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Phase relationships in the La-Ni-Si system at 673 K

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Abstract

The phase relationships in the La–Ni–Si ternary system at 673 K were investigated by X-ray diffraction (XRD), differential thermal analysis (DTA), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). All phase relationships were studied at 673 K. At this temperature, the existence of 14 ternary compounds has been confirmed. This section consists of 35 single-phase regions, 78 two-phase regions, and 47 three-phase regions. At 673 K, the maximum solid solubility of Si in Ni, La₂Ni₇, LaNi₅, and La₂NiSi is about 9, 3, 8.33, and 5 at.%, respectively. Several ternary compounds form a homogeneity region which can be expressed as LaNi_{11.6–9.5}Si_{1.4–3.5}, LaNi_{8.8–8.4}Si_{4.2–4.6}, and LaNi_{7.8–6.5}Si_{5.2–6.5}.

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1. Introduction

In the development of the high-energy density and environment friendly Ni-MH battery, the crucial material having properties required for the MH electrode are AB5-type hydrogen strong systems based on LaNi₅ [1]. The LaNi_{5-x}Si_x (0 < x < 0.08) system has many interesting properties for its application in battery electrodes, e.g. high stability, fast activation, low volume expansion on hydride formation, sinterability, and a suitable plateau pressure. Silicon substitution is cheaper and more effective for obtaining certain properties than cobalt substitution. The LaNi_{5-x}Si_x $(0 \le x \le 0.08)$ system might therefore serve as a basis for the development of low cost, multicomponent alloys in combination with Mm, lanthanum-rich Mm, aluminium, and manganese but without or with very little cobalt [2]. The phase diagrams and thermodynamics are important for the study of phase transformation of materials and for the materials performance. There is some literature reporting that the substitution of small amount of Si for Ni in LaNi₅ alloys can improve its properties including the hydrogen storage ability of LaNi₅ [3].

The phase diagrams of the binary La–Ni, Ni–Si, and La–Si systems were reported in [4,5,6–10], respectively. At 673 K, there are seven intermetallic compounds in the La–Ni system, namely La₇Ni₃, LaNi, La₂Ni₃, La₇Ni₁₆, LaNi₃, La₂Ni₇, and LaNi₅; six intermetallic compounds in the Ni–Si system, namely Ni₃Si, Ni₃₁Si₁₂, Ni₃Si₂, Ni₂Si, NiSi, and NiSi₂; and five intermetallic compounds in the La–Si system, namely LaSi₂, LaSi, La₅Si₄, La₃Si₂, and La₅Si₃. Tables 1 and 2 list the data reported on the crystal structures of the compounds.

2. Experimental

The purities of lanthanum, nickel, and silicon used in this work were 99.9, 99.99, and 99.9%, respectively. Three hundred and fifty-two alloy buttons have been produced. Each sample was prepared with a total weight of 3 g. Weight losses during arc melting were less than 1% of the total mass.

Therefore, the phase relationships in the La–Ni–Si ternary system are well worth studying completely in order to provide information required for improving material properties and for developing new materials. Up to now, the integral phase diagram of the La–Ni–Si system has not been reported. In this paper, we studied the isothermal section of the La–Ni–Si ternary system at 673 K.

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Table 1	
The data on the crystal structures of the compounds of	the La-Ni, Ni-Si and La-Si binary systems

Compound	Space group	Structure type	Lattice parameters				Reference
			a (nm)	b (nm)	<i>c</i> (nm)	γ (°)	
La7Ni3	P6 ₃ mc	Fe ₇ Th ₃	1.0130(9)	_	0.6462(6)	120	[11]
LaNi	Cmcm	BCr	0.3907	1.0180(1)	0.4396	_	[11]
La ₂ Ni ₃	Cmca	La ₂ Ni ₃	0.51183	0.97316	0.79075	-	[11]
La7Ni16	$I\overline{4}2m$	La7Ni16	0.7355	_	1.451	_	[11]
LaNi ₃	R3m	BeNb ₃	0.5086(5)	_	2.501(1)	120	[11]
La2Ni7	$P6_3/mmc$	Ce ₂ Ni ₇	0.5085	_	2.471	120	[11]
LaNi ₅	P6/mmm	CaCu ₅	0.5016	_	0.3983	120	[11]
Ni ₃ Si	Pm3m	AuCu ₃	0.3506	_	_	_	[11]
Ni31Si12	P321	Ni31Si12	0.6671(1)	_	1.228(2)	120	[11]
Ni ₂ Si	Pnma	Co ₂ Si	0.499	0.372	0.706	_	[11]
Ni ₃ Si ₂	$Cmc2_1$	Ni ₃ Si ₂	2.229	1.0805	0.6924	_	[11]
NiSi	Pnma	MnP	0.518	0.334	0.562	_	[11]
NiSi ₂	Fm3m	CaF ₂	0.5406	_	_	_	[11]
LaSi ₂	$I4_1/amd$	ThSi ₂	0.4281	_	1.375	_	[11]
LaSi	Pnma	FeB	0.8404(5)	0.4010(3)	0.6059(3)	_	[11]
La ₅ Si ₄	$P4_{1}2_{1}2$	Zr ₅ Si ₄	0.811	_	1.541	_	[11]
La ₃ Si ₂	P4/mbm	Si ₂ U ₃	0.787(2)	_	0.450(1)	_	[11]
La ₅ Si ₃	I4/mcm	Cr ₅ B ₃	0.7949	_	1.407	-	[11]

These alloy buttons were prepared in an argon atmosphere in a vacuum arc furnace or in a high-frequency induction furnace. Each arc-cast button had been melted three times and turned around after melting for better homogeneity. Small amounts of lanthanum was lost during melting, so an excess of 1 at.% La was used.

After melting, the samples were kept in evacuated sealed silica tubes during homogenization and then they were annealed at different temperatures in order to reach a good homogenization. The homogenization temperature of the alloys were derived from differential thermal analysis (DTA) results of some representative ternary alloys or they were based on the binary phase diagram of the binary La–Ni, Ni–Si, and La–Si systems. The samples in the Ni-rich part, containing more than 75 at.% Ni in the La–Ni binary system or 70 at.% Ni in the Ni–Si binary system or near them

Table 2 The data on the crystal structures of the compounds of the La-Ni-Si ternary system

in the ternary system, were kept at 1123 K for 720 h. The
samples, which contained between 50 and 75 at.% Ni in the
La-Ni binary system or near them in the ternary system,
were homogenized at 973 K for 720 h. The alloy samples
in the Si-rich part, which contained more than 50 at.% Si
in the Ni-Si and La-Si binary system or near them in the
ternary system, were homogenized at 1173 K for 720 h. Sub-
sequently, the alloy samples were cooled at a rate of $10\mathrm{K/h}$
to 673 K and kept at 673 K for 150 h . Then, all of the alloy
samples were quenched into liquid nitrogen.

The homogenized alloy powders or buttons were investigated by X-ray diffraction on a Rigaku D/Max 2500PC X-ray diffractometer (Cu K α , monochromator), using JADE5 software to analyze the angles, ranging from $2\theta =$ 20° to 60° at 40 kV, 25 mA. Some representative alloys were analyzed by an S-570 scanning electron microscope

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Compound	Space group	Structure type	Lattice parameters				Reference
			a (nm)	b (nm)	<i>c</i> (nm)	γ (°)	
LaNiSi	I4 ₁ md	LaPtSi	0.418	_	1.407	_	[11,12]
LaNiSi ₂	Cmcm	CeNiSi ₂	0.42	1.65	0.407	-	[11,12]
LaNi ₂ Si ₂	I4/mmm	Al ₄ Ba	0.4111	_	0.969	-	[11,12]
LaNi9Si2	$I4_1/amd$	BaCd ₁₁	0.9899	_	0.6265	_	[11,12]
La ₂ NiSi	$P6_3/m$	Ce ₅ Ni ₂ Si ₃	1.634(1)	_	0.4322(5)	120	[11,12]
La2NiSi3	P6/mmm	AlB_2	0.4077	_	0.43	120	[11,12]
LaNi11.6-9.5Si1.4-3.5	Fm3c	NaZn ₁₃	1.127	_	-	-	[11,12]
La ₆ Ni ₂ Si ₃	$P6_3/m$	Ce ₆ Ni ₂ Si ₃	1.220(1)	_	0.4350(2)	120	[11,12]
La7Ni2Si5	Pnma	Ce7Ni2Si5	2.363	0.4312	1.409	-	[12]
LaNi _{8.8-8.4} Si _{4.2-4.6}	I4/mcm	Ce ₂ Ni ₁₇ Si ₉	0.785(1)	_	1.151(11)	-	[12–15]
LaNi _{7.8-6.5} Si _{5.2-6.5}	I4/mcm	NaZn ₁₃	1.12	_	_	-	[12–15]
La15Ni4Si13	$P6_3/m$	Ce15Ni4Si13	2.044	_	4.336	120	[12–15]
LaNi ₄ Si		LaNi ₄ Si	0.8382	0.521	0.3989	-	[17]
La14Ni6Si11	C2/m	Ce14Ni6Si11	2.203	1.661	0.4302	113.52(3)	[12–15]

(SEM), electron probe microanalysis (EPMA) or differential thermal analysis (DTA). From all these results, the phase relations in the La–Ni–Si system were determined.

3. Results and discussion

3.1. Binary system

3.1.1. La-Ni system

In [4], the La–Ni phase diagram was assessed, eight kinds of La–Ni compounds La₃Ni, La₇Ni₃, LaNi, La₂Ni₃, La₇Ni₁₆, LaNi₃, La₂Ni₇, and LaNi₅ have been reported (see Table 1). According to [16], one of the major differences between [17,18] is the existence of LaNi₂ or La₇Ni₁₆ in the La–Ni system. Our investigation has shown that the phase is not LaNi₂ but La₇Ni₁₆. The result was obtained by X-ray diffraction analysis, SEM, and EPMA. Secondly, the existence of La₃Ni was confirmed in [16]. In our experiments, five alloy samples near the La₃Ni composition were studied by X-ray diffraction. Our work has proved that the compound of La₃Ni does not exist. The diffraction pattern of La₃Ni consists of that of La and La₇Ni₃.

3.1.2. Ni-Si system

According to the Ni–Si system, there are six kinds of compounds, which are Ni₃Si, Ni₃₁Si₁₂, Ni₂Si, Ni₃Si₂, NiSi, and NiSi₂ (see Table 1). In [11] and JCPDS PDF file, it was reported that the compounds Ni₇₄Si₂₆ and Ni₈₅Si₁₅ maybe exist between Ni and Ni₃Si. But in our investigation, the phases of Ni₇₄Si₂₆ and Ni₈₅Si₁₅ were not found. Their X-ray pattern consists of that of Ni and Ni₃Si.

3.1.3. La-Si system

In the Ni–Si system, five compounds were reported in [11]. These are LaSi₂, LaSi, La₅Si₄, La₃Si₂, and La₅Si₃, which is in accordance with our experimental results. But in JCPDS PDF file, the existence of the LaSi_{2-x} compound has been reported. However, in our work, this compound was not found. The X-ray diagram consists of the patterns of LaSi and LaSi₂.

3.2. Ternary system

Fourteen ternary compounds LaNiSi, LaNiSi₂, LaNi₂Si₂, LaNi₉Si₂, La₂NiSi, La₂NiSi₃, LaNi_{11.6}–9.5Si_{1.4}–3.5, La₆Ni₂Si₃, La₇Ni₂Si₅, LaNi_{8.8}–8.4Si_{4.2}–4.6, LaNi_{7.8}–6.5Si_{5.2}–6.5, La₁₅Ni₄Si₁₃, LaNi₄Si, and La₁₄Ni₆Si₁₁ (see Table 2) were reported. Four of these compounds LaNiSi, La₂NiSi₃, La₂Ni₂₁Si₅, and LaNi₄Si are also reported in the JCPDS PDF file. According to the crystallographic data of LaNiSi₂, LaNi₂Si₂, LaNi₉Si₂, La₂NiSi, LaNi_{11.6}–9.5Si_{1.4}–3.5, La₆Ni₂ Si₃, LaNi_{8.8}–8.4Si_{4.2}–4.6, and La₁₅Ni₄Si₁₃ taken from [12], using the LAZY program [19], we were able to obtain the calculated XRD patterns of the compounds, respectively. The results of XRD analysis of our alloy samples are in good agreement with the respective JCPDS PDF cards or with the calculated XRD pattern.

From our X-ray data, the LaNi_{11.6-9.5}Si_{1.4-3.5} compound with NaZn₁₃-type structure was confirmed to exist in a narrow homogeneity region around the composition La₂Ni₂₁Si₅, as reported earlier already in [11]. In this region, the patterns of the alloy samples are in accordance with that of La₂Ni₂₁Si₅ as well. Similarly, the LaNi_{7.8-6.5}Si_{5.2-6.5} compound with NaZn₁₃-type was confirmed to exist. Also, the LaNi_{8.8-8.4}Si_{4.2-4.6} compound with Ce₂Ni₁₇Si₉-type structure, occurring in a narrow homogeneity region around the composition La₂Ni₁₇Si₉, was confirmed.

In [12,13], a ternary compound La₇Ni₂Si₅ (space group *Pnma*, a = 2.363 nm, b = 0.4312 nm, c = 1.409 nm) with Ce₇Ni₂Si₅-type structure (space group *Pnma*, a = 2.331(3) nm, b = 0.4299(5) nm, c = 1.390(3) nm) is mentioned. In order to identify this phase, we prepared a series of alloy samples near the La₇Ni₂Si₅ region. The results of XRD of these alloy samples showed that the diagram of La₇Ni₂Si₅ is in good agreement with that of Ce₇Ni₂Si₅. Thus, the existence of the La₇Ni₂Si₅ phase was confirmed.

By comparing and analyzing the X-ray diffraction patterns of the alloy samples of the La₁₄Ni₈Si₉ compound, which has been reported to have a structure type with Pearson symbol mP64 [12], our result shows that the phase may not be La₁₄Ni₈Si₉ but La₁₄Ni₆Si₁₁ with Ce₁₄Ni₆Si₁₁-type structure (mC124, a = 3.408(1) nm, b = 0.42456(3) nm, c =2.137(1) nm, $\gamma = 113.52(3)^{\circ}$). Samples in the three-phase regions near the compound were studied by X-ray diffrac-



Fig. 1. The 673 K isothermal section of the phase diagram of the La–Ni–Si ternary system: (a) LaNi_{11.6–9.5}Si_{1.4–3.5}, (b) LaNi_{8.8–8.4}Si_{4.2–4.6}, (c) LaNi_{7.8–6.5}Si_{5.2–6.5}, (d) LaNi₂Si₂, (e) LaNiSi₂, (f) La₂NiSi₃, (g) LaNiSi, (h) La₁₄Ni₆Si₁₁, (i) La₁₅Ni₄Si₁₃, (j) La₇Ni₂Si₅, (k) La₂NiSi, (l) La₆Ni₂Si₃, (m) LaNi₄Si, and (n) LaNi₉Si₂.

tion, and the X-ray diagram of the compound consists of $La_{14}Ni_6Si_{11}$ and two other ternary compounds.

3.3. Solid solubility

At 673 K, the maximum solid solubility of Ni in LaSi₂ is about 4 at.%. The maximum solubilities of Si in Ni, LaNi₅, La₂Ni₇, and La₂NiSi are about 9, 8.33, 3, and 5 at.%, respectively. The single-phase regions a, b, and c correspond to homogeneity ranges expressed as LaNi_{11.6-9.5}Si_{1.4-3.5}, LaNi_{8.8-8.4}Si_{4.2-4.6}, and LaNi_{7.8-6.5}Si_{5.2-6.5}, respectively.

Table 3

Details of three-phase regions in La-Ni-Si system at 673 K

Phase region	Phase
1	$Si + LaNiSi_2 + LaSi_2$
2	$Si + LaNi_2Si_2 + LaNiSi_2$
3	$LaSi_2 + LaNiSi + La_2NiSi_3$
4	$LaNi_2Si_2 + LaNiSi_2 + La_2NiSi_3$
5	$LaNi_2Si_2 + La_2NiSi_3 + LaNiSi$
6	$LaSi + LaSi_2 + La_2NiSi_3$
7	$LaSi + La_5Si_4 + La_2NiSi_3$
8	$La_5Si_4 + La_2NiSi_3 + La_{15}Ni_4Si_{13}$
9	$La_2NiSi_3 + La_{15}Ni_4Si_{13} + La_{14}Ni_6Si_{11}$
10	$La_2NiSi_3 + La_{15}Ni_4Si_{13} + LaNiSi_5$
11	$La_2NiSi_3 + La_{15}Ni_4Si_{13} + La_7Ni_2Si_5$
12	$La_{15}Ni_4Si_{13} + La_7Ni_2Si_5 + La_{14}Ni_6Si_{11}$
13	$La_5Si_4 + La_3Si_2 + La_7Ni_2Si_5$
14	$La_3Si_2 + La_7Ni_2Si_5 + La_6Ni_2Si_3$
15	$La_3Si_2 + La_6Ni_2Si_3 + La_5Si_3$
16	$La_6Ni_2Si_3 + La_5Si_3 + La_7Ni_3$
17	$La + La_6Ni_2Si_3 + La_5Si_3$
18	$La_7Ni_3 + La_6Ni_2Si_3 + La_2NiSi$
19	$La_7Ni_3 + La_2NiSi + LaNi$
20	$La_2NiSi + La_6Ni_2Si_3 + La_7Ni_2Si_5$
21	$La_2NiSi + La_7Ni_2Si_5 + La_{14}Ni_6Si_{11}$
22	$La_2NiSi + LaNiSi + La_{14}Ni_6Si_{11}$
23	$LaNi + La_2NiSi + La_2Ni_3$
24	$La_2Ni_3 + La_2NiSi + LaNiSi$
25	$La_2Ni_3 + LaNiSi + LaNi_2Si_2$
26	$La_2Ni_3 + La_7Ni_{16} + LaNi_2Si_2$
27	$La_7Ni_{16} + LaNi_3 + LaNi_2Si_2$
28	$LaNi_3 + La_2Ni_7 + LaNi_2Si_2$
29	$La_2Ni_7 + LaNi_2Si_2 + LaNi_4Si$
30	$La_2Ni_7 + LaNi_5 + LaNi_4Si$
31	$LaNi_5 + LaNi_4Si + LaNi_9Si_2$
32	$LaNi_5 + LaNi_9Si_2 + LaNi_{11.6-9.5}Si_{1.4-3.5}$
33	$LaNi_9Si_2 + LaNi_{11.6-9.5}Si_{1.4-3.5} + LaNi_4Si$
34	$LaNi_5 + Ni + LaNi_{11.6-9.5}Si_{1.4-3.5}$
35	$Ni + Ni_3Si + LaNi_{11.6-9.5}Si_{1.4-3.5}$
36	$Ni_3Si + Ni_{31}Si_{12} + LaNi_{11.6-9.5}Si_{1.4-3.5}$
37	$Ni_{31}Si_{12} + LaNi_{11.6-9.5}Si_{1.4-3.5} + LaNi_{8.8-8.4}Si_{4.2-4.6}$
38	$LaNi_{11.6-9.5}Si_{1.4-3.5} + LaNi_{8.8-8.4}Si_{4.2-4.6} + LaNi_4Si$
39	$Ni_{31}Si_{12} + Ni_2Si + LaNi_{8.8-8.4}Si_{4.2-4.6}$
40	$LaNi_{8.8-8.4}Si_{4.2-4.6} + LaNi_{7.8-6.5}Si_{5.2-6.5} + Ni_2Si$
41	$LaNi_{8.8-8.4}Si_{4.2-4.6} + LaNi_{7.8-6.5}Si_{5.2-6.5} + LaNi_2Si_2$
42	$LaNi_{8.8-8.4}Si_{4.2-4.6} + LaNi_2Si_2 + LaNi_4Si_1$
43	$Ni_2Si + Ni_3Si_2 + LaNi_{7.8-6.5}Si_{5.2-6.5}$
44	$Ni_3Si_2 + NiSi + LaNi_{7.8-6.5}Si_{5.2-6.5}$
45	$NiSi + NiSi_2 + LaNi_{7.8-6.5}Si_{5.2-6.5}$
46	$NiSi_2 + LaNi_{7.8-6.5}Si_{5.2-6.5} + Si$
47	$LaNi_2Si_2 + Si + LaNi_{7.8-6.5}Si_{5.2-6.5}$

Neither La in Ni nor La in Si forms a range of solid solubility. No solubility of one of the elements in any of the other phases has been observed.

3.4. Isothermal section

By comparing and analyzing the X-ray diffraction patterns of 352 samples, combined with metallography, DTA and EPMA, and identifying the phases presented in each sample, the 673 K isothermal sections of the phase diagram of the La–Ni–Si ternary system were determined (shown in Fig. 1). The isothermal section consists of 35 single-phase, 78 two-phase, and 47 three-phase regions. Details of the three-phase regions are given in Table 3 and Fig. 1.

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References

- R.C. Bowman Jr., C. Witham, B. Fultz, B.V. Ratnakumar, T.W. Ellis, I.E. Anderson, J. Alloys Compd. 253/254 (1997) 613.
- [2] F. Meli, A. Zuettel, L. Schlapbach, J. Alloys Compd. 190 (1992) 17–24.
- [3] S. Srivastava, O.N. Srivastava, J. Alloys Compd. 267 (1998) 240.
- [4] Y.Y. Pan, P. Nash, Binary Alloy Phase Diagrams, ASM International, Materials Park, OH, 1991, pp. 2046–2048.
- [5] P. Nash, A. Nash, Binary Alloy Phase Diagrams, ASM International, Materials Park, OH, 1991, pp. 2859–2861.
- [6] E.I. Gladyshevskii, Izv. Akad. Nauk SSSR, Neorg. Mater. 1 (5) (1965) 706–710 (in Russian).
- [7] E.I. Gladyshevskii, P.I. Kripyakevich, Izv. Akad. Nauk SSSR, Neorg. Mater 1 (5) (1965) 702–705 (in Russian).
- [8] G.S. Snith, A.G. Tharp, Q. Johnson, Acta Crystallogr. 22 (1967) 940.
- [9] E.I. Gladyshevskii, P.I. Kripyakevich, Zh. Strukt. Khim 5 (1964) 853–859 (in Russian);

TR, J. Struct. Chem. USSR 5 (1964) 789-794.

- [10] G. Brauer, H. Haag, Naturwissenschaften 37 (1950) 210–211 (in German).
- [11] P. Villars, Pearson's Handbook of Crystallographic Data, Materials Park, OH, 1997, pp. 2273–2275, 2539–2540, 2294–2295, 2276– 2277.
- [12] K.A. Gschneidner, E. LeRoy Jr., Handbook on the Physics and Chemistry of Rare Earths, vol. 7, pp. 125–128, 28–37.
- [13] Calvert, L., National Research Council of Canada, Ottawa, Canada, ICDD Grant-in-Aid, 1976.
- [14] J. Liang, W.X. Zhao, Acta Phys. Sinica 35 (1986) 505.
- [15] E.R. Hovestreydt, J. Less-Common Met. 102 (1984) L27-L29.
- [16] J. Liu, G. Ke, J. Alloys Compd. 312 (2000) 121-123.
- [17] Y.Y. Pan, P. Nash, in: T.B. Massalski, P.R. Subramanian, H. Okamoto, L. Kacprzak (Eds.), Binary Alloy Phase Diagrams, second ed., ASM International, Materials Park, OH, 1991, pp. 2406–2408.
- [18] H. Okamoto, J. Phase Equilib. 12 (5) (1972) 203-210.
- [19] K. Yvon, W. Jeitschko, E. Parthe, Appl. Crystallogr. 10 (1977) 73.