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Experimental investigation and thermodynamic description of the Li–Si–Ni ternary system

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ABSTRACT

The 150 °C isothermal section of Li–Si–Ni ternary system has been experimentally established. The investigation is based on X-ray powder diffraction and scanning electron microscopy techniques on about 80 ternary alloys, prepared by argon-arc melting of proper elemental ingots. The existence of six ternary compounds, i.e. $\tau_1(LiNi_2Si)$, $\tau_2(Li_{13}Ni_{40}Si_{31})$, $\tau_3(LiNi_6Si_6)$, $\tau_4(Li_{13}Ni_9Si_{18})$, $\tau_5(Li_{0.6}Ni_{5.4}Si_6)$ and τ_6 $(Li_{75}Ni_{20}Si_{128})$ is conformed. Fourteen three-phase regions have been detected, i.e. $Li_{13}Si_4+\tau_1+Li_{22}Si_5$, $Li_{13}Si_4+\tau_1+\tau_2$, $\gamma+\tau_1+\tau_2$, $Li_7Si_3+\tau_4+\tau_2$, $Li_7Si_3+\tau_4+Li_{12}Si_7$, $\tau_6+\tau_4+Li_{12}Si_7$, $\gamma+\tau_1+\beta_1$, $\gamma+\delta+\tau_2$, $\tau_3+\delta+\tau_5$, $\varepsilon+\delta+\tau_5$, $NiSi_2+(Si)+\tau_5$, $(Si)+\tau_5+\tau_4$, $\tau_2+\tau_3+\tau_4$ and $\tau_5+NiSi+NiSi_2$. Furthermore, thermodynamic description of the Li–Ni and Li–Si–Ni systems is carried out with the CALPHAD approach on the basis of the present experimental results and the first-principle calculation of the formation enthalpies for τ_1 and τ_3 ternary compounds. Reasonable agreement of the phase equilibria in the Li–Si–Ni ternary system between the experiment and thermodynamic calculation is achieved.

Introduction

Silicon (Si) is a promising anode material of Li-ion batteries due to its highest theoretic capacity (about 4200 mAh/g) and relatively low working potential (0.5 V vs Li/Li^+). It is considered as a potential alternative of commercial graphite [1–6]. However, rapid capacity decay during alloying and dealloying with lithium followed by electrochemical and mechanical particles disintegrate on a Si anode is thought to be a problem due to severe volume expansion [6–11]. Several approaches have been investigated to overcome this problem. For instance, alloys that consist of Si-containing phase which is electrochemically inactive with lithium can be used to improve the cycling ability. During lithium insertion into the alloy electrodes, Si acts as an active central, which reacts with Li to form Li_xSi alloys; while the other inactive alloy phase plays the role of matrix as an inertia phase, which can buffer silicon volume expansion. Recently, several studies have been carried out on Si–Ni alloys as anode, and successfully improved the cycling performance [12–15]. In order to study the lithiation route of Si–Ni anode materials and to understand the lithium insertion mechanism, it is necessary to investigate the phase relations of the Li–Si–Ni ternary system.

In the present work, the isothermal section of the Li–Si–Ni ternary system at 150 °C has been determined experimentally. Then, combining the earlier thermodynamic assessment for the constituent binary Li–Si [16] and Si–Ni [17] constituent binary systems, and the thermodynamic optimization of Li–Ni binary system in this work, the thermodynamic description of the Li–Si–Ni ternary system has been carried out. The crystallographic parameters for the binary and ternary compounds involved in the present work are listed in Table 1.

2. Experimental procedure

The isothermal section of the Li–Si–Ni ternary system at 150 °C has been constructed by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The nominal compositions of the alloys are detailed in Table 2. The Li–Si–Ni ternary alloys were prepared using metal blocks by arc melting in purified argon atmosphere under a pressure of $\sim 1.01\times10^5$ Pa from a mixture of pure metals (Ni of 99.99 wt% purity, Li of 99.9 wt% purity and Si of 99.99 wt% purity). All materials were weighed with an accuracy of

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Table 1
Crystallographic data of the phases in the Li–Si–Ni ternary system.

Phase	Pearson symbol	Space group	Lattice parameters (nm)			Refs.
			a	*b*	*c*	
Si	*cF8*	*Fd-3m*	0.54307			[18]
Ni	*cF4*	*Fm-3m*	0.35238			[18]
$Li_{22}Si_5$	cF432	*F23*	1.8751			[19]
$Li_{13}Si_4$	oP34	*Pbam*	0.7990	1.521	0.443	[19]
Li_7Si_3	hR6.67	*R-3m*	0.4435		1.8134	[19]
$Li_{12}Si_7$	oP152	*Pnma*	0.8610	1.9738	1.4341	[19]
$\beta_1(Ni_3Si)$	*cF4*	Pm-3m	0.3500			[19]
$\beta_2(Ni_3Si)$	*mC16*	C2/c	0.6970	0.6250	0.5070	[20]
$\beta_3(Ni_3Si)$	*mC16*	C2/c	0.704	0.626	0.508	[20]
$\gamma(Ni_5Si_2)$	*hP43*	P312	0.66619		1.2258	[18]
$\theta(Ni_2Si)$	*hP6*	$P6_3$ /mcm	0.3805		0.4890	[18]
$\delta(Ni_2Si)$	*oP12*	Pnma	0.4990	0.3720	0.7060	[18]
$\varepsilon(Ni_3Si_2)$	*oC80*	$Cmc2_1$	1.2229	1.0805	0.6924	[18]
NiSi	*oP8*	Pnma	0.5180	0.3340	0.5620	[18]
$NiSi_2$	*cF12*	Fm-3m	0.5406			[18]
$\tau_1(LiNi_2Si)$	*cF16*	*Fm-3m*	0.55524			[21]
$\tau_2(Li_{13}Ni_{40}Si_{31})$	*hP168*	*P6/mmm*	1.70924		0.78487	[22]
$\tau_3(LiNi_6Si_6)$	*hP39*	*P6/mmm*	0.8461		0.75915	[23]
$\tau_4(Li_{13}Ni_9Si_{18})$	*cI160*	*Im-3*	1.2741			[24]
$\tau_5(Li_{0.6}Ni_{5.4}Si_6)$	*mS24*	*C12/m1*	1.10848	0.37428	0.81222	[25]
$\tau_6(Li_{75}Ni_{20}Si_{128})$	*hP223*	*P6₃/mmc*	1.2870		2.1446	[26]

Table 2
Summary of the Li–Si–Ni alloys identified by XRD and SEM

Alloy no.	Nominal composition (at%)			Phase
	Li	Si	Ni	
A1	50	43	7	$\tau_4+\tau_6+Li_{12}Si_7$
A2	5	32	63	$Ni_5Si_2+Ni_2Si+\tau_2$
A3	6	45	49	$\tau_3+Ni_2Si+\tau_5$
A4	1	40	59	$Ni_3Si_2+Ni_2Si+\tau_5$
A5	3	65	32	$NiSi_2+(Si)+\tau_5$
A6	15	55	30	$(Si)+\tau_5+\tau_4$
A7	60	22	18	$Li_{13}Si_4+\tau_1+Li_{22}Si_5$
A8	50	25	25	$Li_{13}Si_4+\tau_1+Li_{13}Ni_{40}Si_{31}$
A9	20	27	53	$Ni_5Si_2+\tau_1+Li_{13}Ni_{40}Si_{31}$
A10	50	34	16	$Li_7Si_3+\tau_4+Li_{13}Ni_{40}Si_{31}$
A12	10	25	65	$Ni_5Si_2+\tau_1+Ni_3Si$
A13	22	41	37	$\tau_2+\tau_3+\tau_4$
A14	4	51	45	$NiSi+NiSi_2+\tau_5$

0.001 g. To ensure homogeneity, the ingots were melted five times and inverted after every melting. After melting, the weight losses of alloys were checked. The Li–Si–Ni ternary alloys were sealed under pure argon at 1 bar in special adapted tantalum containers using electric arc welding, and the sealed tantalum container was sealed into evacuated quartz tubes. To ensure the establishment of an equilibrium state, all samples were annealed at 150 °C for 960 h. The treatment was completed with rapid water quenching to preserve the equilibrium state at annealing temperatures. The quenched samples were cut into two parts. One piece was prepared for metallographic examination and the other for X-ray diffraction analysis.

The metallographic specimens were prepared in a conventional way for microstructure examination. The morphology of all phases in the alloys was studied using both optical microscopy (OM) and a JSM-6360LV scanning electron microscopy (SEM). The phase relations of the alloys were confirmed by XRD patterns generated by a D/max-rA X-ray diffractometer with Cu Kα-radiation.

3. Evaluation of the available information

3.1. The Li–Si and Si–Ni binary systems

The Li–Si system has been assessed by Okamoto et al. [27] firstly. Braga et al. [28] re-optimized this system using more interaction parameters for the liquid phase. Due to the inconsistency between the phase diagram data and the thermodynamic data, Braga et al. [28] provided two sets of parameters to better describe the phase diagram data and the thermodynamic data, respectively. Recently, Wang et al. [16] and Braga et al. [29] all critically assessed all the original experimental data of the Li–Si system, a good agreement were obtained between the assessment results and the experiment data, respectively. The thermodynamic parameters assessed by Wang et al. [16] are adopted in this work and the calculated Li–Si phase diagram is shown in Fig. 1.

The phase equilibria of the Si–Ni system have been reviewed by Nash et al. [20] firstly. This binary system was then successively assessed by Du et al. [30], Tokunaga et al. [31], Miettinen [17] and