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Phase equilibria of the La–Ni–Cu ternary system at 673 K: Thermodynamic modeling and experimental validation

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ABSTRACT

Phase equilibria and thermodynamic properties in the La–Ni–Cu ternary system were studied by coupling thermodynamic modeling and experimental validation. A set of self-consistent thermodynamic descriptions for phases in the La–Ni–Cu system were obtained on the basis of those three constituent binary and ternary experimental data in the literature. The isothermal section at 673 K and the mixing enthalpy of liquid calculated from the currently constructed ternary thermodynamic description were favorably compared with available experimental data. Three key alloy samples were then selected, synthesized and annealed at 673 K in order to further validate the calculated phase equilibria. These alloys were analyzed by means of inductively coupled plasma (ICP), X-ray diffraction (XRD), scanning electron microscopy (SEM)/back-scattered electrons (BSE) and energy disperse spectroscopy (EDS), and the experimental results were in reasonable agreement with the calculated phase equilibrium relationships.

1. Introduction

Rare earth (RE)-Ni based alloys are one of the most promising candidates for the hydrogen storage materials. In the La–Ni–Cu system, $LaCu_2$ as well as $LaNi_5$, are the main hydrogen storage alloys [1–4]. According to the available literature, the phase relationships near the $LaCu_2$ phase region were not consistent. Therefore, it is important to understand the phase equilibria and thermodynamic information on this region in the La–Ni–Cu system. The present work focused on the thermodynamic modeling of the La–Ni–Cu ternary system with the Calphad (Calculation of Phase Diagrams) method. Experimental validation was carried out in the $LaCu_2$ and LaNi two-phase region to confirm the calculated phase equilibria.

The La–Ni binary system was thermodynamically studied by several researchers [5–7]. Dischinger and Schaller [5] found a new compound, La_4Ni_{17}, which cannot be supported by other papers. $LaNi_5$ was described by a three-sublattice model by Liu and Jin [6], which is too complicated for the construction of multicomponent system. Du et al. [7] treated $LaNi_5$ as the stoichiometric compound and assessed the La–Ni binary system, which agreed well with the experimental data. The available thermodynamic description of La–Cu system was reported by Du et al. [8], which was consistent with the experimental data. The Ni–Cu system was thermodynamically calculated by Mey [9] and Jansson [10], both of which showed a good agreement with experimental data. However, the magnetic effect was not taken into account in Jansson's work [10].

The isothermal sectional phase diagram of the ternary system La–Ni–Cu at 673 K was constructed by Liu et al. [11] by means of XRD, differential thermal analysis (DTA), optical microscope (OM) and electron probe microscopy analysis (EPMA). They found a new ternary compound $La_{10}Cu_{85}Ni_5$, which has a face-centered cubic (fcc) structure, the space group of *Fm3c* and the lattice constant of 1.158 nm. However, there has been no other information on the $La_{10}Cu_{85}Ni_5$ until now. The integral enthalpies of mixing of La–Ni–Cu liquid alloys at 1123 K were determined using solution calorimetry by Zhou and Sommer [12]. Pasture et al. [13] measured the enthalpies of formation of $LaNi_{5-x}Cu_x$ ($x = 0, 1, 2, 3, 4, 5$) compounds using a calorimetric method and found that the enthalpies of formation increased linearly from $LaNi_5$ to $LaCu_5$. In this work, the experimental data in Refs. [11,12] as well as our experimental results are used for the assessment.

2. Thermodynamic modeling

The Gibbs energy functions of pure elements La, Ni and Cu are taken from the SGTE compilation [14]. The thermodynamic models and parameters of La–Ni, La–Cu and Cu–Ni binary systems reported in Refs. [7–9] are adopted. However, some parameters of La–Cu binary system are modified to ensure that the phase relationships among $LaCu_6$, $LaCu_5$ and $La_{10}Cu_{85}Ni_5$ are consistent with the

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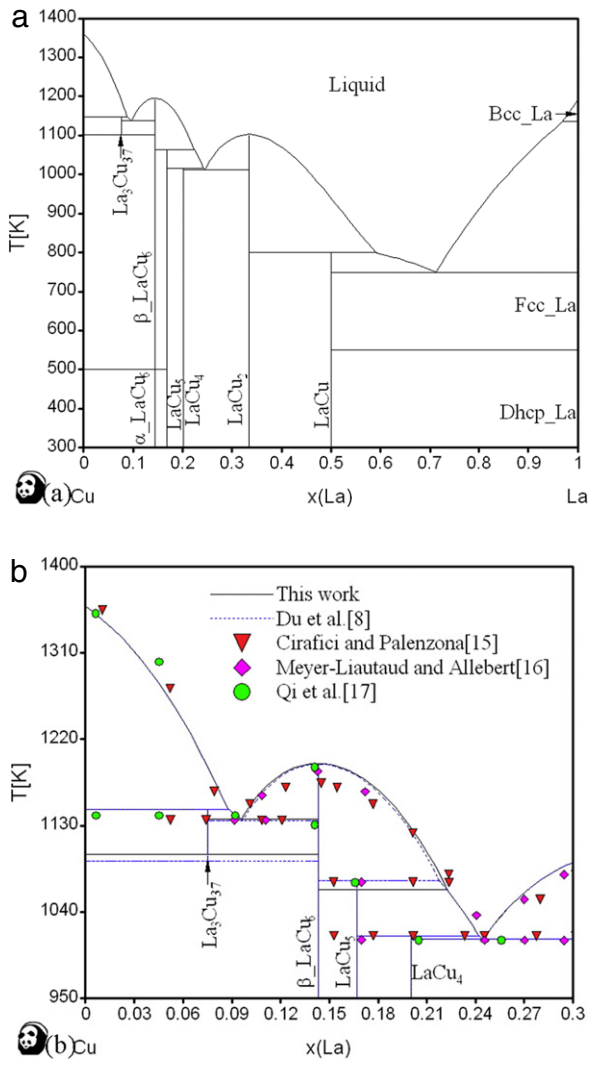

Fig. 1. Calculated phase diagram of La–Cu binary system using the revised parameters (a) and comparison with calculated results from Ref. [8] and the experimental data (b).

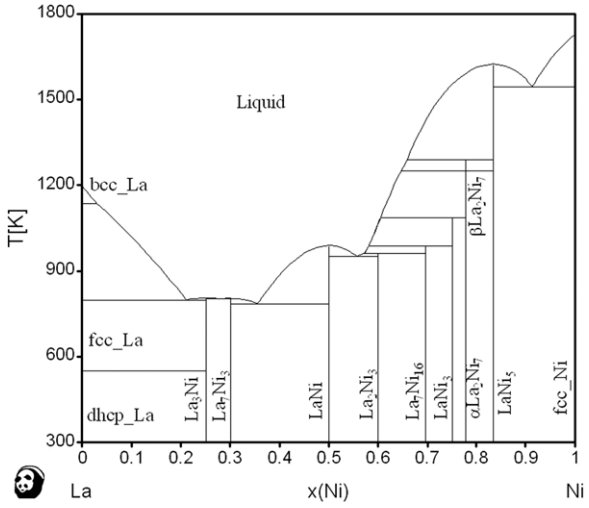

Fig. 2. Calculated phase diagram of La–Ni binary system.

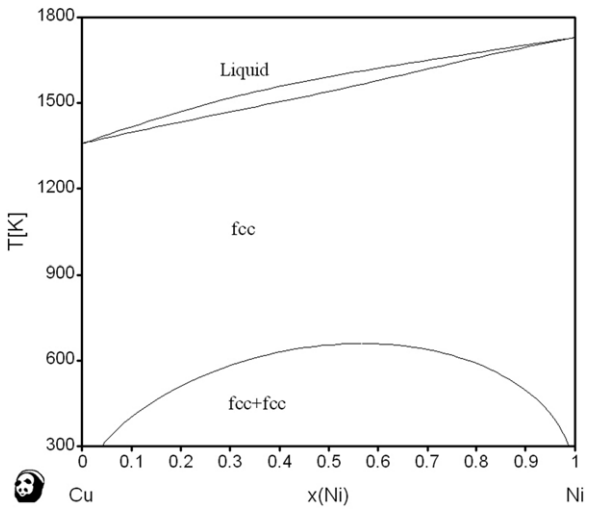

Fig. 3. Calculated phase diagram of Cu–Ni binary system.

experimental ones. The calculated phase diagram of La–Cu, La–Ni and Ni–Cu binary systems are shown in Figs. 1–3, respectively. The La–Cu phase diagram calculated using the revised parameters is shown in Fig. 1(a), however, comparison between the revised part and the experimental data [15–17] as well as that reported in Ref. [8] was presented in Fig. 1(b). The calculation in this work was not better than that reported by Du et al. [8] but within the uncertainty range. It should be noted that the main purpose of revised La–Cu phase diagram is not to make improvement but to ensure that the phase relationships are consistent with the experimental ones in the ternary.

Five solution phases, liquid, body-centered cubic (bcc), fcc, double hexagonal close-packed (dhcp) and hexagonal close-packed (hcp), were described using the substitutional regular solution model, which is described as

$$\begin{aligned} G^{\phi} &= \sum_{i=1}^{c} x_i G_i^{\circ,\phi} + RT \sum_{i=1}^{c} x_i \ln x_i + G^{ex,\phi} \\ &= x_{\mathrm{La}} G_{\mathrm{La}}^{\circ,\phi} + x_{\mathrm{Ni}} G_{\mathrm{Ni}}^{\circ,\phi} + x_{\mathrm{Cu}} G_{\mathrm{Cu}}^{\circ,\phi} \\ &\quad + RT(x_{\mathrm{La}} \ln x_{\mathrm{La}} + x_{\mathrm{Ni}} \ln x_{\mathrm{Ni}} + x_{\mathrm{Cu}} \ln x_{\mathrm{Cu}}) + G^{ex,\phi} \end{aligned} \quad (1)$$

where x_i is the mole fraction of the elements i (i = La, Ni, Cu); $G_i^{\circ,\phi}$ is the Gibbs energy of the element i at 298.15 K in its standard element reference (SER) state; $G^{ex,\phi}$ is the excess Gibbs energy, expressed by the Redlich–Kister polynomial,

$$G^{ex,\phi} = \sum_{\substack{i,j=1 \\ (i \neq j)}}^{c} x_i x_j \sum_{k=0}^{m} L_{(i,j)}^{k} (x_i - x_j)^k + x_i x_j x_l L_{(i,j,l)}^{\circ} \quad (2)$$

where $L_{(i,j)}^{k}$ is the interaction parameter between elements i and j, $L_{(i,j,l)}^{\circ}$ is the ternary interaction parameter.

The maximum solid solubility of Ni in LaCu and $LaCu_2$ is 4 at.% and 15 at.%, respectively. The homogeneities of Cu in α-La_2Ni_7, $LaNi_3$, La_7Ni_{16}, La_2Ni_3 and LaNi are 2 at.%, 2 at.%, 3 at.%, 3 at.% and 5 at.%, respectively. $LaCu_5$ and $LaNi_5$ form a continuous solid solution [11]. In the present work, LaCu, $LaCu_2$, α-La_2Ni_7, $LaNi_3$, La_7Ni_{16}, La_2Ni_3, LaNi and $La(Cu, Ni)_5$ are described by the two sublattice model formula $(La)_m(Cu, Ni)_n$, namely, $(La)_1(Cu, Ni)_1$, $(La)_1(Cu, Ni)_2$, $(La)_2(Cu, Ni)_7$, $(La)_1(Cu, Ni)_3$, $(La)_7(Cu, Ni)_{16}$, $(La)_2(Cu, Ni)_3$, $(La)_1(Cu, Ni)_1$ and $(La)_1(Cu, Ni)_5$, respectively, with La on the first sublattice and Cu and Ni on the second one. The Gibbs energy per mole of formula unit $(La)_m(Cu, Ni)_n$ can be expressed:

$$\begin{aligned} G^{\mathrm{La}_m(\mathrm{Cu,Ni})_n} &= y'_{\mathrm{Ni}} G^{\circ}_{\mathrm{La:Ni}} + y'_{\mathrm{Cu}} G^{\circ}_{\mathrm{La:Cu}} + nRT(y'_{\mathrm{Cu}} \ln y'_{\mathrm{Cu}} + y'_{\mathrm{Ni}} \ln y'_{\mathrm{Ni}}) \\ &\quad + y'_{\mathrm{Cu}} y'_{\mathrm{Ni}} L^{\mathrm{La}_m(\mathrm{Cu,Ni})_n}_{\mathrm{La:Cu,Ni}} \end{aligned} \quad (3)$$

where y'_{Cu} and y'_{Ni} represent the site fractions of Cu and Ni on the first sublattice; the $G^{\circ}_{\mathrm{La:Cu}}$ and $G^{\circ}_{\mathrm{La:Ni}}$ are the Gibbs energies

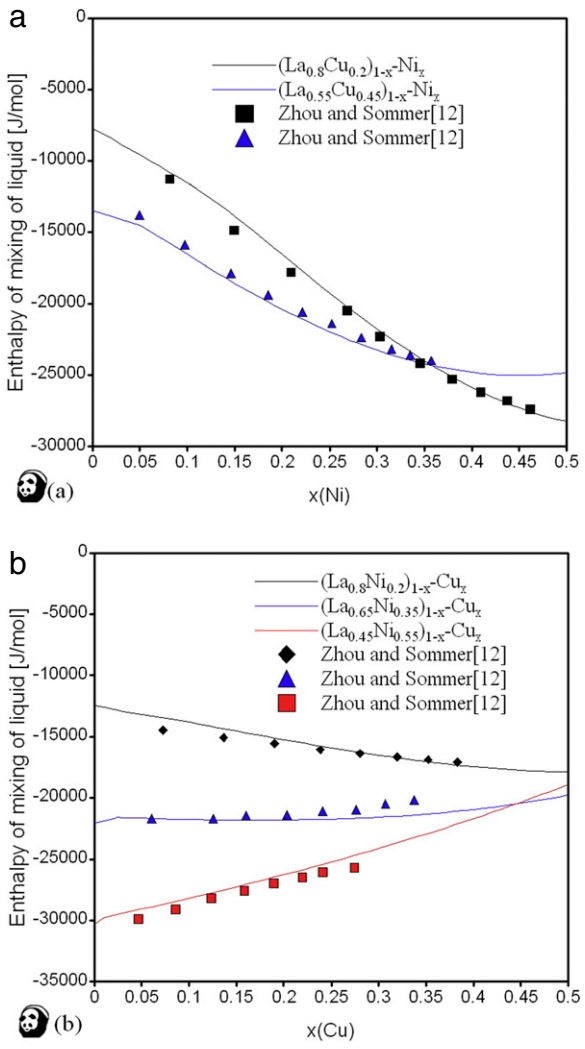

Fig. 4. Calculated enthalpies of mixing of liquid $(Cu_yLa_{1-y})_{1-x} - Ni_x$ ($y = 0.2, 0.45$) (a) and $(La_yNi_{1-y})_{1-x} - Cu_x$ ($y = 0.8, 0.65, 0.45$) (b) compared with the experimental data at 1123 K.

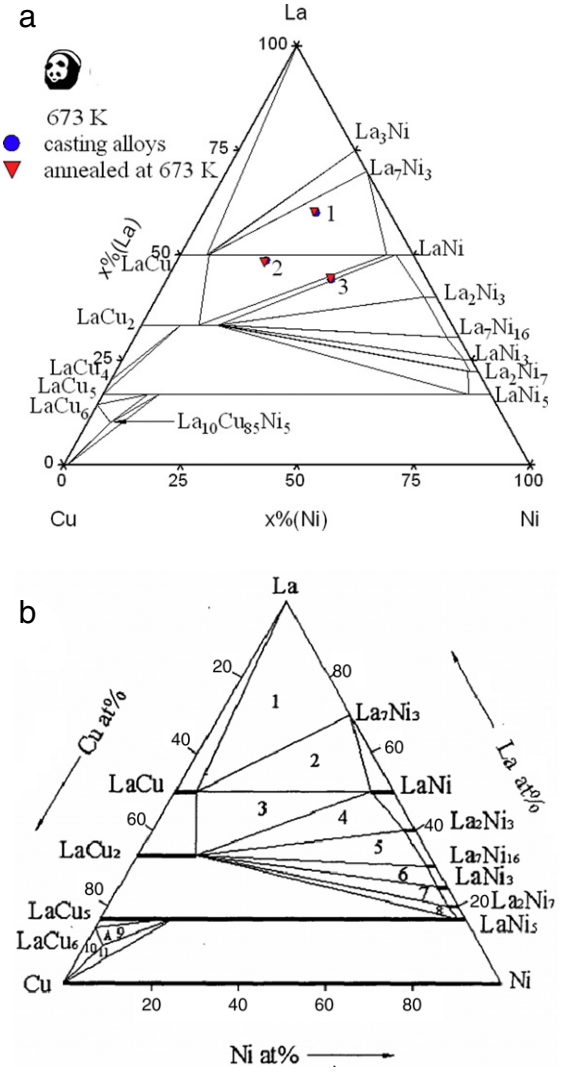

Fig. 5. The calculated isothermal section (a) and the experimental isothermal section [11] (b) at 673 K.

of the compounds La_mCu_n and La_mNi_n when the first and second sublattices are occupied by only one element La and Cu or Ni, respectively, which are relative to the enthalpies of pure dhcp for La and fcc for Cu and Ni in their SER state; $L^{La_m(Cu,Ni)_n}_{La:Cu,Ni}$ is the interaction parameters between the element Cu and Ni on the second sublattice.

Liu et al. [11] reported a new ternary compound $La_{10}Cu_{85}Ni_5$ in the La–Ni–Cu system. However, there is no other information about it. In the present work, $La_{10}Cu_{85}Ni_5$ is treated as stoichiometric compound and the Gibbs energy per mole of formula unit $(La)_{10}(Cu)_{85}(Ni)_5$ is

$$G^{La_{10}Cu_{85}Ni_5} = 10G^{\circ,dhcp}_{La} + 85G^{\circ,fcc}_{Cu} + 5G^{\circ,fcc}_{Ni} + G_f \quad (4)$$

where $G^{\circ,dhcp}_{La}$, $G^{\circ,fcc}_{Cu}$ and $G^{\circ,fcc}_{Ni}$ are the Gibbs energies of La, Cu and Ni in the SER state, respectively. G_f is the Gibbs energy of formation per mole of $La_{10}Cu_{85}Ni_5$.

3. Experimental details

Three alloy samples were synthesized from high purity La (99.99%), Ni (99.999%), and Cu (99.999%) using the medium frequency induction furnace in an ultrahigh-purity Ar (99.999%) atmosphere. The Cu–Ni alloys were melted first and then the refined La was added. Each alloy was melted and flipped several times to ensure good homogeneity. All the alloys were wire cut as the size of 4 × 4 × 10 mm and annealed in an evacuated quartz tube at 673 K for 87 days. Subsequently, the evacuated quartz tubes were dropped into cold water for rapid cooling.

The compositions of casting and annealed alloys were analyzed by Optima 7300DV ICP. XRD, carried out on a DLMAX-2200 diffractometer (CuKα radiation, $10^\circ \le 2\theta \le 90^\circ$, 8°/min) operated at 40 kV and 40 mA, was used to determinate the structure of the alloys. The Materials Data Inc. software Jade 5.0 and a Powder Diffraction File were used to analyze the XRD patterns. The JSM-6700F SEM/BSE and the EDS were used to analyze the annealed alloy samples.

4. Results and discussion

4.1. Optimization results and discussion

The ternary interaction parameters of liquid were optimized using the integral enthalpy of mixing of liquid at 1123 K. The thermodynamic parameters for the intermetallic compounds were optimized based on the phase relationships at 573 and 673 K, where it is assumed that the homogeneity ranges in the binary compounds at 573 K are the same as those at 673 K. It should be noted that the experimental isothermal section at 673 K

Table 1
The thermodynamic models and parameters of compounds in the La–Ni–Cu ternary system.

Phase	Model	Parameters	Ref.
Liquid	(Cu, Ni, La)1	${}^{0}L^{\text{Liquid}}_{(\text{La,Ni})} = -116{,}299 + 19.815T$	
		${}^{1}L^{\text{Liquid}}_{(\text{La,Ni})} = -63{,}813 + 40.941T$	[7]
		${}^{0}L^{\text{Liquid}}_{(\text{La,Cu})} = -103{,}584 + 342.112T - 40.1841T\ln(T)$	[7]
		${}^{1}L^{\text{Liquid}}_{(\text{La,Cu})} = -706{,}35 + 205.618T - 24.1452T\ln(T)$	[8]
		${}^{1}L^{\text{Liquid}}_{(\text{La,Cu})} = -103{,}936 + 450.826T - 52.4266T\ln(T)$	[8]
		${}^{0}L^{\text{Liquid}}_{(\text{La,Ni,Cu})} = -30{,}086$	[8]
		${}^{1}L^{\text{Liquid}}_{(\text{La,Ni,Cu})} = 100{,}000$	This work
FCC	(Cu, Ni, La)1	${}^{0}L^{\text{FCC}}_{(\text{La,Cu})} = 100{,}000$	[8]
		${}^{0}L^{\text{FCC}}_{(\text{Cu,Ni})} = 8983 + 2.691T$	[9]
		${}^{1}L^{\text{FCC}}_{(\text{Cu,Ni})} = -1446 + 0.681T$	[9]
		$T_{c(\text{Cu,Ni})}^{\text{Liquid}} = 633$	[9]
		$B_{M(\text{Cu,Ni})}^{\text{Liquid}} = 0.520$	[9]
BCC	(Cu, Ni, La)1	${}^{0}L^{\text{BCC}}_{(\text{La,Cu})} = 100{,}000$	[8]
DHCP	(Cu, Ni, La)1	${}^{0}L^{\text{DHCP}}_{(\text{La,Cu})} = 100{,}000$	[8]
La_3Ni	(La)3(Ni)1	$G^{\text{La:Ni}}_{\text{La}_3Ni} - 3G^{0,\text{Dhcp}}_{\text{La}} - G^{0,\text{fcc}}_{\text{Ni}} = -60{,}909 - 0.702T$	[7]
La_7Ni_3	(La)7(Ni)3	$G^{\text{La:Ni}}_{\text{La}_7Ni_3} - 7G^{0,\text{Dhcp}}_{\text{La}} - 3G^{0,\text{fcc}}_{\text{Ni}} = -180{,}100 + 1.054T$	[7]
LaNi	(La)1(Ni, Cu)1	$G^{\text{La:Ni}}_{\text{LaNi}} - G^{0,\text{Dhcp}}_{\text{La}} - G^{0,\text{Fcc}}_{\text{Cu}} = -51{,}390 - 0.055T$	[7]
		$G^{\text{La:Cu}}_{\text{LaNi}} - G^{0,\text{Dhcp}}_{\text{La}} - G^{0,\text{Fcc}}_{\text{Cu}} = 10{,}000$	This work
		${}^{0}L^{\text{La:Ni,}Cu}_{\text{LaNi}} = -27{,}426$	This work
		${}^{1}L^{\text{La:Ni,}Cu}_{\text{NiLa}} = 13{,}500$	This work
		${}^{2}L^{\text{La:Ni,}Cu}_{\text{LaNi}} = -74{,}500$	This work
$LaNi_3$	(La)1(Ni, Cu)3	$G^{\text{La:Ni}}_{\text{LaNi}_3} - G^{0,\text{Dhcp}}_{\text{La}} - 3G^{0,\text{fcc}}_{\text{Ni}} = -108{,}154 + 15.857T$	[7]
		$G^{\text{La:Cu}}_{\text{LaNi}_3} - G^{0,\text{Dhcp}}_{\text{La}} - 3G^{0,\text{fcc}}_{\text{Cu}} = 20{,}000$	This work
		${}^{0}L^{\text{La:Ni,}Cu}_{\text{LaNi}_3} = -94{,}055 + 77.501T$	This work
α-La_2Ni_7	(La)2(Cu, Ni)7	$G^{\text{La:Ni}}_{\alpha\text{-La}_2\text{Ni}_7} - 2G^{0,\text{Dhcp}}_{\text{La}} - 7G^{0,\text{Fcc}}_{\text{Ni}} = -239{,}869 + 37.356T$	[7]
		$G^{\text{La:Cu}}_{\alpha\text{-La}_2\text{Ni}_7} - 2G^{0,\text{Dhcp}}_{\text{La}} - 7G^{0,\text{Fcc}}_{\text{Cu}} = 45{,}000$	This work
		${}^{0}L^{\text{La:Ni,}Cu}_{\alpha\text{-La}_2\text{Ni}_7} = -171{,}558 - 115.046T$	This work
β-La_2Ni_7	(La)2(Ni)7	$G^{\text{La:Ni}}_{\beta\text{-La}_2\text{Ni}_7} - 2G^{0,\text{Dhcp}}_{\text{La}} - 7G^{0,\text{Fcc}}_{\text{Ni}} = -237{,}259 + 35.267T$	[7]
La_2Ni_3	(La)2(Ni, Cu)3	$G^{\text{Ni:La}}_{\text{Ni}_3\text{La}_2} - 2G^{0,\text{Dhcp}}_{\text{La}} - 3G^{0,\text{Fcc}}_{\text{Ni}} = -138{,}509 + 14.109T$	[7]
		$G^{\text{Cu:La}}_{\text{Ni}_3\text{La}_2} - 2G^{0,\text{Dhcp}}_{\text{La}} - 3G^{0,\text{Fcc}}_{\text{Cu}} = 25{,}000$	This work
		${}^{0}L^{\text{Ni,Cu:La}}_{\text{Ni}_3\text{La}_2} = -138{,}246 - 30.144T$	This work
La_7Ni_{16}	(La)7(Ni, Cu)16	$G^{\text{La:Ni}}_{\text{La}_7\text{Ni}_{16}} - 7G^{0,\text{Dhcp}}_{\text{La}} - 16G^{0,\text{Fcc}}_{\text{Ni}} = -639{,}390 + 91.778T$	[7]
		$G^{\text{La:Cu}}_{\text{La}_7\text{Ni}_{16}} - 7G^{0,\text{Dhcp}}_{\text{La}} - 16G^{0,\text{Fcc}}_{\text{Cu}} = 18{,}000 - 76.364T$	This work
		${}^{0}L^{\text{La:Ni,}Cu}_{\text{La}_7\text{Ni}_{16}} = -506{,}931 + 449.928T$	This work
LaCu	(La)1(Cu, Ni)1	$G^{\text{La:Cu}i}_{LaCu} - G^{0,\text{Dhcp}}_{\text{La}} - G^{0,\text{Fcc}}_{\text{Cu}} = -32{,}457 + 10.856T$	[8]
		$G^{\text{La:Ni}}_{\text{LaCu}} - G^{0,\text{Dhcp}}_{\text{La}} - G^{0,\text{Fcc}}_{\text{Ni}} = 10{,}000$	This work
		${}^{0}L^{\text{La:Ni,Cu}}_{\text{LaCu}} = 5168$	This work
		${}^{1}L^{\text{La:Ni,Cu}}_{\text{LaCu}} = -147{,}168$	This work
$LaCu_2$	(La)1(Cu, Ni)2	$G^{\text{La:Cu}}_{\text{LaCu}_2} - G^{0,\text{Dhcp}}_{\text{La}} - 2G^{0,\text{fcc}}_{\text{Cu}} = -48{,}445 + 3.484T$	[8]
		$G^{\text{La:Ni}}_{\text{LaCu}_2} - G^{0,\text{Dhcp}}_{\text{La}} - 2G^{0,\text{fcc}}_{\text{Ni}} = 20{,}000$	This work
		${}^{0}L^{\text{La:Cu,Ni}}_{\text{LaCu}_2} = -142{,}075$	This work
		${}^{1}L^{\text{La:Cu,Ni}}_{\text{LaCu}_2} = -80{,}250$	This work
$LaCu_4$	(La)1(Cu)4	$G^{\text{La:Cu}}_{\text{LaCu}_4} - G^{0,\text{Dhcp}}_{\text{La}} - 4G^{0,\text{fcc}}_{\text{Cu}} = -66{,}273 + 7.727T$	[8]

Table 1 (*continued*)

Phase	Model	Parameters	Ref.
α-$LaCu_6$	(La)1(Cu)6	$G^{La:Cu}_{LaCu_6} - G^{0,Dhcp}_{La} - 6G^{0,fcc}_{Cu} = -65{,}039 - 0.106T$	This work
β-$LaCu_6$	(La)1(Cu)6	$G^{La:Cu}_{LaCu_6} - G^{0,Dhcp}_{La} - 6G^{0,fcc}_{Cu} = -60{,}257 - 9.669T$	This work
La_3Cu_{37}	(La)3(Cu)37	$G^{La:Cu}_{La_3Cu_{37}} - 3G^{0,Dhcp}_{La} - 37G^{0,fcc}_{Cu} = -71{,}251 - 129.229T$	[8]
$La(Cu, Ni)_5$	(La)1(Cu,Ni)5	$G^{La:Ni}_{La(Cu,Ni)_5} - G^{0,Dhcp}_{La} - 5G^{0,fcc}_{Ni} = -154{,}674 + 30.622T$	[7]
		$G^{La:Cu}_{La(Cu,Ni)_5} - G^{0,Dhcp}_{La} - 5G^{0,fcc}_{Cu} = -65{,}041 - 0.019T$	[8]
		${}^0L^{La:Cu,Ni}_{La(Cu,Ni)_5} = 29{,}354 + 30.025T$	This work
$La_{10}Cu_{85}Ni_5$	(La)10(Cu)85(Ni)5	$G^{La:Cu:Ni}_{La10Cu85Ni5} - 10G^{0,Dhcp}_{La} - 85G^{0,Fcc}_{Cu} - 5G^{0,Fcc}_{Ni} = -757{,}211 - 18.005T$	This work

Table 2
The crystallographic data of solid phases in the La–Ni–Cu system.

Phase name	Pearson symbol	Space group	Prototype	Lattice parameters/nm	
				a	*c*
(αLa)	hP4	$P6_3/mmc$	αLa	0.3770	–
(γLa)	cI2	Im3m	W	0.4260	–
(βLa)	cF4	$Fm\bar{3}m$	Cu	0.5303	–
Ni	cF4	$Fm\bar{3}m$	Cu	0.3523	–
Cu	cF4	$Fm\bar{3}m$	Cu	0.3614	–
La_3Ni	oP16	Pnma	CFe_3	0.6601	0.5111
La_7Ni_3	hP20	$P6_3/mc$	Fe_3Th_7	1.0130	0.6462
LaNi	oC8	Cmcm	CrB	0.3907	0.4396
La_2Ni_3	oC20	Cmca	La_2Ni_3	0.5114	0.7908
$LaNi_2$	cF24	$Fd\bar{3}m$	Cu_2Mg	0.7340	–
La_7Ni_{16}	Tl46	$1\bar{4}2m$	La_7Ni_{16}	0.7355	1.4511
$LaNi_3$	hR24	$R\bar{3}m$	Be_3Nb	0.5086	2.5011
α-La_2Ni_7	hP36	$P6_3/mmc$	Ce_2Ni_7	0.5058	2.4710
β-La_2Ni_7	hP18	$R\bar{3}m$	Co_2Er_7	0.5056	3.6981
$LaNi_5$	hP6	P6/mmm	$CaCu_5$	0.5013	0.3987
LaCu	oP8	Pnma	BFe	0.7543	0.5724
$LaCu_2$	hP3	$1\bar{4}2m$	AlB_2	0.4346	0.3807
α-$LaCu_6$	mP28	$P2_1/c(14)$	$LaCu_6$	0.5143	0.8144
$LaCu_5$	hP6	P6/mmm	$CaCu_5$	0.5189	0.4107
$LaCu_4$	tI90	$1\bar{4}m2$	–	–	–
La_3Cu_{37}	–	–	–	–	–
α-$LaCu_6$	mP28	P21/C	$\alpha LaCu_6$	0.51467	0.8146
β-$LaCu_6$	oP28	Pnma	$\beta CeCu_6$	0.8165	1.023
$La_{10}Cu_{85}Ni_5$	cF*	$Fm\bar{3}c$	–	1.1580	–

were reported in Ref. [11]. The phase equilibria at 573 K were experimentally validated and details on the results as well as the calculated 573 K isothermal section were published in the Ref [18]. The assessment of the thermodynamic parameters was carried out with Pandat software. Although $LaCu_4$ and La_3Ni were not detected in Liu's work [11], they were identified in Refs. [16,19], so they were considered in the present work. The thermodynamic models and parameters of compounds in the La–Ni–Cu ternary system are listed in Table 1. The crystal structure information of phases was listed in Table 2.

According to the Table 1, the mixing enthalpies of liquid $(Cu_yLa_{1-y})_x - Ni_{1-x}$ ($y = 0.2, 0.45$) and $(La_yNi_{1-y})_x - Cu_{1-x}$ ($y = 0.8, 0.65, 0.45$) at 1123 K are calculated, as shown in Fig. 4(a) and (b), respectively. The calculated results agree well with the experimental data.

The 673 K isothermal section calculated from the currently constructed database as well as the experimental one [11] is presented in Fig. 5(a) and (b). La_3Ni and $LaCu_4$ were not included in Ref. [11], as shown in Fig. 5(b). However, La_3Ni has been determined in Ref. [19] and considered in the assessment of La–Ni binary phase diagrams [5–7]. In addition, when Ghosh [20] summarized the information on the La–Ni–Cu system, the La_3Ni phase was included, and the phase relationship is consistent with the present assessed results. The existence and crystal structure

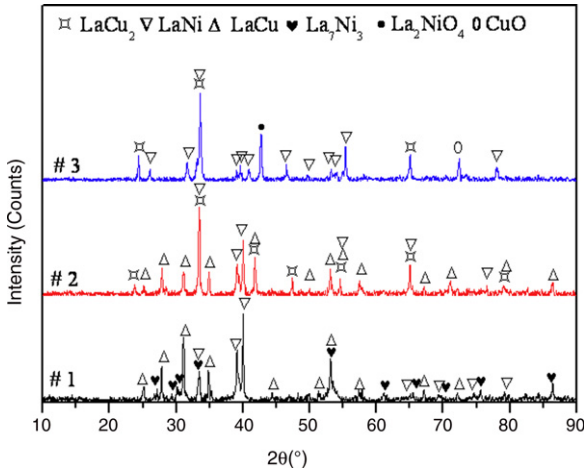

Fig. 6. The XRD patterns of annealed alloys.

of $LaCu_4$ was confirmed by Meyer-Liautaud and Allibert [16], and considered in the Ref. [8]. Moreover, $LaCu_4$ is not used for hydrogen storage, so it was included and extrapolated based on the binary parameters. In addition, LaNi and $LaCu_2$ two-phase

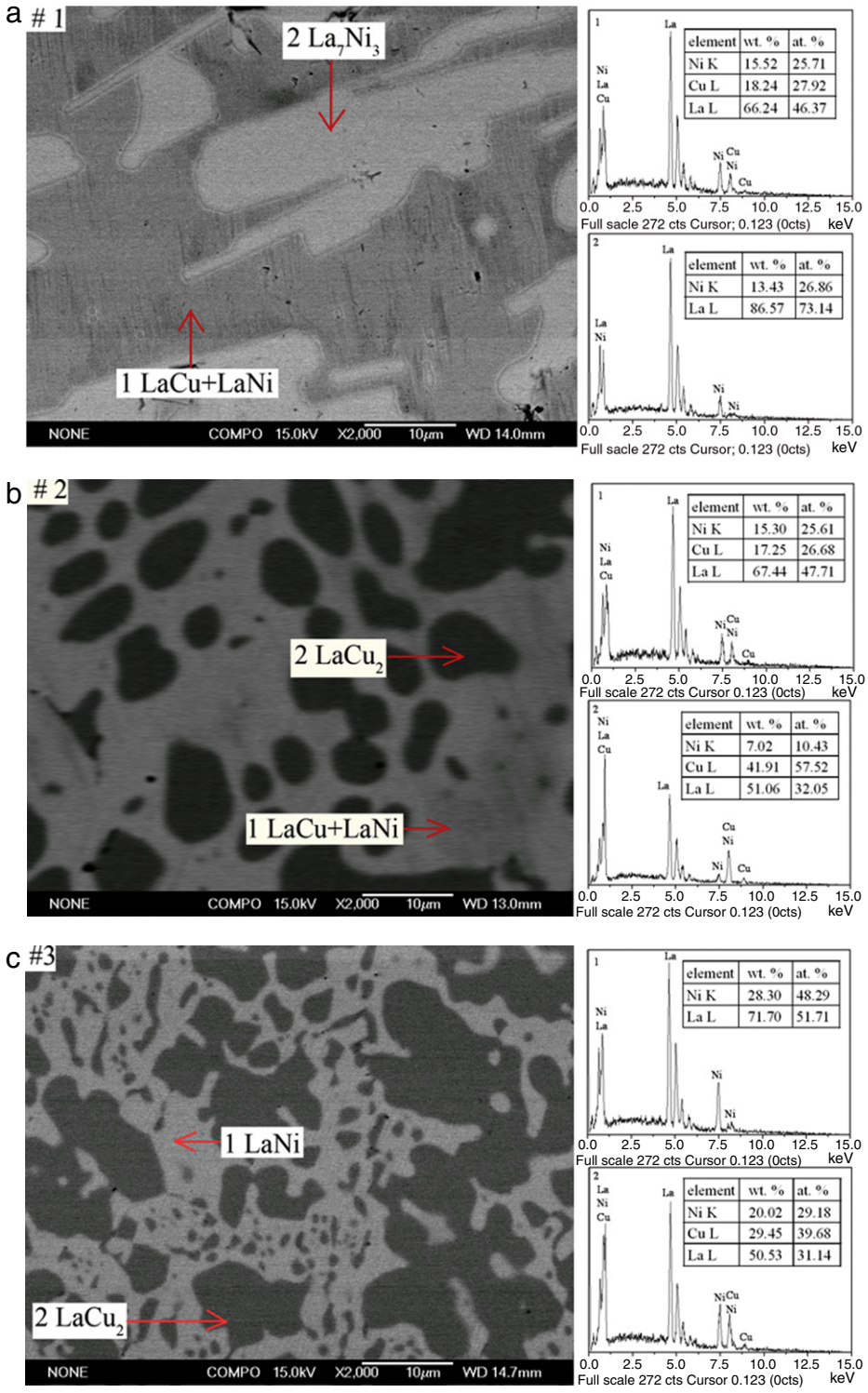

Fig. 7. BSE images and the EDS results of alloys # 1(a), # 2(b) and # 3(c).

region is larger than that reported in the literature. Near this region, there are several hydrogen storage alloys, i.e. $LaCu_2$, LaNi and La_7Ni_3 [1,2,21]. A combination of experimental measurements and computational methods is an efficient approach to determine the phase equilibria in multi-component systems. In order to identify the phase equilibrium relationships in this region, three alloys (marked as 1, 2 and 3 in Fig. 5(a)) were prepared and analyzed.

4.2. Experimental results and discussion

The compositions of the casting and annealed alloys analyzed by ICP are marked in Fig. 5(a) and listed in Table 3, from which it can be seen that there is no significant difference in the composition before and after annealing at 673 K.

Fig. 6 shows the XRD patterns of the annealed alloys, which indicates that #1 is composed of three phases La_7Ni_3, LaNi and

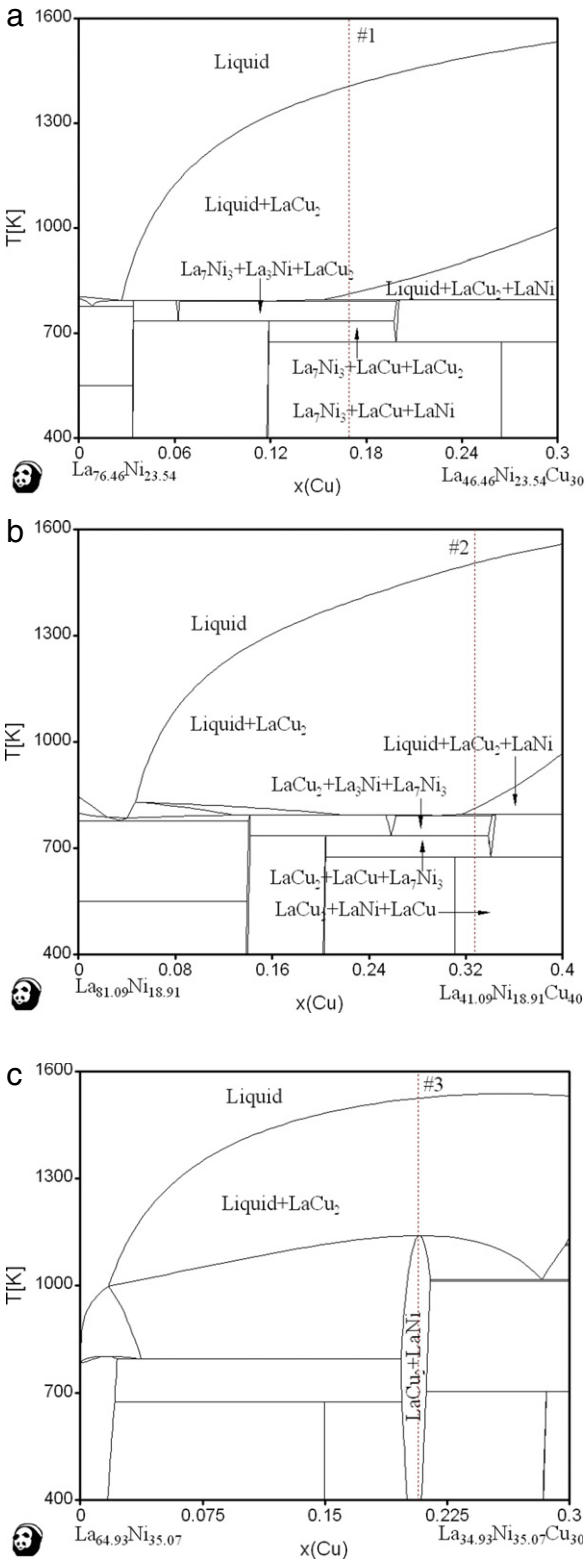

Fig. 8. The vertical sections of #1 (a), #2 (b) and #3 (c).

Table 3
The composition of the casting and annealed alloys (at.%).

Sample	Casting alloys			Annealed at 673 K		
	La	Ni	Cu	La	Ni	Cu
#1	60.00	24.12	15.88	60.26	23.54	16.20
#2	48.56	19.15	32.28	48.19	18.87	32.94
#3	44.15	35.31	20.54	44.36	34.98	20.66

LaCu, #2 has three phases $LaCu_2$, LaNi and LaCu, and #3 has $LaCu_2$, LaNi and trace amounts of La_2NiO_4 and CuO, which may be caused by the oxidation during the melting.

The BSE and EDS results of the annealed alloys are shown in Fig. 7(a), (b) and (c), respectively. It seems that #1 and #2 in Fig. 7(a) and (b) are composed of two phases. Actually, the composition ratio of La content to the total amount of Cu and Ni in the gray region (marked as 1) is approximately 1 to 1. The solid solubility of Ni in LaCu is 4 at.% and that of Cu in LaNi is 5 at.%, as reported in the Ref. [11]. Moreover, the atomic number of Ni is so close to Cu that they cannot be distinguished clearly in the BSE image. In addition, there is an invariant reaction, $LaCu_2 + La_7Ni_3 \xrightarrow{674\ K} LaCu + LaNi$, in the isoplethal sections with constant Ni content for #1 (23.54 at.% Ni) and #2 (18.91 at.% Ni), as shown in Fig. 8(a) and (b), respectively. The invariant reaction suggests that LaCu and LaNi appear simultaneously in the solid phases so that they cannot be distinguished in the BSE image. Therefore, we believe that the regions marked as 1 in Fig. 8(a) and (b) are the mixture of LaNi and LaCu. The light gray region marked as 2 in Fig. 8(a) is La_7Ni_3, and the black region marked as 2 in Fig. 8(b) is $LaCu_2$. The BSE and EDS results are consistent with the XRD results. That is to say, the sample #1 is composed of La_7Ni_3, LaNi and LaCu and #2 has LaNi, LaCu and $LaCu_2$ three phases. Fig. 7(c) presents the BSE image of #3 annealed at 673 K, which indicates the existence of a two-phase mixture. Also, the EDS results suggest that #3 is composed of two phases, LaNi and $LaCu_2$, which were marked as 1 and 2 in Fig. 8(c), respectively. No invariant reaction is found in the section (35.07 at.% Ni) through the sample #3, as shown in Fig. 8(c), so the phenomenon found in #1 and #2 does not existed in #3. That is to say, #3 is composed of LaNi and $LaCu_2$.

5. Conclusions

In the present work, a thermodynamic description of the La–Ni–Cu ternary system was established and experimental validated. The 673 K isothermal section and the enthalpy of mixing of liquid were calculated and agreed well with experimental data. Three key sample alloys were prepared and microstructurally characterized, and the results suggested that the LaNi and $LaCu_2$ two-phase field was larger than that reported in the literature. All of the experimental results showed an agreement with the calculated phase diagram.

Acknowledgments

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Appendix. Supplementary data

Supplementary material related to this article can be found online at doi:10.1016/j.calphad.2011.10.004.

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