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Contribution to the investigation of ternary Lu–Ni–Sn system

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ABSTRACT

The phase equilibria in the Lu–Ni–Sn ternary system were studied at 770 K (up to 50 at.% Sn) and 670 K (more than 50 at.% Sn) by means of X-ray and metallographic analyses in the whole concentration range. The Lu–Ni–Sn system is characterized by formation of 10 ternary intermetallic compounds at investigated temperatures: $LuNi_5Sn$ ($CeCu_5Au$-type), $LuNi_4Sn$ ($MgCu_4Sn$-type), Lu_6Ni_2Sn (Ho_6Co_2Ga-type), Lu_2Ni_2Sn (Mo_2FeB_2-type), $LuNi_2Sn$ ($MnCu_2Al$-type), $LuNi_{2-x}Sn$ ($YbNi_{2-x}Sn$-type), LuNiSn (TiNiSi-type), $LuNiSn_2$ ($LuNiSn_2$-type), Lu_2NiSn_6 (Lu_2NiSn_6-type), and $LuNiSn_4$ ($LuNiSn_4$-type). Three new binary compounds, $LuNi_3$ ($PuNi_3$-type), Lu_3Ni_2 (Er_3Ni_2-type), and Lu_3Ni (Fe_3C-type), were found in the Lu–Ni system.

1. Introduction

Among the R–Me–Sn ternary systems (R – rare earths, Me – transition elements) the ternary systems with rare earth metals, nickel and tin are characterized by a large number of the intermediate ternary phases, especially in the Ni-rich corner of the R–Ni–Sn phase diagrams, where the formation of numerous ternary stannides with structures being a derivative of the $CaCu_5$ structure type was observed.

The studied R–Ni–Sn systems where R = La, Ce, Nd, Gd, Dy, and Y [1–6] are rather complicated and clearly showed the *f*-element contribution to the chemical and structural characteristics of intermediate ternary phases realized in different structure types in Ni- and Sn-rich parts of the R–Ni–Sn systems passing from light rare earths to the elements of Y group. The similarity in the interaction of the components in all related R–Ni–Sn systems is displayed by the formation of equiatomic RNiSn (TiNiSi-type) compounds, while at $RNiSn_2$ and RNi_5Sn stoichiometry two ($CeNiSi_2$ (La–Sm), $LuNiSn_2$ (Y, Gd–Lu)) and three ($CeNi_5Sn$ (La–Nd), $CeCu_{4.38}In_{1.62}$ (Sm–Tm), $CeCu_5Au$ (Lu)) different structure types were found.

According to the previous study of the phase equilibria in the Lu–Ni–Sn ternary system at 770 K (up to 50 at.% Sn) and 670 K (more than 50 at.% Sn) 12 ternary compounds were found as reported in Refs. [6,7], but the crystal structure was determined for Lu_6Ni_2Sn, $LuNi_4Sn$, $LuNi_2Sn$, LuNiSn, $LuNiSn_2$, and Lu_2NiSn_6. Later we found a new compound at high tin content, $LuNiSn_4$, crystallized in own type with modulated structure [8], and the crystal structure of the stannide $LuNi_5Sn$ ($CeCu_5Au$-type structure) was determined by X-ray single crystal method [9]. With regard to the work in progress on the R–Ni–Sn ternary systems formed by the rare earths of Yttrium group, and the limited results appear for some cases in the Lu–Ni–Sn system, such as the structural characterization of the compounds with approximate compositions, i.e. $\sim Lu_2NiSn_7$, $\sim Lu_{43}Ni_{40}Sn_{17}$, $\sim Lu_{48}Ni_{40}Sn_{12}$ and $\sim Lu_{62}Ni_{33}Sn_5$, it was decided to fill this gap, especially in Ni- and Sn-rich region of the Lu–Ni–Sn system.

In the present paper the results of X-ray and EPMA analyses of the phase equilibria in the Lu–Ni–Sn system at 770 K (up to 50 at.% Sn) and 670 K (more than 50 at.% Sn) and the crystal structure data of new ternary compounds are reported.

2. Experimental

The samples were prepared by a direct arc melting of the constituent elements (lutetium, purity of 99.9 wt.%; nickel, purity of 99.99 wt.%; and tin, purity of 99.999 wt.%) under high purity Ti-gettered argon atmosphere on a water-cooled copper crucible. The weight losses of the initial total mass were lower than 1 wt.%. The alloys were annealed at 770 K (up to 50 at.% Sn) and 670 K (more than 50 at.% Sn) in the evacuated quartz tubes for 720 h, and subsequently quenched in ice water.

X-ray phase analysis of the samples was carried out using the powder patterns obtained on DRON-2.0M diffractometer (Fe K_α radiation). The observed diffraction intensities were compared with reference powder patterns of binary and known ternary phases. The compositions of the obtained samples were examined by scanning electron microscopy (SEM) using REMMA-102-02 scanning microscope. Quantitative electron probe microanalysis (EPMA) of the phases was carried out by using an energy-dispersive X-ray analyzer with the pure elements as standards (an acceleration voltage was 20 kV; *K*- and *L*-lines were used). The data for the crystal structure refinements were collected at room temperature using STOE STADI P powder diffractometer (Cu $K_{\alpha1}$ radiation, curved germanium (1 1 1) monochromator).

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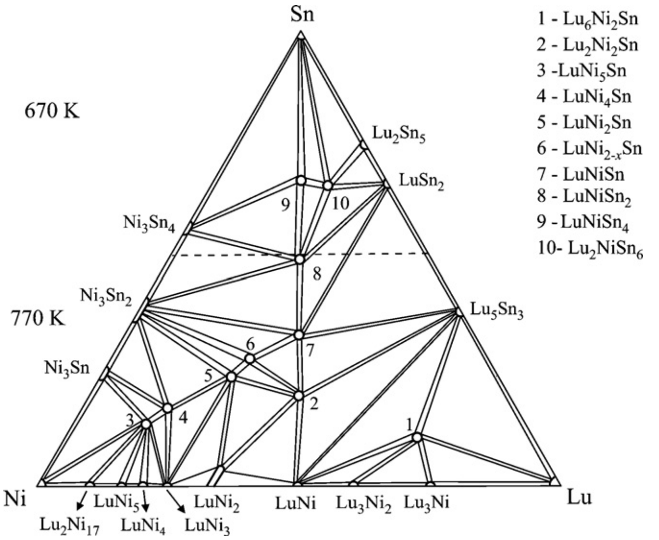

Fig. 1. Isothermal sections of the Lu–Ni–Sn phase diagram at 770 K (up to 50 at.% Sn) and 670 K (more than 50 at.% Sn).

Calculations of the unit cell parameters and theoretical patterns were performed using the WinPLOTR program package [10].

3. Results and discussion

3.1. Binary systems

In the Ni–Sn system we confirmed the existence of Ni_3Sn (Mg_3Cd-type), Ni_3Sn_2 (Ni_3Sn_2-type), and Ni_3Sn_4 (Ni_3Sn_4-type) binaries at 670 and 770 K in agreement with [11,12], the samples near NiSn stoichiometry contain two phases—Ni_3Sn_4 and Ni_3Sn_2 at investigated temperatures. The Lu–Sn diagram used for our investigation was taken from Ref. [11], three binary phases $LuSn_2$, Lu_5Sn_3, and the phase with approximate composition $LuSn_3$ (unknown structure) were observed. More recently the formation of a new phase Lu_2Sn_5 crystallized in Er_2Ge_5-type was reported in [13]. During our investigation we have synthesized all the samples in the Lu–Sn system with the stoichiometry corresponding to the literature data. Phase analysis of the corresponding samples confirmed a formation Lu_2Sn_5, $LuSn_2$, and Lu_5Sn_3 binaries under our conditions. The $LuSn_3$ compound was not observed at investigated temperature.

In the Lu–Ni binary system we have synthesized all compounds according to the literature data. Phase analysis of the corresponding samples confirmed a formation of Lu_2Ni_{17} (Th_2Ni_{17}-type), $LuNi_5$ ($CaCu_5$-type), $LuNi_4$ (own type), $LuNi_2$ ($MgCu_2$-type), and LuNi (FeB-type) binaries. Taking into account that the phase diagram of the Lu-Ni system was not constructed until present, we also prepared the additional samples near $Lu_{25}Ni_{75}$, $Lu_{40}Ni_{60}$, and $Lu_{75}Ni_{25}$ stoichiometry, and the phase analysis the powder patterns of the corresponding ingots resulted the formation of three new $LuNi_3$ ($PuNi_3$-type, $a = 0.49218(1)$ nm, $c = 2.40870(3)$ nm), Lu_3Ni_2 (Er_3Ni_2-type, $a = 0.83720(1)$ nm, $c = 1.55314(4)$ nm),

Table 1
Composition and lattice parameters of the samples of the $LuNi_{2-x}Sn_x$ solid solution.

Composition	Lattice parameter (nm) a	V (nm^3)
$Lu_{33}Ni_{67}$	0.7077(5)	0.3544
$Lu_{33}Ni_{62}Sn_5$	0.7081(4)	0.3551
$Lu_{33}Ni_{60}Sn_7$	0.7084(5)	0.3555
[a]$Lu_{33}Ni_{57}Sn_{10}$	0.7085(3)	0.3556

[a] Two phase sample.

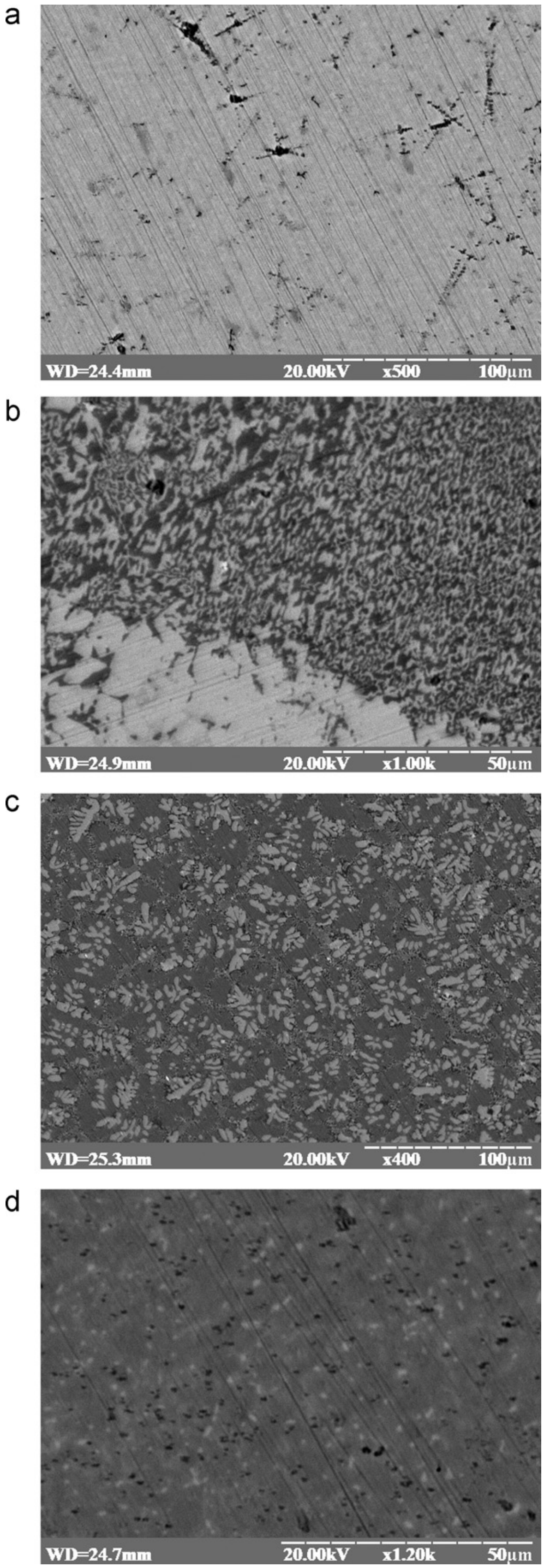

Fig. 2. Electron microphotographs of the alloys: (a) $Lu_{73}Sn_{27}$–Lu_3Ni; (b) $Lu_{20}Ni_{35}Sn_{45}$–$LuNiSn_2$ (gray phase); Ni_3Sn_4 (gray dark phase); (c) $Lu_{17}Ni_{50}Sn_{33}$–Ni_3Sn_2 (gray phase); $LuNi_{2-x}Sn$ (gray light phase); (d) $Lu_{45}Ni_{32}Sn_{23}$–Lu_2Ni_2Sn (gray main phase); Lu_5Sn_3 (light phase).

Table 2
Crystallographic characteristics of ternary compounds in the Lu–Ni–Sn system.

No.	Compound	Space group	Structure type	Lattice parameters (nm)			Ref.
				a	*b*	*c*	
1	Lu_6Ni_2Sn	*Immm*	Ho_6Co_2Ga	0.9141	0.9279	0.9710	[14]
2	$LuNi_5Sn$	*Pnma*	$CeCu_5Au$	0.79841(2)	0.48328(1)	1.01907(4)	[9]
3	$LuNi_4Sn$	*F*−43*m*	$MgCu_4Sn$	0.6981			[15]
4	$LuNi_2Sn$	*Fm*3*m*	$MnCu_2Al$	0.6345			[15]
5	Lu_2Ni_2Sn	*P*4/*mbm*	Mo_2FeB_2	0.7238(3)		0.3602(1)	This work
6	$LuNi_{2\text{-}x}Sn$	$P6_3/mmc$	$YbNi_{2-x}Sn$	0.44035(1)		1.51289(3)	This work
7	LuNiSn	*Pnma*	TiNiSi	0.6932(4)	0.4398(3)	0.7604(5)	[16]/This work
8	$LuNiSn_2$	*Pnma*	$LuNiSn_2$	1.5944	0.4361	1.4345	[17]
9	$LuNiSn_4$	*Cmmm*	$LuNiSn_4$	0.4397	2.8100	0.4362	[8]
10	Lu_2NiSn_6	*Cmmm*	Lu_2NiSn_6	0.4301	2.2278	0.4366	[18]

and Lu_3Ni (CFe_3-type, $a = 0.67504(1)$ nm, $b = 0.92991(1)$ nm, $c = 0.61630(1)$ nm) compounds. The detailed description of the crystal structure refinements for three new Lu–Ni binaries will be published in our next manuscript, which is currently in press. Thus, according to obtained results we may note that eight binary compounds form in Lu–Ni system at 770 K.

The formation of the $LuNi_{2-x}Sn_x$ solid solution formed by substitution of the nickel atoms by tin in $LuNi_2$ ($MgCu_2$-type) up to 5 at.% Sn was found. The compositions and values of the lattice parameters are given in Table 1.

3.2. Isothermal sections of the Lu–Ni–Sn ternary system

The isothermal sections of the Lu–Ni–Sn ternary system have been constructed at 770 K (up to 50 at.% Sn) and 670 K (more than 50 at.% Sn) using X-ray and EPMA analyses of 115 ternary and binary alloys. The isothermal sections of this system are presented in Fig. 1. The microphotographs of some alloys are shown in Fig. 2.

The presence of the earlier known Lu_6Ni_2Sn (Ho_6Co_2Ga-type) [14], $LuNi_4Sn$ ($AuBe_5$-type), $LuNi_2Sn$ ($MnCu_2Al$-type) [15], LuNiSn (TiNiSi-type) [16], $LuNiSn_2$ ($LuNiSn_2$-type) [17], Lu_2NiSn_6 (Lu_2NiSn_6-type) [18], $LuNiSn_4$ ($LuNiSn_4$-type) [8], and $LuNi_5Sn$ [9] compounds was confirmed and new ternary stannides were found: Lu_2Ni_2Sn, and $LuNi_{2-x}Sn$. Crystallographic characteristics of the ternary compounds in the Lu–Ni–Sn system are listed in Table 2.

The crystal structure refinements were performed by powder method on $Lu_{25}Ni_{45}Sn_{30}$ sample (Fig. 3) using the starting model of the $YbNi_{2\text{-}x}Sn$ structure type (space group $P6_3/mmc$). The presence of diffraction peaks belonging to the LuNiSn compound was taken into account during the crystal structure refinement. The final atomic parameters for $LuNi_{2-x}Sn$ ($a = 0.44035(1)$ nm, $c = 1.51289(3)$ nm, $R_{Bragg} = 0.034$, $R_p = 0.053$, $R_{wp} = 0.083$) are listed in Table 3. The analysis of the $LuNi_{2-x}Sn$ structure showed that interatomic distances Lu–Ni3 (0.260 nm), Sn1–Ni3 (0.255 nm) and Ni2–Sn2 (0.254 nm) are shorter then the sum of the respective atomic radii and, like in the case of $YbNi_{2-x}Sn$ structure, it is associated with the incomplete occupancy of the atomic sites for Ni2 and Ni3 atoms.

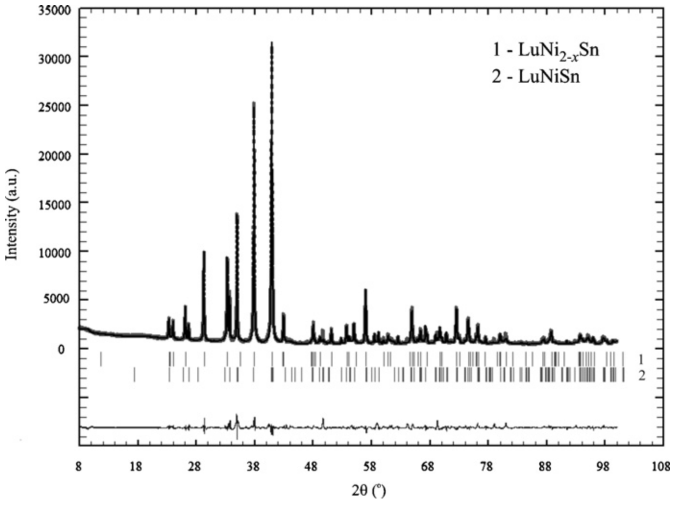

Fig. 3. The observed, calculated and difference X-ray patterns of the $Lu_{25}Ni_{45}Sn_{30}$ sample.

Table 3
Atomic parameters for the $LuNi_{2-x}Sn$ compound.

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*
Lu	4*f*	1/3	2/3	0.63277(6)
Ni1	4*f*	1/3	2/3	0.05423(19)
[a]Ni2	2*b*	0	0	1/4
[b]Ni3	4*e*	0	0	0.1687(4)
Sn1	2*a*	0	0	0
Sn2	2*c*	1/3	2/3	1/4

[a] Ni2 = 0.55(1).
[b] Ni3 = 0.45(2).

As for the LuNiSn stannide only lattice parameters were known, we have also refined its crystal structure using powder patterns of $Lu_{25}Ni_{45}Sn_{30}$ sample ($a = 0.6932(4)$ nm, $b = 0.4398(3)$ nm, $c = 0.7604(5)$ nm, $R_{Bragg} = 0.043$, $R_p = 0.074$, $R_{wp} = 0.098$) with atomic coordinates presented in Table 4.

Detailed phase analysis of the samples near $\sim Lu_{43}Ni_{40}Sn_{17}$ and $\sim Lu_{48}Ni_{40}Sn_{12}$ compositions, identified earlier as two different phases [6,7], indicated that in both samples only one ternary compound was observed. The results of microprobe analysis confirmed the presence of ternary compound with stoichiometry Lu_2Ni_2Sn. The powder pattern of the $Lu_{45}Ni_{30}Sn_{25}$ sample (Fig. 4) was indexed on the basis of the tetragonal lattice with cell parameters $a = 0.7238(3)$ nm, $c = 0.3602(1)$ nm, and indicated that this compound belongs to the Mo_2FeB_2 type structure (space group *P*4/*mbm*). The crystal structure of the Lu_2Ni_2Sn compound was determined using X-ray powder diffraction method ($R_{Bragg} = 0.032$, $R_p = 0.075$, $R_{wp} = 0.095$). Refined atomic coordinates are listed in Table 5.

The formation of the ternary phases, namely $\sim Lu_2NiSn_7$, $\sim Lu_{48}Ni_{40}Sn_{12}$, and $\sim Lu_{62}Ni_{33}Sn_5$, reported in the previous study [6,7] of this system was not confirmed in the present inves-

Table 4
Atomic parameters for the LuNiSn compound.

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*
Lu	4*c*	0.9976(11)	1/4	0.7005(1)
Ni	4*c*	0.2002(7)	1/4	0.0759(10)
Sn	4*c*	0.3103(2)	1/4	0.4116(3)

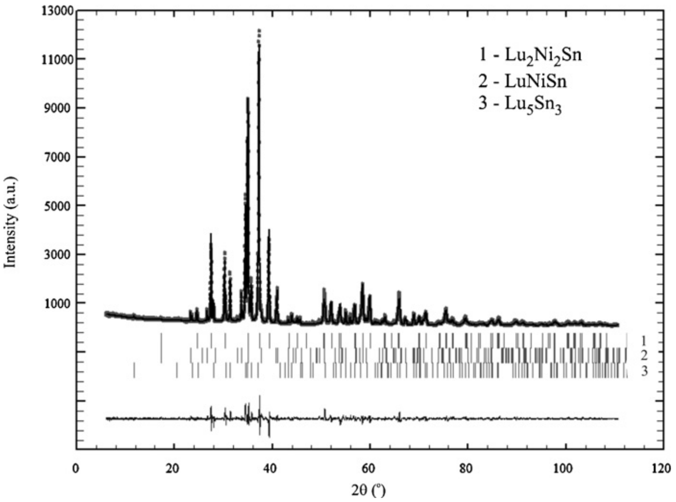

Fig. 4. The observed, calculated and difference X-ray patterns of the $Lu_{45}Ni_{30}Sn_{25}$ sample.

Table 5
Atomic parameters for the Lu_2Ni_2Sn compound.

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*
Lu	4*h*	0	0	0
Ni	4*f*	1/3	2/3	1/2
Sn	2*b*	0	0	1/4

tigation. Powder XRD analysis of the corresponding samples revealed that they belong to the two-phases and three-phases fields involving Lu_2NiSn_6, Lu_2Ni_2Sn and Lu_6Ni_2Sn ternary phases, respectively.

Comparing the present study of the Lu–Ni–Sn system and data reported in Refs. [6,7] we may note a formation of ten ternary phases at investigated temperatures. The chemical and structural characterization of the unknown ternary and binary compounds, performed in our work, allowed us to complete the phase diagram of the Lu–Ni–Sn system. It should be to note that the Lu–Ni–Sn ternary system differs essentially from the other related R–Ni–Sn systems with heavy rare-earths investigated at the present. The main difference between Gd–Ni–Sn, Dy–Ni–Sn and Lu–Ni–Sn systems lies in the formation of the $LuNi_4Sn$ and $LuNi_2Sn$ phases in Lu systems and the absence of the compounds with such stoichiometry in Gd- and Dy-systems. Besides, $LuNi_5Sn$ and Lu_2Ni_2Sn are not isostructural to the RNi_5Sn and R_2Ni_2Sn stannides in the related systems.

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