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New binary compounds in the Lu–Ni system

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The binary system Lu–Ni was studied by means of X-ray powder diffraction and metallographic analysis in the whole concentration range. The presence 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) was confirmed and three new binary compounds, $LuNi_3$ ($PuNi_3$ type), Lu_3Ni_2 (Er_3Ni_2 type) and Lu_3Ni (Fe_3C type), were found. The crystal structures of the latter were refined to R_{Bragg} = 0.03-0.04. Electronic structure calculations performed for Lu_3Ni confirmed the metallic character of the bonding, with some additional electron density between Lu and Ni atoms.

Intermetallics / Crystal structure / X-ray diffraction / Electronic structure / Bonding

1. Introduction

The binary *R*–Ni systems, where *R* is a rare earth metal, are characterized by the formation of a high number of compounds over the whole concentration range [1]. Most of them have been studied completely and the corresponding phase diagrams constructed. However, the Tm–Ni and Lu–Ni systems have only been studied with the aim to find binary compounds and to study their crystallographic parameters and physical properties. Five Lu–Ni binary compounds were found in the region 50-100 at.% Ni: LuNi (FeB type) [2], $LuNi_2$ ($MgCu_2$ type) [3], $LuNi_4$ (own type) [4], $LuNi_5$ ($CaCu_5$ type) [5], and Lu_2Ni_{17} (Th_2Ni_{17} type) [6], whereas in the Tm–Ni system the formation of Tm_2Ni_{17} (Th_2Ni_{17} type) [6], $TmNi_5$ ($CaCu_5$ type) [5], $TmNi_3$ ($PuNi_3$ type) [7], $TmNi_2$ ($TmNi_2$ type) [8], TmNi (FeB type) [9], and Tm_3Ni (Fe_3C type) [10] binaries was observed. Taking into account the existence in the other *R*–Ni systems of series of isostructural compounds RNi_3, R_3Ni and R_3Ni_2, it would be of interest to clarify the situation concerning the existence of these compounds with Lu. The study of the formation and characterization of binary phases formed in the *R*–Ni systems is part of our ongoing research project on the investigation of *R*–Ni–Sn ternary systems.

In this paper we report the crystal structures of new binaries in the Lu–Ni system, the results of a crystal chemical analysis and electronic structure calculations for Lu_3Ni.

2. Experimental

The samples were prepared by direct, twofold arc melting of the constituent elements (lutetium, 99.9 wt.% purity; nickel, 99.99 wt.% purity) under high-purity Ti-gettered argon on a water-cooled copper hearth. The weight losses with respect to the initial total mass were lower than 1 wt.%. The alloys were annealed separately at 870 K and 1070 K in evacuated quartz tubes for 720 h, and subsequently quenched in ice water.

X-ray phase analysis of the samples was carried out using powder patterns obtained on a DRON-2.0m diffractometer (Fe *Kα* radiation). The observed diffraction intensities were compared with reference powder patterns of known binary phases. The compositions of the samples were examined by Scanning Electron Microscopy (SEM), using a REMMA-102-02 scanning microscope. Quantitative electron probe microanalysis (EPMA) of the phases was carried out using an energy-dispersive X-ray analyzer with the pure elements as standards (the acceleration voltage was 20 kV; *K*- and *L*-lines were used). The data for the crystal structure refinements were collected at room temperature on a STOE STADI P powder diffractometer (Cu $K\alpha_1$ radiation). Rietveld refinements were performed with the WinPLOTR program package [11]. The electronic structure calculations were performed by the full potential linearized augmented planewave method (FLAPW) in the general gradient approximation (GGA), using the cell parameters and atomic coordinates refined in this work.

Table 1 Atomic and isotropic displacement parameters for the $LuNi_3$ compound (R_{Bragg} = 0.044, R_p = 0.068, R_{wp} = 0.092).

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*	$B_{iso}\times10^2$ (nm^2)
Lu1	3*a*	0	0	0	0.94(5)
Lu2	6*c*	0	0	0.8605(1)	0.90(4)
Ni1	3*b*	0	0	½	0.43(12)
Ni2	6*c*	0	0	0.6659(1)	1.08(10)
Ni3	18*h*	0.8399(27)	0.1840(27)	0.5851(1)	0.74(1)

Table 2 Atomic and isotropic displacement parameters for the Lu_3Ni compound (R_{Bragg} = 0.032, R_p = 0.050, R_{wp} = 0.065).

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*	$B_{iso}\times10^2$ (nm^2)
Lu1	8*d*	0.1800(1)	0.0631(1)	0.1813(2)	0.50(3)
Lu2	4*c*	0.0312(2)	¼	0.6348(3)	0.64(5)
Ni	4*c*	0.3983(8)	¼	0.4523(8)	1.61(16)

Table 3 Atomic and isotropic displacement parameters for the Lu_3Ni_2 compound (R_{Bragg} = 0.026, R_p = 0.050, R_{wp} = 0.065).

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*	$B_{iso}\times10^2$ (nm^2)
Lu1	3*a*	0	0	0	1.74(14)
Lu2	6*c*	0	0	0.2087(2)	0.51(10)
Lu3	18*f*	0.0975(2)	0.4140(2)	0.0729(1)	0.61(4)
Ni	18*f*	0.3127(6)	0.2521(6)	0.1024(4)	1.30(13)

3. Results and discussion

Samples with compositions corresponding to all of the already known Lu–Ni compounds were synthesized. The phase analysis of these samples confirmed the formation of LuNi (FeB type), $LuNi_2$ ($MgCu_2$ type), $LuNi_4$ (own type), $LuNi_5$ ($CaCu_5$ type), and Lu_2Ni_{17} (Th_2Ni_{17} type) at both 870 and 1070 K. Taking into account that the phase diagram of the Lu–Ni system has yet not been constructed, we decided to look for the possible existence of other binary compounds in the Lu–Ni system. Additional samples near the compositions $Lu_{25}Ni_{75}$ and $Lu_{75}Ni_{25}$ were prepared and annealed at 870 and 1070 K. The powder patterns of the ingots showed the formation of three new compounds: $LuNi_3$, Lu_3Ni and Lu_3Ni_2, at both temperatures. The composition of the three new phases was confirmed by microprobe analysis.

The crystal structure refinements showed that the $LuNi_3$ compound belongs to the $PuNi_3$ type (space group *R*-3*m*, *a* = 0.49218(4) nm, *c* = 2.40870(3) nm) and is thus isotypic to the other *R*Ni_3 binaries. Refined atomic coordinates and displacement parameters are listed in Table 1. The observed, calculated, and difference X-ray patterns for the $LuNi_3$ compound are shown in Fig. 1.

The second binary compound, Lu_3Ni, was found to be isostructural to the Fe_3C type (space group *Pnma*, *a* = 0.67504(1) nm, *b* = 0.92991(1) nm, *c* = 0.61630(1) nm). Refined atomic coordinates and displacement parameters are listed in Table 2.

Detailed phase analysis of the sample of composition $Lu_{70}Ni_{30}$ showed the presence of two phases, Lu_3Ni and an additional, unknown phase. The powder pattern reflections of the unknown phase were well indexed in a hexagonal cell (space group *R*-3) with the lattice parameters *a* = 0.83720(1) nm, *c* = 1.55314(4) nm. A detailed crystal structure investigation performed on the $Lu_{70}Ni_{30}$ sample showed that the structure of the new binary phase belongs to the Er_3Ni_2 structure type (space group *R*-3) [12]. The final atomic parameters, refined to R_p = 0.050, R_{wp} = 0.065, R_{Bragg} = 0.026, are listed in Table 3. The observed, calculated, and difference X-ray patterns for the $Lu_{70}Ni_{30}$ sample are presented in Fig. 2.

We performed a crystal chemical analysis of the structure of Lu_3Ni and found that the distances between Ni and Lu (0.27-0.28 nm) are considerably shorter than the sum of their atomic radii (0.297 nm), but are very close to the sum of the corresponding covalent radii (0.271 nm). The Lu-Lu distances (~0.34 nm) are close to the sum of the atomic radii (0.346 nm). According to this, we may expect some localized bonding between Ni and Lu atoms and somewhat weaker interactions between Lu atoms.

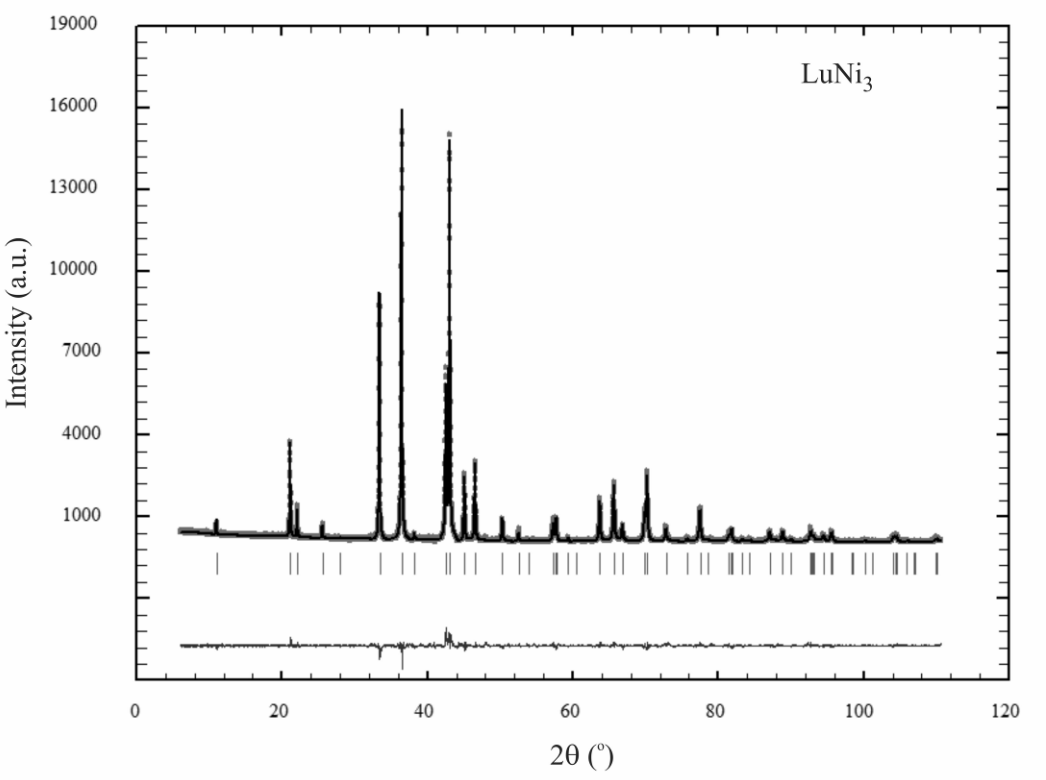

Fig. 1 The observed, calculated, and difference X-ray patterns of the $LuNi_3$ compound (annealed at 870 K).

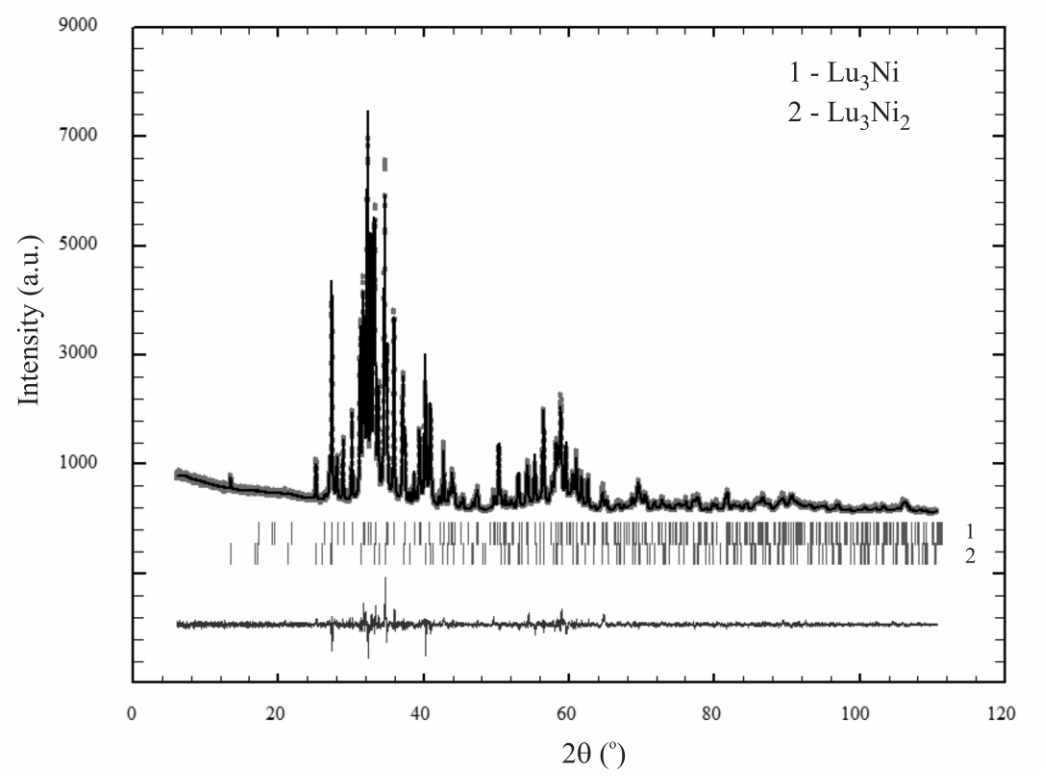

Fig. 2 The observed, calculated, and difference X-ray patterns of the $Lu_{70}Ni_{30}$ sample (annealed at 870 K).

Table 4 Crystallographic data for the binary compounds in the Lu–Ni system.

No	Compound	Structure type	Space group	Unit cell parameters, nm		
				a	*b*	*c*
1	Lu_2Ni_{17}	Th_2Ni_{17}	$P6_3/mmc$	0.821	–	0.7998
2	$LuNi_5$	$CaCu_5$	*P6/mmm*	0.4834	–	0.3969
3	$LuNi_4$	$LuNi_4$	$P3_112$	0.4872	–	3.048
4	$LuNi_3$[a]	$PuNi_3$	*R*-3*m*	0.49218(1)	–	2.40870(3)
5	$LuNi_2$	$MgCu_2$	*Fd*-3*m*	0.7064	–	–
6	LuNi	FeB	*Pnma*	0.6912	0.4073	0.5366
7	Lu_3Ni_2[a]	Er_3Ni_2	*R*-3	0.83720(1)	–	1.55314(4)
8	Lu_3Ni[a]	Fe_3C	*Pnma*	0.67504(1)	0.92991(1)	0.61630(1)

[a] this work; for literature references see the text

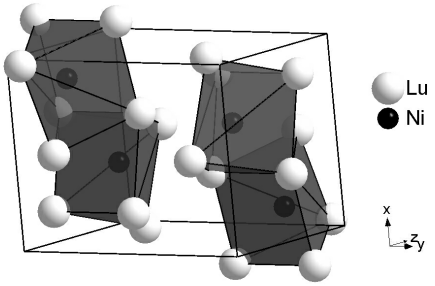

Fig. 3 Coordination polyhedrons of the Ni atoms in the structure of Lu_3Ni.

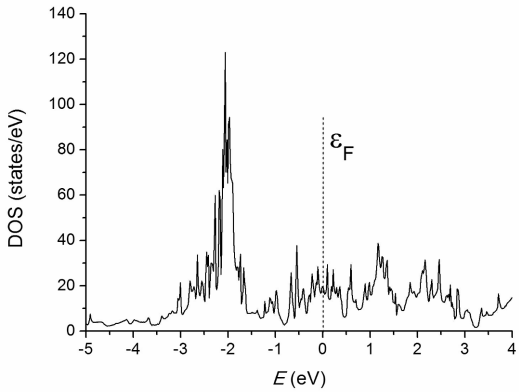

Fig. 4 Total DOS in Lu_3Ni from electronic structure calculations.

The coordination polyhedrons of the Ni atoms are slightly distorted trigonal prisms (Fig. 3).

To verify our assumption about the bonding in the Lu_3Ni compound we performed electronic structure calculations. The total density of states (DOS) distribution shows that Lu_3Ni is a typical metal with metallic type of conductivity and no energy gap is observed at the Fermi level (Fig. 4). The analysis of the calculated electron density shows that there is some additional electron density between Lu and Ni atoms (Fig. 5), which is in a good agreement with the crystal chemical analysis and confirms that the Ni atoms are more strongly bonded to the six Lu atoms forming the trigonal prisms around them. However, the bonding between Ni and Lu is not covalent, as one might deduce from the analysis of the interatomic distances. It is still metallic with somewhat higher electron density between the atoms.

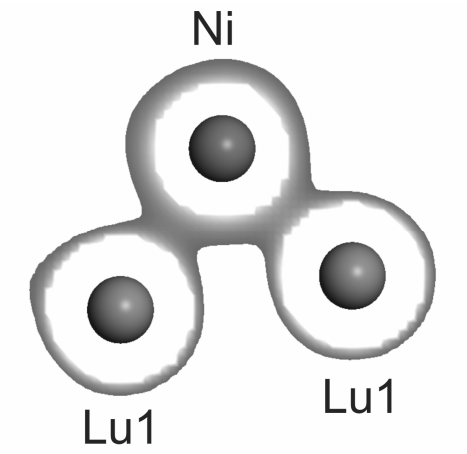

Fig. 5 Electron density distribution in the 0.33-0.50 e/Å^3 range between Lu1 and Ni atoms in the structure of Lu_3Ni from electronic structure calculations.

An analysis of the results obtained here on the Lu–Ni system and the data reported previously allow us to state the formation of eight binary phases in the temperature range from 870 to 1070 K (Table 4). As regards the stoichiometry and crystal structure of the intermediate phases we can note the similarity of the Lu–Ni system with the other *R*–Ni systems, especially those with rare earths of the yttrium group.

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