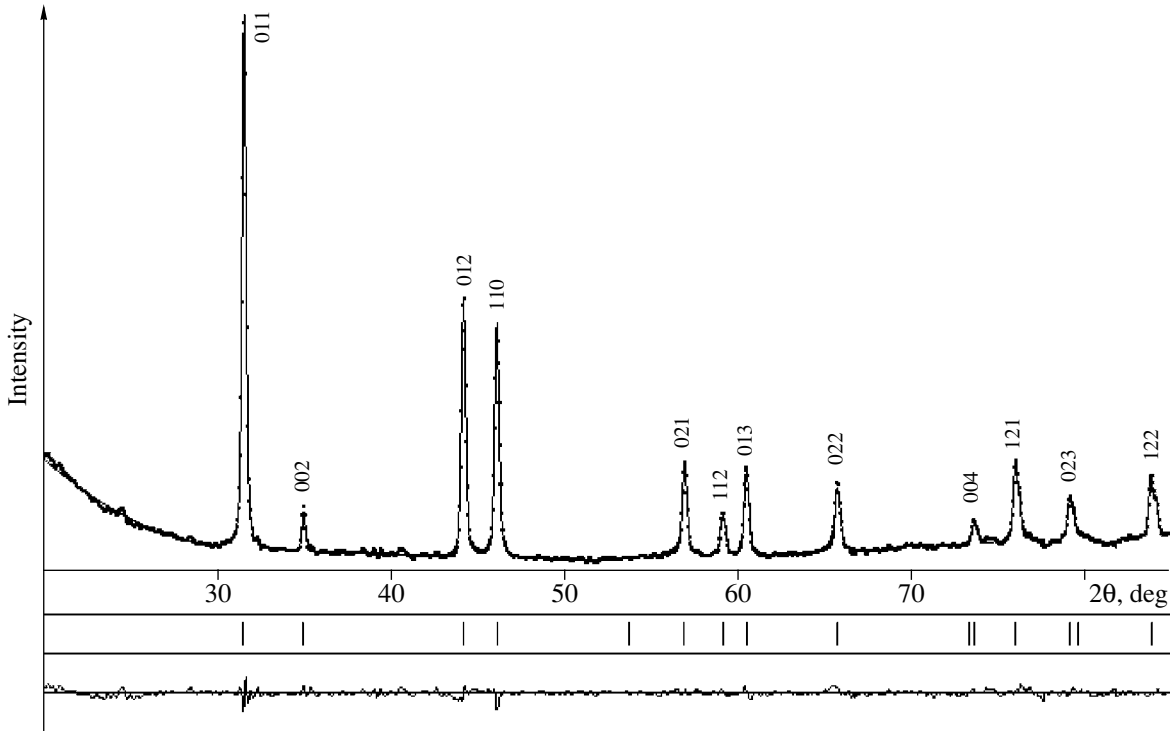

Fig. 2. XRD pattern of NiSb ($Nb_{0.1}Ni_{0.9}Sb$ sample, CuK_α radiation).

Table 2. Crystal data for NiSb ($Nb_{0.1}Ni_{0.9}Sb$ sample), intensity data collection conditions, and refinement statistics

Refined composition	NiSb
Space group	$P6_3/mmc$
a, Å	3.9399(5)
c, Å	5.1413(9)
V, Å^3	69.12(3)
Formula units per cell, Z	2
Calculated density, g/cm^3	8.676(4)
Diffractometer	DRON-3M
Radiation; wavelength, nm	Cu; λ = 0.154185
Absorption coefficient, cm^{-1}	1721.34
[111] texture	2.0700
Refinement parameters	5
Refinement procedure	Full profile
Atomic positions	2
$2\theta_{max}$; $\sin\theta_{max}/\lambda$, Å^{-1}	85.27; 0.439
R_I; R_p	0.0453; 0.1203

Those samples contained, in addition to $Nb_{28}Ni_{33.5}Sb_{12.5}$, other phases. XRD examination of the three-phase samples showed that the lattice parameters of $Nb_{28}Ni_{33.5}Sb_{12.5}$ were slightly increased in the Nb_3Sb + NiSb + $Nb_{28}Ni_{33.5}Sb_{12.5}$ region (a = 1.3278(4) nm, b = 1.6532(5) nm, c = 0.5049(2) nm) and slightly reduced in the NiSb + NbNi + $Nb_{28}Ni_{33.5}Sb_{12.5}$ region (a = 1.3206(6) nm, b = 1.6480(9) nm, c = 0.5036(2) nm) in comparison with the single-phase material (a = 1.320(8) nm, b = 1.6551(5) nm, c = 0.5019(2) nm). Thus, we are led to conclude that $Nb_{28}Ni_{33.5}Sb_{12.5}$ has a narrow homogeneity range, no broader than 2 mol %, at a constant Sb content. For this reason, the composition region of this ternary compound in Fig. 1 is shown by a dashed line. Solid solutions based on Nb–Ni or Nb–Sb binary compounds were not detected.

Solubility of Nb in NiSb and Ni in $NbSb_2$. Nb–Ni–Sb samples close in composition to NiSb (NiAs) were XRD single-phase. To assess Nb solubility in NiSb, we prepared samples containing 5 mol % Nb and different Ni : Sb ratios within the homogeneity range of $Ni_{1.12–0.94}Sb_{0.88–1.06}$ (0.44, 0.46, 0.50, and 0.52 mol % Sb). The structure of the $Nb_{0.1}Ni_{0.9}Sb$ sample (a = 0.39399(5) nm, c = 0.51413(9) nm) was refined using powder XRD data with the aim of ascertaining whether Nb may substitute for Ni or Sb in NiSb.

The XRD pattern of that sample is shown in Fig. 2. The crystal data and intensity data collection conditions are summarized in Table 2. The structure was refined in space group $P6_3/mmc$ using the atomic parameters in the NiAs structure [4] as input data. The Nb occupancy was free to refine on both the Ni (2a) and Sb (2c) sites. Final refinement converged to R_I = 0.045 at the composition NiSb (Table 3), indicating that NiSb dissolves no Nb.

The sample with the bulk composition ≃$NbNiSb_3$ was found to contain needlelike single crystals. According to x-ray spectrochemical analysis results (JEOL JSM-6400 scanning electron microscope, Laboratoire de Chimie du Solide et Inorganique Moléculaire, Université Rennes 1, France), the approximate composition of one of the crystals was ≃$NbSb_2$. The crystal structure of $NbSb_2$ was solved earlier by Rehr and Kauzlarich [6]. Determining the Nb and Sb site compositions, we might assess the homogeneity range of $NbSb_2$ and find out whether it dissolves Ni or not. Intensity data for that crystal were collected on the Nonius Kappa diffractometer (Table 4).

The observed reflections could be indexed in a monoclinic cell, possible space group $C2$, with lattice parameters a = 1.02395(2) nm, b = 0.36318(1) nm, c = 0.83322(2) nm, and β = 120.035(14)°. The structure was solved by the direct method in space group $C2/m$ using CSD (Table 4). The final difference Fourier map showed no foreign atoms. To determine site compositions, first a random mixture of Nb and Ni atoms was placed in the Nb site, and then the Nb and Sb atoms were permitted to occupy both sites at random. The lowest agreement factor was obtained with both sites occupied only by Nb and Sb. The atomic position coordinates and thermal parameters in the structure of $NbSb_2$ (R_F = 0.026 and R_w = 0.038 for 1031 indepen-

Table 3. Atomic position coordinates and thermal parameters in the structure of NiSb ($Nb_{0.1}Ni_{0.9}Sb$ sample)

Atom (site composition)	Position	x	y	z	$B_{iso} \times 10^2$, nm^2
Ni (1.00(4)Ni + 0.00(4)Nb)	2a	0	0	0	0.7(3)
Sb (1.00(3)Sb + 0.00(3)Nb)	2c	1/3	2/3	1/4	0.2(2)

Table 4. Crystal data for $NbSb_2$ (sample of composition ~$NbNiSb_3$), intensity data collection conditions, and refinement statistics

Refined composition	$NbSb_2$
Space group	*C*2/*m*
a, Å	10.2395(2)
b, Å	3.6318(1)
c, Å	8.3322(2)
β, deg	120.035(1)°
V, Å^3	268.25(2)
Formula units per cell, *Z*	3
Calculated density, g/cm^3	8.3302(7)
Absorption coefficient, cm^{-1}	239.15
Diffractometer	Nonius Kappa CCD
Radiation; wavelength, nm	Mo; λ = 0.071073
Measured reflections	4879
Independent reflections	2923 ($I > 1\sigma(I)$)
Observed reflections	1031 ($I > 4\sigma(I)$)
Refinement procedure	$F^2(hkl)$
Atomic positions	3
Refinement parameters	268
$2\theta_{max}$; $\sin\theta_{max}/\lambda$, Å^{-1}	84.22; 0.942
R_F; R_w	0.0261; 0.0377

dent *hkl* reflections considered observed on the criterion $F_{hkl} > 4\sigma(F_{hkl})$) are listed in Table 5. Refinement in space group *C*2 converged to the same *R*-factor, but preference was given to the higher symmetry space group *C*2/*m*.

The bond distances in $NbSb_2$ (Table 6) are close to the sums of the corresponding atomic radii (r_{Nb} = 0.147 nm, r_{Sb} = 0.141 nm [7]).

Thus, our results confirm earlier data on the crystal structure of $NbSb_2$ [6] and indicate that it has no homogeneity range and dissolves no Ni.

DISCUSSION

As a result of systematic studies of the Nb–Ni–Sb system, we constructed its phase diagram at 1070 K in the region 0–67 mol % Sb and at 870 K at higher Sb contents. The only ternary compound in the system is $Nb_{28}Ni_{33.5}Sb_{12.5}$. Although the binary compounds in the Nb–Ni system have some homogeneity ranges, there is no Nb or Ni solubility in the binary antimonides of this system, as evidenced by the present structural data for NiSb and $NbSb_2$ in three-phase samples. The ternary compound $Nb_{28}Ni_{33.5}Sb_{12.5}$ has a narrow homogeneity range.

Just as the Nb–Fe–Sb and Nb–Co–Sb systems [4], the Nb–Ni–Sb contains only one ternary compound and no solid solutions based on binary compounds, but the ternary compounds in the first two systems, NbFeSb and NbCoSb, have the MgAgAs structure [8]. The Nb–Ni–Sb system shows less similarity to the Zr(Hf)–Ni(Co,Fe)–Sb systems, which contain substantially more ternary compounds, with different crystal structures [4]. This is attributable to the larger differences in atomic radius and electronegativity between the transition metals in the Zr and Hf systems (r_{Nb} = 0.1468 nm, r_{Zr} = 0.1602 nm, r_{Ni} = 0.1246 nm, χ_{Nb} = 1.6, χ_{Zr} = 1.4, χ_{Ni} = 1.7) [7, 10]. Consequently, phase relations in ternary systems of two transition metals and antimony are influenced by the size factor and the difference in chemical properties between the transition metals.

Substantially more complex phase relations occur in analogous phosphorus systems. In particular, the Nb–Ni–P system contains eight ternary compounds [11], none of which are isostructural with any phase in the Nb–Ni–Sb or Zr(Hf)–Fe(Co,Ni)–Sb systems. The reason for this is that phosphorus is a typical nonmetal,

Table 5. Atomic position coordinates and thermal parameters ($B \times 10^2$, nm^2) in the structure of $NbSb_2$ (sample of composition ≃$NbNiSb_3$)

Atom	Position	ι	*y*	*z*	B^*_{iso}	B_{11}	B_{22}	B_{33}	B_{13}
Nb	4*i*	0.84791(4)	0	0.30972(5)	0.233(9)	0.24(1)	0.27(1)	0.21(1)	0.128(9)
Sb(1)	4*i*	0.59493(3)	0	0.38735(4)	0.327(6)	0.349(8)	0.350(7)	0.373(8)	0.249(7)
Sb(2)	4*i*	0.14750(3)	0	0.03457(4)	0.338(6)	0.329(8)	0.404(7)	0.321(8)	0.192(7)

* $B_{12} = B_{23} = 0$.

Table 6. Bond distances in the structure of $NbSb_2$

Atoms	δ, Å	Atoms	δ, Å
Nb–2Nb	3.6318(1)	Sb1–2Nb	2.9113(5)
2Sb(2)	2.8382(4)	2Nb	2.9211(4)
Sb(2)	2.8924(5)	Nb	2.9675(6)
2Sb(1)	2.9113(5)	2Sb(1)	3.3074(4)
2Sb(1)	2.9211(4)	Sb(1)	3.3101(5)
Sb(1)	2.9675(6)	2Sb(2)	3.6169(4)
Nb	3.1416(6)	2Sb(1)	3.6318(1)
		2Sb(2)	3.7164(4)
		Sb2–Sb2	2.7773(6)
		2Nb	2.8382(4)
		Nb	2.8924(5)
		2Sb(2)	3.0408(4)
		2Sb(1)	3.6169(4)
		2Sb(2)	3.6318(1)
		2Sb(1)	3.7164(4)

while antimony has metallic properties ($\chi_{Sb} = 1.8$, $\chi_P = 2.1$ [10]). Moreover, the atomic radius of phosphorus is notably smaller ($r_{Sb} = 0.141$ nm, $r_P = 0.110$ nm) [7].

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