

## The Y–Ni–Cu ternary system at 600°C

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The isothermal section of the Y–Ni–Cu phase diagram at 600°C has been investigated by means of X-ray diffraction and microstructure analyses. The homogeneity ranges of the solid solutions  $\text{YNi}_{5-x}\text{Cu}_x$  ( $0 \leq x \leq 4.6$ ) (structure type  $\text{CaCu}_5$ , space group  $P6/mmm$ ,  $a = 0.48861(2)–0.50080(4)$ ,  $c = 0.39592(2)–0.40740(4)$  nm),  $\text{Y}_2\text{Ni}_{17-x}\text{Cu}_x$  ( $0 \leq x \leq 7.8$ ) (structure type  $\text{Th}_2\text{Ni}_{17}$ , space group  $P6_3/mmc$ ,  $a = 0.8314(1)–0.8387(1)$ ,  $c = 0.8042(1)–0.8117(1)$  nm),  $\text{YCu}_{6-7}\text{Ni}_x$  ( $0 \leq x \leq 0.28$ ) (structure type  $\text{TbCu}_7$ , space group  $P6/mmm$ ,  $a = 0.49470(4)–0.49540(4)$ ,  $c = 0.4133(4)–0.4227(4)$  nm) were refined. It was found that the maximal solubility of the third component does not exceed 3.8 at.% in  $\text{Y}_2\text{Cu}_7$  and less than 1 at.% in  $\text{Y}_2\text{Ni}_7$ ,  $\text{YCu}$ , and  $\text{YCu}_4$ . The crystal structure of a single crystal of composition  $\text{YNi}_4\text{Cu}$  ( $\text{YNi}_{5-x}\text{Cu}_x$  solid solution) was investigated by X-ray diffraction:  $a = 0.4899(2)$ ,  $c = 0.3979(3)$  nm,  $R_1 = 0.028$  for 57 independent reflections with  $I_0 \geq 2\sigma(I_0)$ ,  $wR_2 = 0.058$ . A new ternary compound,  $\text{YNi}_{2.85-0.75}\text{Cu}_{1.15-3.25}$ , of unknown structure with an extended homogeneity range, was found.

Intermetallics / Rare-earth metal system / Phase diagram / X-ray diffraction

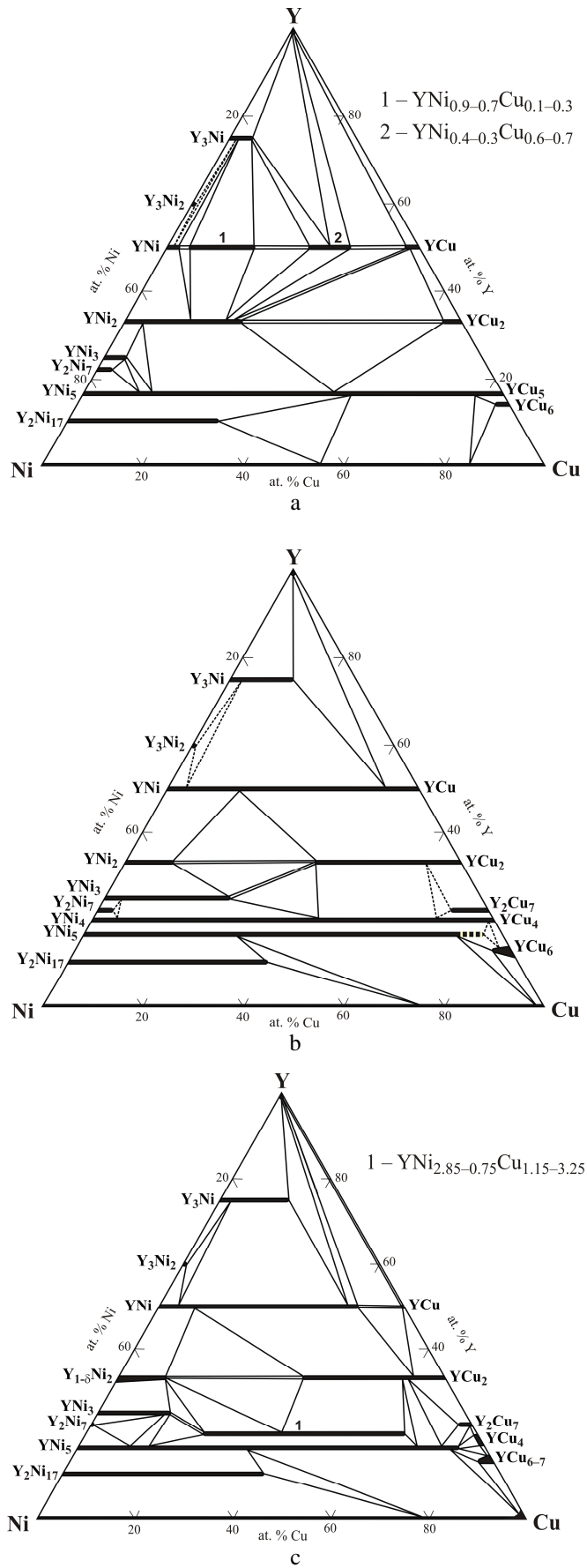
### Introduction

The phase equilibria in the Y–Ni–Cu ternary system have previously been investigated near the Ni–Cu side with low content of Y ( $\leq 16.7$  at.%) at 500°C [1], and in the whole concentration range at 600°C [2] by X-ray diffraction (XRD), and at 700°C using diffusion couples and key alloys [3]. The isothermal sections of the Y–Ni–Cu phase diagram at 600°C [2] and at 700°C [3] are presented in Fig. 1 a,b.

A large number of studies of the ternary Y–Ni–Cu system were dedicated to the crystal structures [4-12], magnetism [6], hydrogen sorption [7-9], and electrical [10,11] properties of the solid solutions based on the binary Y–Ni and Y–Cu compounds. However, there are some significant differences between the results of these studies. The authors of [2] reported the existence of two ternary compounds at the isoconcentrate of 50 at.% Y, whereas in [3] the existence of extended solid solutions between the isostructural binary compounds  $\text{YNi}$  and  $\text{YCu}$  (both indicated as FeB structure type) was found. The data on the crystal structures and the homogeneity ranges of some solid solutions based on the binary compounds of the Y–Ni and Y–Cu systems are contradictory (see Table 1). In particular, the results of [2] differ significantly from the data of [1,3-6,12].

The binary systems Ni–Cu [13-15], Y–Ni [16-24] and Y–Cu [25-32], which form the ternary Y–Ni–Cu system, have been widely studied, including the phase diagrams over the whole concentration ranges. The Ni–Cu system [13] is a simple isomorphous system with continuous liquid and solid solutions separated by a narrow two-phase region. The data on some of the binary Y–Ni and Y–Cu compounds are contradictory, in particular as they were investigated under different conditions.

The Y–Ni phase diagram was first investigated by Beaudry and Daane [16] using metallographic and thermal analyses and X-ray diffraction. The existence of nine binary compounds  $\text{Y}_2\text{Ni}_{17}$  (unknown structure),  $\text{YNi}_5$  (structure type (ST)  $\text{CaCu}_5$ , space group (SG)  $P6/mmm$ ),  $\text{YNi}_4$  (unknown structure),  $\text{Y}_2\text{Ni}_7$  (unknown structure),  $\text{YNi}_3$  (ST  $\text{PuNi}_3$ , SG  $R-3m$ ),  $\text{YNi}_2$  (ST  $\text{MgCu}_2$ , SG  $Fd-3m$ ),  $\text{YNi}$  (ST FeB, SG  $Pnma$ ),  $\text{Y}_3\text{Ni}_2$  (ST  $\text{Y}_3\text{Ni}_2$ , SG  $P4_12_12$ ), and  $\text{Y}_3\text{Ni}$  (ST  $\text{Fe}_3\text{C}$ , SG  $Pnma$ ) was detected. Later, Buschow [17] reported the crystal structure of the compound  $\text{Y}_2\text{Ni}_{17}$  (ST  $\text{Th}_2\text{Ni}_{17}$ , SG  $P6_3/mmc$ ). The phase  $\text{YNi}_4$  with unknown structure was not found in [2,23,24,33], but is present on the phase diagrams of the binary and ternary systems reported in [3,16,22,25]. The authors of [19-21] reported two types of structure for  $\text{Y}_2\text{Ni}_7$ : a hexagonal structure of the  $\text{Ce}_2\text{Ni}_7$  type (SG  $P6_3/mmc$ ) and a rhombohedral structure of the  $\beta\text{-Gd}_2\text{Co}_7$  type (SG  $R-3m$ ).



**Fig. 1** Isothermal sections of the Y–Ni–Cu system at 600°C [2] (a), 700°C [3] (b), and 600°C (present investigation) (c).

**Table 1** Crystallographic data and solubility of the third component in solid solutions based on the binary Y–Ni and Y–Cu compounds in the Y–Ni–Cu system.

Solid solution	Structure type	Space group	Unit cell parameters, nm			Solubility of the 3 <sup>rd</sup> component, at.% (T, °C)	Ref.
			<i>a</i>	<i>b</i>	<i>c</i>		
Y <sub>3</sub> Ni <sub>1-x</sub> Cu <sub>x</sub>	Fe <sub>3</sub> C	<i>Pnma</i>	0.6917-	0.9644-	0.6357-	14 (600)	[12] <sup>a</sup>
			0.6923	0.9721	0.6412	4.1 (600)	[2]
						12.04 (700)	[3]
Y <sub>3</sub> Ni <sub>2</sub>	Y <sub>3</sub> Ni <sub>2</sub>	<i>P4<sub>1</sub>2<sub>1</sub>2</i>	0.7098	–	3.6060	<1 (600)	[12] <sup>a</sup>
						<1 (600)	[2]
YNi <sub>1-x</sub> Cu <sub>x</sub>	FeB	<i>Pnma</i>	0.7148-	0.4122-	0.5512-	42 (600)	[12] <sup>a</sup>
			0.7094	0.4450	0.5405	5.7 (600)	[2]
						50 <sup>b</sup> (700)	[3]
YCu <sub>1-x</sub> Ni <sub>x</sub>	CsCl	<i>Pm-3m</i>	0.3474(1)	–	–	<1 (600)	<sup>a</sup>
						4.9 (600)	[2]
						5.5 (690)	[10]
Y <sub>0.95</sub> Ni <sub>2-x</sub> Cu <sub>x</sub>	TmNi <sub>2</sub>	<i>F-43m</i>	1.4347-	–	–	10 (600)	[12] <sup>a</sup>
			1.4373			23.7 (600)	[2]
YNi <sub>2-x</sub> Cu <sub>x</sub>	MgCu <sub>2</sub>	<i>Fd-3m</i>				9.67 (700)	[3]
						13.4 (800)	[5]
YCu <sub>2-x</sub> Ni <sub>x</sub>	KHg <sub>2</sub>	<i>Imma</i>	0.4301-	0.6874-	0.7297-	29 (600)	[12] <sup>a</sup>
			0.4192	0.6471	0.7299	3.9 (600)	[2]
						28 (700)	[3]
						33 (800)	[5]
YNi <sub>3-x</sub> Cu <sub>x</sub>	PuNi <sub>3</sub>	<i>R-3m</i>	0.4978-	–	2.4450-	14 (600)	[12] <sup>a</sup>
			0.4994		2.4476	16.67 (500)	[8]
						5 (600)	[2]
						12 (600)	[1]
						25 (700)	[3]
α-Y <sub>2</sub> Ni <sub>7-x</sub> Cu <sub>x</sub>	β-Gd <sub>2</sub> Co <sub>7</sub>	<i>R-3m</i>	0.49525(3)	–	3.6314(3)	<1 (600)	<sup>a</sup>
						4.1 (600)	[2]
						3.08 (700)	[3]
Y <sub>2</sub> Cu <sub>7-x</sub> Ni <sub>x</sub>	CeCu <sub>3.6</sub>	<i>P6/m</i>	1.1571(4)	–	0.8669(6)	3.8 (600)	<sup>a</sup>
			crystal structure is not established			7.5 (700)	[3]
YNi <sub>4</sub>	compound is not found					– (600)	<sup>a</sup>
YNi <sub>4-x</sub> Cu <sub>x</sub>	crystal structure is unknown					80 <sup>b</sup> (700)	[3]
YCu <sub>4-x</sub> Ni <sub>x</sub>	crystal structure is unknown					<1 (600)	<sup>a</sup>
YNi <sub>5-x</sub> Cu <sub>x</sub>	CaCu <sub>5</sub>	<i>P6/mmm</i>	0.48861(2)-	–	0.39592(2)-	77 (600)	<sup>a</sup>
			0.50080(4)		0.40740(4)	72 (500)	[1]
						83 <sup>b</sup> (600)	[2,12]
						75 (700)	[3]
						66.7 (800)	[4]
YCu <sub>5</sub>	compound is not found					– (600)	<sup>a</sup>
YCu <sub>6-7</sub> Ni <sub>x</sub>	TbCu <sub>7</sub>	<i>P6/mmm</i>	0.49470(4)-	–	0.4133(4)-	3.5 (600)	<sup>a</sup>
			0.49540(4)		0.4227(4)	3.3 (600)	[2]
						11 (600)	[12]
						3.9 (700)	[3]
Y <sub>2</sub> Ni <sub>17-x</sub> Cu <sub>x</sub>	Th <sub>2</sub> Ni <sub>17</sub>	<i>P6<sub>3</sub>/mmc</i>	0.8314(1)-	–	0.8042(1)-	~41 (600)	<sup>a</sup>
			0.8387(1)		0.8117(1)	35 (500)	[1]
						30.3 (600)	[2]
						37 (700)	[3]
						30.5 (950)	[6]

<sup>a</sup> results of this work; <sup>b</sup> continuous solid solution

The rhombohedral structure is stable at low temperatures, whereas the hexagonal one is the high-temperature modification. The phase transformation from one type of structure to another occurs *via* a sluggish martensitic-type process [20]. These structures are closely related, since both are derivatives of the hexagonal  $\text{CaCu}_5$  structure type [34]. The authors of [18] pointed out that the  $\text{YNi}_2$  compound has a structure derived from the ideal cubic  $\text{MgCu}_2$  structure with the defect composition  $\text{Y}_{0.95}\text{Ni}_2$ . It can be described as a superstructure of  $\text{MgCu}_2$  with doubled  $a$  lattice parameter and space group  $F\text{-}43m$  with the  $4a$  site only partially occupied by Y atoms.

The phase equilibria in the Y–Cu system have been studied in [25–29]. All the authors confirmed the existence of the intermetallic compounds  $\text{YCu}$  (ST CsCl, SG  $Pm\text{-}3m$ ) and  $\text{YCu}_2$  (ST  $\text{KHg}_2$ , SG  $Imma$ ). Some authors reported the existence of a high-temperature modification of the compound  $\text{YCu}_2$  above 860°C [14,28,29] (the structure is unknown). The phase  $\text{Y}_2\text{Cu}_7$  was not found in [25,30,31], however it is present on the phase diagrams of the binary and ternary systems reported in [3,14,26–29,32]. The authors of [32] determined the crystal structure of the  $\text{Y}_2\text{Cu}_7$  compound, which was found to adopt the structure type  $\text{CeCu}_{3.6}$  (SG  $P6/m$ ,  $a = 1.1627$ ,  $c = 0.8698$  nm). According to the data of [25,31], the phase  $\text{YCu}_4$  with unknown crystal structure exists in a narrow homogeneity range, whereas in [3,14,27–29,32] it is shown as a compound with constant stoichiometric composition. Some authors attribute this phase to the hexagonal structure type  $\text{CaCu}_5$  [2,13,26,33], while in [32] the crystal structure of  $\text{YCu}_4$  was determined as an original monoclinic structure type (SG  $P2/n$ ,  $a = 0.8765$ ,  $b = 0.5000$ ,  $c = 0.4105$  nm,  $\gamma = 91.09^\circ$ ). The phase with  $\text{TbCu}_7$ -type structure (SG  $P6/mmm$ ) was in [14,26,31] attributed the composition  $\text{YCu}_7$ , whereas by other researchers [29,31,32] it was reported to occur at the composition  $\text{YCu}_6$  with a narrow ( $< 1$  at.%) homogeneity range.

These inconsistencies in the literature on the compositions and crystal structures of the binary compounds of the Y–Ni and Y–Cu systems, and on the solubility of the third components in the binary compounds, prompted us to conduct additional research of the system Y–Ni–Cu at 600°C, the results of which are presented in this article.

## Experimental

The alloys were prepared by arc melting of the elements with not less than 99.9 wt.% purity under argon. During the arc melting the weight losses were less than 1 wt.% of the total mass of the ingots. The alloys were annealed in evacuated quartz ampoules at 600°C for 1000 h. Bulk and powdered samples were stable in air over months. The annealed binary alloys

of the Y–Cu system with an Y content of ~10–30 at.% were subjected to re-crystallization. For that purpose 0.5 g-specimens were ground into powder, cold-pressed into pellets, separately sealed in evacuated quartz ampoules, and exposed to prolonged thermal annealing at 600°C for 4500 h.

The phase analysis of the alloys was carried out with the CSD program package [35] on powder XRD data, obtained with DRON-2.0 (Fe  $K\alpha$ -radiation) and STOE STADI P (Mo  $K\alpha_1$ , Cu  $K\alpha_1$ ) diffractometers. Small and irregularly shaped single crystals were selected from crushed, annealed samples and sealed in Lindemann-glass capillaries under argon atmosphere. These crystals were first examined by the Buerger precession technique in order to establish their quality for subsequent intensity collection. Diffraction data of a crystal were collected at room temperature on a STOE IPDS I image plate diffractometer with monochromatized Ag  $K\alpha$  radiation and oscillation of the crystal around the  $\omega$ -axis. The starting atomic parameters were derived by direct methods using the program SIR97 [36] and subsequently refined with the program SHELXL-97 [37] in the WinGX program package [38] (full-matrix least-squares on  $F^2$ ) with anisotropic atomic displacements.

Metallographic, quantitative and qualitative composition analyses of polished samples and single crystals were performed by energy-dispersive X-ray spectroscopy analysis (EDX) on a scanning electron microscope VEGA TS 5130 MM with an Oxford Si-detector.

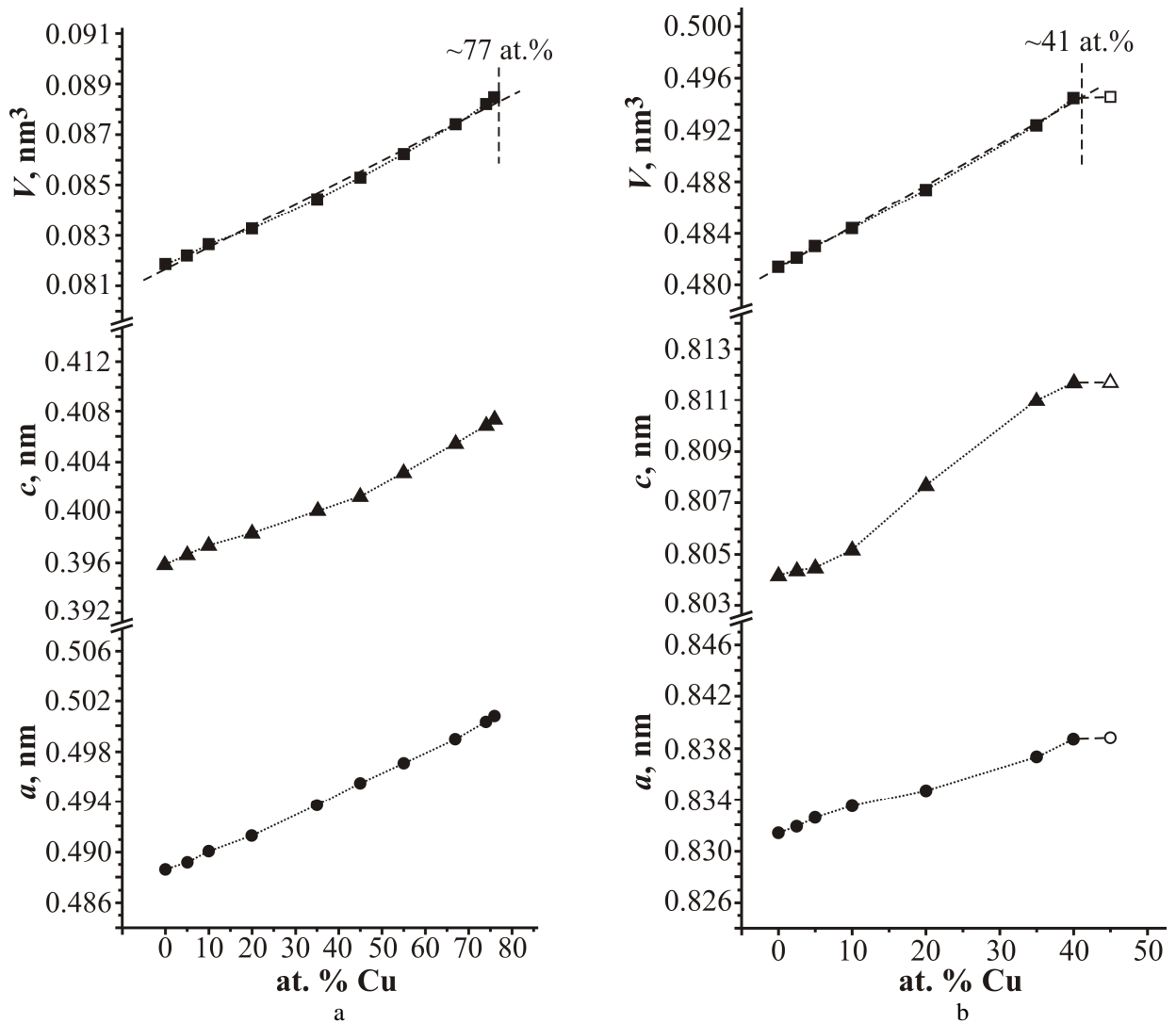
## Results and discussion

The isothermal section of the Y–Ni–Cu phase diagram at 600°C was investigated by means of XRD and metallographic analyses of 144 binary and ternary alloys and is presented in Fig. 1c.

The existence of the compounds  $\text{Y}_3\text{Ni}$ ,  $\text{Y}_3\text{Ni}_2$ ,  $\text{YNi}$ ,  $\text{Y}_{1.6}\text{Ni}_2$ ,  $\text{YNi}_3$ ,  $\alpha\text{-Y}_2\text{Ni}_7$ ,  $\text{YNi}_5$ , and  $\text{Y}_2\text{Ni}_{17}$  was confirmed (see Fig. 1). The solubilities of Cu observed in these compounds agree with those given in our previous work [12] (see Table 1). Like in our earlier research of the related system Y–Zr–Ni under similar conditions [39], in the present work we encountered a problem regards the  $\text{YNi}_4$  compound, reported earlier [3,16,22,25]. Based on the results of powder XRD and EDX we conclude that it does not exist at 600°C. The results of these studies will be given in more detail in a separate publication. It should be noted that one of our previous works was devoted to the refinement of the phase equilibria in the related Dy–Ni system concerning the possible existence of a  $\text{DyNi}_4$  compound, which was also not found [40]. The continuous solid solution between  $\text{YNi}_4$  and  $\text{YCu}_4$  at 600°C reported in [3], was not confirmed. No significant solubility of the third component in  $\alpha\text{-Y}_2\text{Ni}_7$  was found (see Table 1).

In the present work, the results of [2,12] concerning the existence of a continuous solid solution between  $\text{YNi}_5$  (ST  $\text{CaCu}_5$ , SG  $P6/mmm$ ) and  $\text{YCu}_5$  (attributed to ST  $\text{CaCu}_5$  in [2,13,26,33]) were not confirmed. The pure  $\text{YCu}_5$  compound is probably not thermodynamically stable at 600°C (see below). We refined the homogeneity range of the solid solution  $\text{YNi}_{5-x}\text{Cu}_x$ :  $0 \leq x \leq 4.6$ , using EDX technique (see Table 1). A significantly higher solubility of copper (~41 at.%), in comparison with previous works, was found in the  $\text{Y}_2\text{Ni}_{17}$  compound (see Table 1). It may be described by the formula  $\text{Y}_2\text{Ni}_{17-x}\text{Cu}_x$  ( $0 \leq x \leq 7.8$ ). The variations of the unit cell parameters and the cell volumes within the  $\text{YNi}_{5-x}\text{Cu}_x$  ( $0 \leq x \leq 4.6$ ) and  $\text{Y}_2\text{Ni}_{17-x}\text{Cu}_x$  ( $0 \leq x \leq 7.8$ ) solid solutions are presented in Fig. 2. Substitution of copper for nickel is accompanied by an almost linear change of the unit cell volumes within the solid solutions. The presence of  $\text{YCu}$  (ST  $\text{CsCl}$ , SG  $Pm-3m$ )

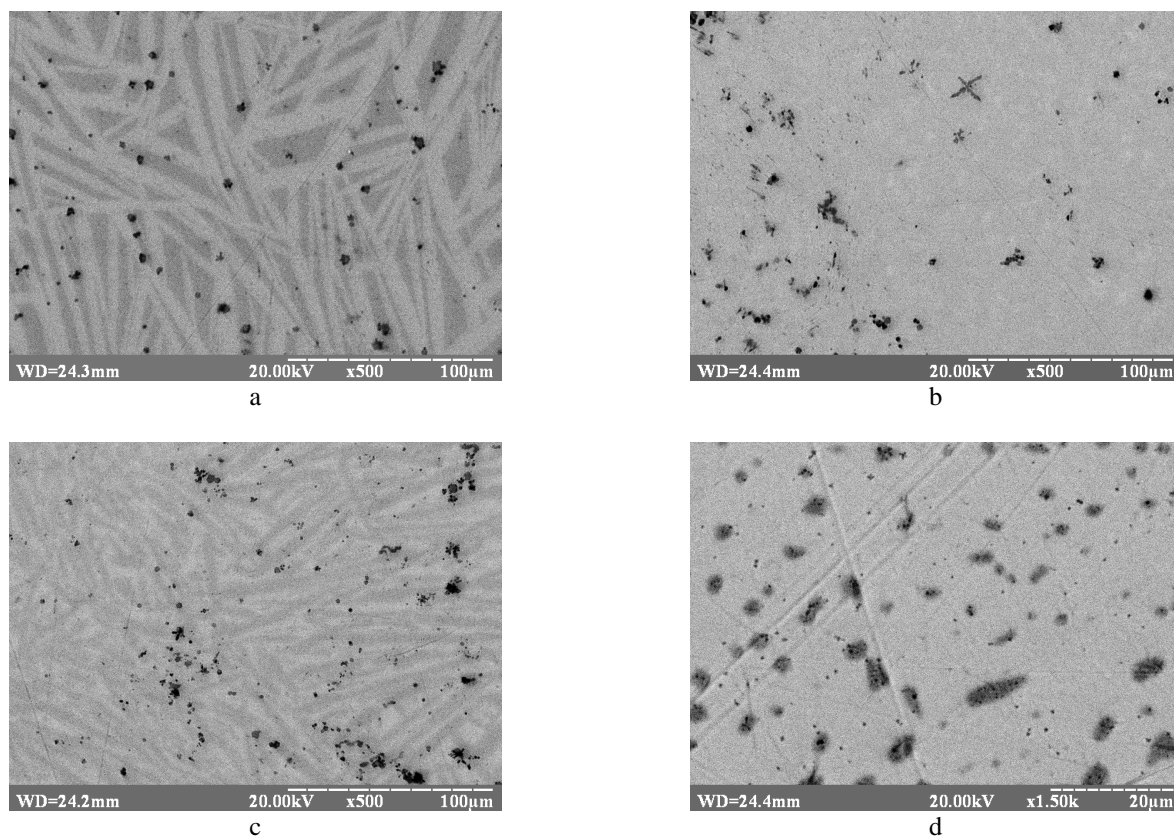
and  $\text{YCu}_2$  (ST  $\text{KHg}_2$ , SG  $Imma$ ) in the phase equilibria in the Y–Ni–Cu system at 600°C was confirmed (see Fig. 1). In [2] two ternary compounds,  $\text{YNi}_{0.9-0.7}\text{Cu}_{0.1-0.3}$  (ST  $\text{FeB}$ , SG  $Pnma$ ,  $a = 0.7103$ ,  $b = 0.4188$ ,  $c = 0.5491$  nm) and  $\text{YNi}_{0.3-0.4}\text{Cu}_{0.7-0.6}$  (unknown structure), which are in equilibrium at 600°C (Fig. 1a), were reported to occur along the 50 at.% Y isoconcentrate. However, according to the data of [3], a continuous solid solution exists between the binary compounds  $\text{YNi}$  and  $\text{YCu}$  at 700°C (see Fig. 1b). In the present investigation we confirmed the results of our previous work [12] on the solubility of copper in the  $\text{YNi}$  compound (see Table 1). The  $\text{YCu}$  compound does not dissolve detectable amounts of nickel. In contradiction with [3],  $\text{YCu}$  with  $\text{CsCl}$ -type structure is stable at 600°C, which makes impossible the formation of a continuous solid solution  $\text{YNi}_{1-x}\text{Cu}_x$  between  $\text{YCu}$  and  $\text{YNi}$ , the latter crystallizing in another structure type ( $\text{FeB}$ ).



**Fig. 2** Variation of the unit cell parameters and cell volumes within the homogeneity ranges  $\text{YNi}_{5-x}\text{Cu}_x$  ( $0 \leq x \leq 4.6$ ) (a),  $\text{Y}_2\text{Ni}_{17-x}\text{Cu}_x$  ( $0 \leq x \leq 7.8$ ) (b).

In order to resolve the contradictory literature data on the Y–Cu binary compounds reported in [13–15,25–32], special efforts were made to obtain homogenous samples. Prolonged annealing with preliminary grinding of the alloys with an Y content of ~10–30 at.% was applied and the powder was pressed into pellets in order to accelerate re-crystallization of the samples. The results of the X-ray phase analysis of as-cast alloys and alloys annealed at 600°C indicated the existence in this concentration region of three phases with the following Y contents: ~14 at.% (YCu<sub>7</sub>), ~20 at.% (YCu<sub>4</sub>) and ~22 at.% (Y<sub>2</sub>Cu<sub>7</sub>). According to our data, the YCu<sub>7</sub> compound (ST TbCu<sub>7</sub>, SG *P6/mmm*) has a narrow homogeneity range from ~13 to 15 at.% Y, which is in good agreement with the data of [31] on as-cast alloys. This result allowed us to assume the YCu<sub>6</sub> and YCu<sub>7</sub> compounds, reported in [14,26,29,31,32] as different ones, to be the same compound, which we denote here as YCu<sub>6–7</sub>. It should be noted that the alloys with an Y content of 19–23 at.% are very hard and their X-ray diffraction reflections are very blurred, probably due to the existence of internal stresses or defects, which were not removed even after prolonged annealing. In this case mainly the EDX method was used for the determination of the phase equilibria. Backscattered electron images of alloys of the Cu-rich corner of the

Y–Ni–Cu system annealed at 600°C are presented in Fig. 3, and their phase compositions are given in Table 2. The alloy of composition Y<sub>17</sub>Cu<sub>83</sub>, from the presumed homogeneity range of the YCu<sub>4</sub> compound [25,31], was found to be a two-phase sample (Fig. 3a, Table 2) and contained the phases YCu<sub>4</sub> and Y<sub>2</sub>Cu<sub>7</sub>. The diffuse X-ray powder pattern (Fig. 4a) is very similar to that reported in [28,31]. These authors ascribed the unusual features of the diffractogram to the occurrence of random, non-periodic defects in the parent CaCu<sub>5</sub>-like type structure. We did not confirm the literature data on the crystal structure of the compound YCu<sub>4</sub>: own structure type (SG *P2/n*) in [32], or structure type CaCu<sub>5</sub> [2,13,26,33]. The homogeneity range extends from 17 to 20 at.% Y at 600°C. The same sample Y<sub>17</sub>Cu<sub>83</sub> (see Fig. 3a, Table 2, Fig. 4a) was subjected to re-crystallization. The XRD pattern of the re-crystallized sample is presented in Fig. 4b. Unfortunately, as a result of this treatment it absorbed some oxygen (the presence of Y<sub>2</sub>O<sub>3</sub> proves this), which, possibly, stabilized the CaCu<sub>5</sub>-type structure of the main phase (see Fig. 4). The alloy annealed at 600°C, corresponding to the Y<sub>2</sub>Cu<sub>7</sub> compound (composition Y<sub>22</sub>Cu<sub>78</sub>), was single-phase according to the EDX analysis (Fig. 3b, Table 2). Its powder diffraction pattern (Fig. 5a) could not be indexed due to blurry XRD peaks.



**Fig. 3** Backscattered electron image of alloys Y<sub>17</sub>Cu<sub>83</sub> (a): dark phase – YCu<sub>4</sub> (Y<sub>17.11</sub>Cu<sub>82.89</sub>), light phase – Y<sub>2</sub>Cu<sub>7</sub> (Y<sub>21.5</sub>Cu<sub>77.5</sub>); Y<sub>22</sub>Cu<sub>78</sub> (b): Y<sub>2</sub>Cu<sub>7</sub> (Y<sub>26.15</sub>Cu<sub>73.85</sub>); Y<sub>27</sub>Cu<sub>68</sub>Ni<sub>5</sub> (c): dark phase – Y<sub>2</sub>Cu<sub>7</sub> (Y<sub>23.6</sub>Cu<sub>72.6</sub>Ni<sub>3.8</sub>), light phase – YCu<sub>2</sub> (Y<sub>35.3</sub>Cu<sub>57.0</sub>Ni<sub>7.7</sub>); Y<sub>13</sub>Cu<sub>76</sub>Ni<sub>11</sub> (d): light phase – YNi<sub>5</sub> (Y<sub>16.6</sub>Cu<sub>70.6</sub>Ni<sub>12.8</sub>); dark phase – Cu (Cu<sub>98.1</sub>Y<sub>1.9</sub>).

**Table 2** XRD and EDX data for alloys of the Y–Cu and Y–Cu–Ni systems.

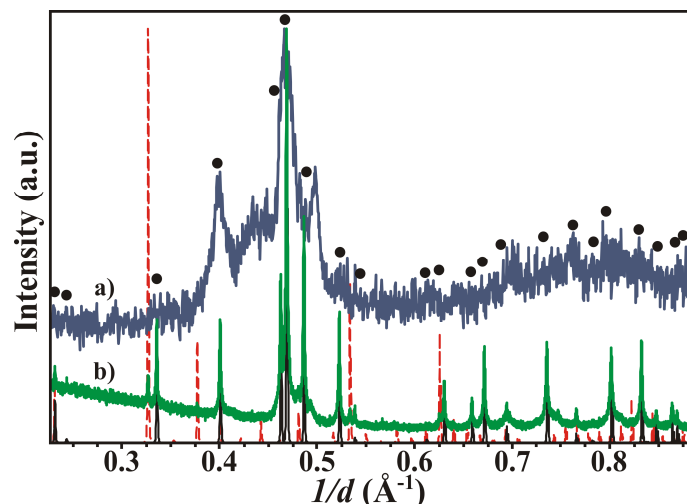
Nominal sample composition	XRD data	EDX data
Y <sub>17</sub> Cu <sub>83</sub>	YCu <sub>4</sub> Y <sub>2</sub> Cu <sub>7</sub>	Y <sub>17.11</sub> Cu <sub>82.89</sub> Y <sub>21.5</sub> Cu <sub>77.5</sub>
Y <sub>22</sub> Cu <sub>78</sub>	Y <sub>2</sub> Cu <sub>7</sub>	Y <sub>26.15</sub> Cu <sub>73.85</sub>
Y <sub>27</sub> Cu <sub>68</sub> Ni <sub>5</sub>	Y <sub>2</sub> Cu <sub>7</sub> YCu <sub>2</sub>	Y <sub>23.6</sub> Cu <sub>72.6</sub> Ni <sub>3.8</sub> Y <sub>35.3</sub> Cu <sub>57.0</sub> Ni <sub>7.7</sub>
Y <sub>13</sub> Cu <sub>76</sub> Ni <sub>11</sub>	YNi <sub>5</sub> Cu	Y <sub>16.6</sub> Cu <sub>70.6</sub> Ni <sub>12.8</sub> Cu <sub>98.1</sub> Y <sub>1.9</sub>

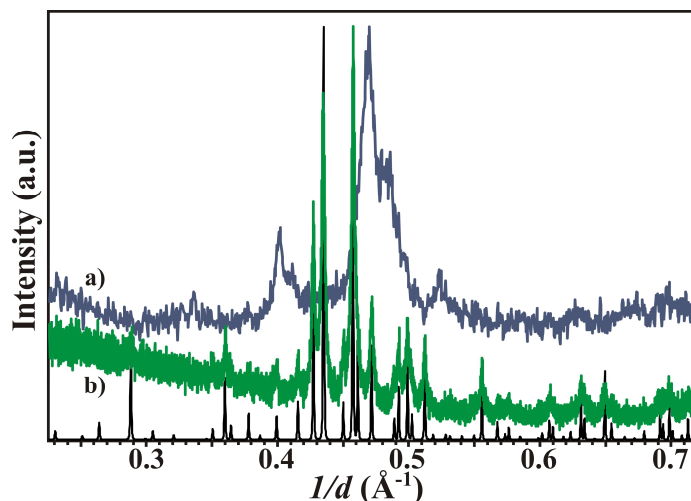
The authors of [3,14,26–29] also failed to determine the crystal structure of Y<sub>2</sub>Cu<sub>7</sub>, and only in [32] the crystal structure of the Y<sub>2</sub>Cu<sub>7</sub> compound is stated to adopt the structure type CeCu<sub>3.6</sub> (SG *P6/m*). We exposed the Y<sub>22</sub>Cu<sub>78</sub> alloy to a re-crystallization process. It was found that the CeCu<sub>3.6</sub>-type of crystal structure of Y<sub>2</sub>Cu<sub>7</sub> only forms after re-crystallization, as it is shown in Fig. 5b. In this case no oxygen impurities were found, which proves that the structure is not impurity-stabilized, compared to the CaCu<sub>5</sub>-type structure of YCu<sub>4</sub>, which is sensitive to oxygen impurities (Fig. 4).

The highest solubility of copper in Y<sub>2</sub>Cu<sub>7</sub> is 3.8 at.% at 600°C, according to the EDX results (Fig. 3c, Table 2). In [12] the solubility of nickel in YCu<sub>7</sub> was reported to be ~11 at.%. That is inconsistent with the results of [2,3] (see Table 1). We conducted an EDX analysis of the alloy Y<sub>13</sub>Cu<sub>76</sub>Ni<sub>11</sub> (Fig. 3d, Table 2), which did not reveal the presence of the YCu<sub>7</sub> phase in the sample, indicating a significantly lower solubility of nickel in YCu<sub>7</sub>, which does not exceed 3.5 at.% at 600°C. The YCu<sub>4</sub> phase does practically not dissolve the third component in the Y–Ni–Cu system at 600°C.

One ternary compound, with the extended homogeneity range YNi<sub>2.85–0.75</sub>Cu<sub>1.15–3.25</sub>, was found to occur in the Y–Ni–Cu system along the 20 at.% Y

isoconcentrate at 600°C. We failed to determine its crystal structure as the powder XRD profile was very blurred. This is probably due to the existence of internal stresses or defects, which were not removed even after prolonged annealing procedure at 1000°C. Our attempts to find single crystals of the new compound failed. Instead of the new compound (which was the main phase in the sample), a single crystal within the homogeneity range of the YNi<sub>5–x</sub>Cu<sub>x</sub> (0 ≤ x ≤ 4.6) solid solution was extracted from a crushed sample of composition Y<sub>20</sub>Ni<sub>60</sub>Cu<sub>20</sub> (annealed at 1000°C). The composition YNi<sub>4</sub>Cu was found by EDX analysis. Single-crystal XRD data confirmed that the crystal structure was of the CaCu<sub>5</sub> structure type. All relevant crystallographic data are listed in Table 3. The atomic coordinates and displacement parameters for the YNi<sub>4</sub>Cu single crystal are gathered in Table 4 and 5, respectively. The results of the investigation indicated that the Wyckoff positions 1a and 3g are fully occupied by Y and Ni atoms, respectively, and the 2c site is occupied by a statistical mixture of 25 at.% Ni + 75 at.% Cu. In this case we obtained satisfactory values of the displacement parameters and the lowest *R*-values. As one can see from Table 1, the concentration ranges of the solid solutions in the Y–Ni–Cu system vary at different temperatures of annealing. Comparing the results of the present investigation with the data of investigations of alloys annealed at different temperatures [1,3–6,8,10], it appears that an increase of the annealing temperature leads to an increase of the solubility of the third component in the binary compounds of the Y–Ni and Y–Cu systems (Table 1). Replacement of Ni atoms (*r* = 0.124 nm) by larger Cu atoms (*r* = 0.128 nm) leads to an increase of the unit cell parameters and of the unit cell volumes of alloys within the homogeneity ranges of the solid solutions. The variation of the unit cell parameters is, however, non-linear [3–6,12]. There are both slight positive and negative deviations from Vegard's rule.

**Fig. 4** XRD patterns of the Y<sub>17</sub>Cu<sub>83</sub> sample: a) annealed at 600°C (unknown structure); b) after re-crystallization (ST CaCu<sub>5</sub> (bottom, solid lines; positions of peaks indicated by circles) and Y<sub>2</sub>O<sub>3</sub> (bottom, dashed lines)).



**Fig. 5** XRD patterns of the  $Y_{22}Cu_{78}$  sample: a) annealed at 600°C (unknown structure); b) after re-crystallization (ST CeCu<sub>3.6</sub>, SG *P6/m* (bottom)).

**Table 3** Crystal and structure refinement data for YNi<sub>4</sub>Cu.

Empirical formula	YNi <sub>4</sub> Cu
Space group	<i>P6/mmm</i>
Z	1
Unit cell parameters	
<i>a</i> , nm	0.4899(2)
<i>c</i> , nm	0.3979(3)
Unit cell volume, nm <sup>3</sup>	0.0827(1)
Calculated density, g/cm <sup>3</sup>	7.776
Absorption coefficient, mm <sup>-1</sup>	24.219
Crystal size, mm <sup>3</sup>	0.12 × 0.08 × 0.03
Radiation and wavelength, nm	Ag Kα, 0.056086
Diffractometer	STOE IPDS I
Refined parameters	11
Refinement	<i>F</i> <sup>2</sup>
2θ <sub>max</sub>	46.72
<i>h</i> , <i>k</i> , <i>l</i>	-6 < <i>h</i> < 6 -6 < <i>k</i> < 6 -5 < <i>l</i> < 5
Collected reflections	931
Independent reflections	65 ( <i>R</i> <sub>int</sub> = 0.087)
Reflections with <i>I</i> <sub>0</sub> ≥ 2σ( <i>I</i> <sub>0</sub> )	57 ( <i>R</i> <sub>σ</sub> = 0.035)
Final <i>R</i> <sub>1</sub> indices ( <i>R</i> <sub>1</sub> all data) <sup>a</sup>	0.028 (0.039)
Weighted <i>wR</i> <sub>2</sub> factor ( <i>wR</i> <sub>2</sub> all data) <sup>b</sup>	0.058 (0.062)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.22
Extinction coefficient	0.08(2)
Largest difference peak and hole / (e·Å <sup>-3</sup> )	2.0/-2.7

$$^a R_1(F) = [\sum(|F_o| - |F_c|)] / \sum|F_o|;$$

$$^b wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$$

**Table 4** Atomic coordinates and displacement parameters (×10<sup>2</sup> nm<sup>2</sup>) for YNi<sub>4</sub>Cu.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Y	1 <i>a</i>	0	0	0	0.0080(5)
Ni	3 <i>g</i>	½	0	½	0.0052(5)
<i>M</i>	2 <i>c</i>	⅔	⅓	0	0.0065(2)

$$M = 0.25Ni + 0.75Cu$$



**Table 5** Anisotropic displacement parameters <sup>a</sup> ( $\times 10^2$  nm<sup>2</sup>) for YNi<sub>4</sub>Cu.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$
Y	0.0049(6)	0.0049(6)	0.0142(9)	0.0024(3)
Ni1	0.0058(6)	0.0018(7)	0.0067(8)	0.0009(4)
Ni2	0.0055(3)	0.0055(3)	0.001(2)	0.0027(3)
Cu	0.0065(2)	0.0065(2)	0.0065(2)	0.0032(4)

<sup>a</sup>  $U_{13} = U_{23} = 0$ 

The Y–Ni–Cu system studied here is similar to other RE–Ni–Cu (RE = Gd, Dy, Ho) systems [41–43] in many aspects. All these systems are characterized by the formation of ternary compounds at a low (20–25 at.%) RE content and the presence of solid solutions of Cu/Ni substitution based on Y–Ni and Y–Cu binary compounds.

### Conclusions

The phase equilibria in the Y–Ni–Cu ternary system and the Y–Ni and Y–Cu binary systems at 600°C have been re-investigated in order to resolve some controversial data on compositions and crystal structures of binary and ternary phases. The presence of the YNi<sub>4</sub> compound at 600°C was not confirmed. The homogeneity ranges of the solid solutions YNi<sub>5–x</sub>Cu<sub>x</sub> ( $0 \leq x \leq 4.6$ ), Y<sub>2</sub>Ni<sub>17–x</sub>Cu<sub>x</sub> ( $0 \leq x \leq 7.8$ ), YCu<sub>6–7</sub>Ni<sub>x</sub> ( $0 \leq x \leq 0.28$ ) were refined. The maximal solubility of the third component does not exceed 3.8 at.% in Y<sub>2</sub>Cu<sub>7</sub> and is less than 1 at.% in Y<sub>2</sub>Ni<sub>7</sub>, YCu, and YCu<sub>4</sub>. The crystal structure of a single crystal of composition YNi<sub>4</sub>Cu (CaCu<sub>5</sub>-type structure, YNi<sub>5–x</sub>Cu<sub>x</sub> solid solution) was investigated by single-crystal X-ray diffraction. One new ternary compound with an extended homogeneity range, YNi<sub>2.85–0.75</sub>Cu<sub>1.15–3.25</sub>, was found to occur in the Y–Ni–Cu system at 600°C. Its crystal structure is unknown.

A long-time special procedure for re-crystallization was needed to reach equilibrium state for the Y–Ni and Y–Cu samples in the 15–25 at.% Y region. After this treatment, the Y<sub>2</sub>Cu<sub>7</sub> compound with CeCu<sub>3,6</sub>-type structure and the YCu<sub>6–7</sub> compound (unknown structure) were obtained.

The previously reported YCu<sub>5</sub> and YCu<sub>4</sub> compounds crystallizing in CaCu<sub>5</sub>-type structures are stabilized by oxygen.

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