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Thermodynamic description of Si-B binary system

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Abstract

The Si-B binary system was thermodynamically assessed and described using the CompuTherm Pandat software. The solution phases, including Liquid, diamond-Si and β-B were treated as substitutional solution phases, of which the Gibbs energies were expressed with Redlich-Kister polynomial functions. Meanwhile, the compounds, SiB3, SiB6, SiBn, were modeled as stoichiometric compounds. The thermodynamic parameters formulating the Gibbs energies of various phases were obtained and the equilibrium and transition of phases were discussed. The existent forms for Si-B phases in MG-Si melt were forecast.

Keywords: CompuTherm, Si-B binary system, thermodynamic, metallurgical grade silicon

1. Introduction

Presently, the metallurgical process that metallurgical grade silicon (MG-Si) is used as raw material and purified to 6N (99.9999%) or so purity is an important method for preparing solar grade silicon (SoG-Si). The MG-Si melt is a complicated system in which includes many impurity elements such as Fe, Al, Ca, Ti, P, B, C, O etc, and to a large extent, these impurity elements will impact on the photoelectric conversion efficiency of SoG-Si [1,2]. It is crucial to the removal of impurities with the metallurgical process, so it is necessary to previously investigate the phase equilibria among silicon and other components in silicic systems [3]. A challenging problem with metallurgical process is the boron removal for MG-Si and the Si-B binary system plays an important role here.

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The purpose of this work is to evaluate the Si-B binary system by means of the CompuTherm technology (software Pandat 7.0) and to generate a reliable description of thermodynamic properties and phase diagrams for the Si-B binary system.

2. Evaluation of experimental information

2.1 Phase diagram

The present Si-B binary diagram is based on the evaluation of various computational techniques by utilizing the enthalpy function. The calculations were done by assuming Henrian behavior for the solid solutions. The calculated liquidus curve agreed with the experimental features of the diagram only upon weighting the solubility data. Detailed review of the Si-B system was studied by R.W. Olesinski and G.J. Abbaschian [4]. There are six phases, liquid, diamond-Si, β-B SiB_3, SiB_6 and SiB_n reported so far for this system. J. Hesse [5], J.C. Viala and J. Bouix [6] also made some comprehensive studies of the Si-B binary system. Their studies revealed that the assessed Si-B phase diagram includes the intermediate phases SiB_6 and SiB_3. It is generally agreed that SiB_3, sometimes erroneously identified as SiB_4, is unstable above 1473K～1673K. B. Armas [7], G. Male and D. Salanoubat [8] proved the formation of a B-rich solid phase, SiB_n, distinct from, although isotypic with, the solubility of Si in B. The calculated coordinates of the eutectic and SiB_n peritectic points agree well with the experimental data. G.N. Makarenko and O.I. Popova [9] found that the phase SiB_4 was obtained by amorphous boron powder and silicon for the B-Si system, but it is not found in the assessed Si-B binary phase diagram.

2.2 Thermodynamic model

The Gibbs Energy Model is usually used to calculate the thermodynamic process for phase diagram. The Si-B binary system includes six phases: liquid, diamond-Si, β-B, SiB_3, SiB_6 and SiB_n. The Gibbs free energies of pure elements with respect to temperature $G_i^{o,\varphi}(T) = G_i^{\varphi}(T) - H_i^{\mathrm{SER}}$ are represented by Eq. (1):

$$G_i^{o,\varphi}(T) = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} + \ldots \quad (1)$$

The $G_i^{o,\varphi}(T)$ data are referred to the constant enthalpy value of the standard element reference H_i^{SER} at 298.15K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE) [10]. The $G_i^{o,\varphi}(T)$ may be given for several temperature ranges, where the coefficients *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h* have different values.

3. Results and discussion

The crystal structures of these phases are listed in Table 1. It includes a peritectic reaction L+(B)↔ SiB_n at 2293K, involving the B-rich intermediate phase SiB_n (n～23), a peritectic reaction L+ SiB_n ↔ SiB_6 involving the intermediate phase SiB_6 at 2123K, a eutectic reaction L↔(Si)+SiB_6 at 8 at.% B and 1658K, and a peritectoid reaction (Si)+SiB_6↔SiB_3 involving the intermediate phase SiB_3 at around 1543K.

Table 1. Phases and structures of Si-B

Phase	Prototype	Pearson symbol	Space group
liquid	—	—	—
diamond-Si	C(diamond)	cF8	$Fd\bar{3}m$
β-B	β-B	hR105	$R\bar{3}m$
SiB_3	B_4C	hR15	$R\bar{3}m$
SiB_6	SiB_6	oP280	Pnnm
SiB_n	B	hR12	$R\bar{3}m$

The thermodynamic parameters for phases in Si-B binary system have been made from CompuTherm Pandat7.0 software, and the parameters of various phases in the Si-B binary system are listed in Table 2.

Table 2. Thermodynamic parameters of the Si-B binary system

Phase	Thermodynamic parameters
Liquid	$L^{0,liq} = 17631.9 - 1.7632T$ $L^{1,liq} = -3526.99 + 0.3527T$
diamond-Si	$G_{Si:B}^{dia\text{-}Si} = -8162.61 + 137.237T - 22.8318T\ln T - 0.0019129T^2 + 176667T^{-1} - 3.552e^{-9}T^3$
β-B	$L^{\beta-B} = -725614 + 72.5614T$
SiB_3	$G^{SiB_3} = 0.25G^{dia\text{-}Si} + 0.75G^{\beta-B} - 2400480 + 240.048T$
SiB_6	$G^{SiB_3} = 0.14G^{dia\text{-}Si} + 0.86G^{\beta-B} - 1571560 + 1571.56T$
SiB_n	$G^{SiB_n} = \frac{1}{n+1}G^{dia\text{-}Si} + \frac{n}{n+1}G^{\beta-B} - 281574 + 28.1574T$

Note: Gibbs energies are expressed in $J \cdot mol^{-1}$. Lattice stabilities of elements Si and B are referred to CompuTherm Pandat 7.0.

Fig.1 shows the calculated Si-B binary phase diagram with CompuTherm Pandat7.0 software and the B-rich side in Fig.2 displays the transition among phases in detail. Table 3 lists all invariant reactions in this binary system. The peritectoid reaction Diamond_Si+SiB_6↔SiB_3 at 1543K, the eutectic reaction Liquid↔Diamond_Si+SiB_6 at 1658K, the peritectic reactions Liquid+SiB_n↔SiB_6 at 2122K and Liquid+Bata_B↔SiB_n at 2310K are respectively listed. According to the B-rich side in Fig.2, it was found that the SiB_3 and SiB_n are solid solution phases and the SiB_6 is a stoichiometric compound which is consistent with V. Babizhetskyy's studies [12]. In detail, Fig.2 also shows the equilibrium and transition among phases in Si-B system.

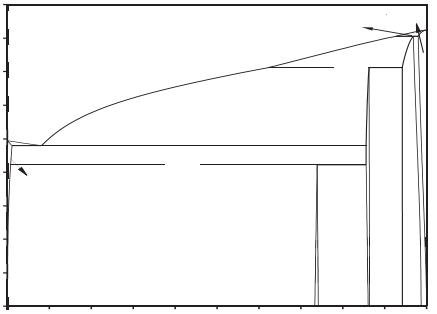

Fig.1. Calculated phase diagram of Si-B binary system

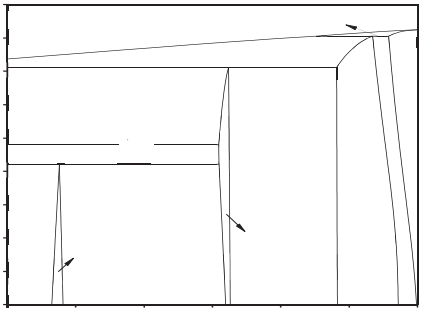

Fig.2. B-rich side of Si-B binary system

Table 3. Invariant reactions in the Si-B system

Reaction	Type	Phase	x_B	x_{Si}	T/K
		Diamond_Si	0.007	0.993	
Diamond_Si+SiB_6↔SiB_3	peritectoid	SiB_3	0.738	0.262	1543
		SiB_6	0.855	0.145	
		Diamond_Si	0.011	0.989	
Liquid↔Diamond_Si+SiB_6	eutectic	Liquid	0.081	0.919	1658
		SiB_6	0.854	0.146	
		Liquid	0.621	0.379	
Liquid+SiB_n↔SiB_6	peritectic	SiB_6	0.862	0.138	2122
		SiB_n	0.941	0.059	
		Liquid	0.926	0.074	
Liquid+Bata_B↔SiB_n	peritectic	SiB_n	0.967	0.033	2310
		Bata_B	0.979	0.021	

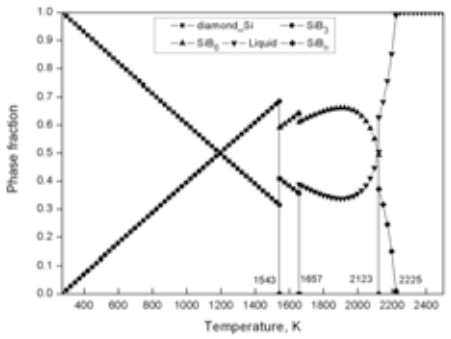

Fig.3. Equilibrium and transition of phases in Si-B system

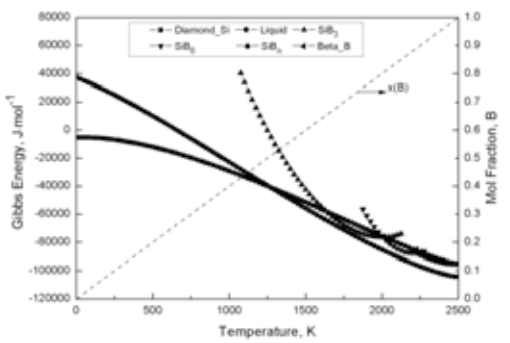

Fig.4. Gibbs energies of phases in Si-B system

The Gibbs energies and components of Si-B phases at different temperature are calculated and shown in Fig.4. With the increase of temperature, the Gibbs energies for Si-B phases become more negative. The phases SiB_6, SiB_n, Beta_B only exist above 1657K, so it can be forecast that only the phases SiB_3 and Diamond_Si exist in Si-B system to the MG-Si melt besides phase Liquid, which is consistent with Si-B binary phase diagram.

4. Conclusions

(1) The thermodynamic assessmen for the Si-B binary system has been performed and described using the CompuTherm of thermodynamic properties and phase diagrams method.

(2) The thermodynamic parameters for the solution phases Liquid, diamond-Si and β-B and the compounds SiB_3, SiB_6, SiB_n have been obtained and the equilibrium and transition of phases were studied.

(3) The Gibbs energies for Si-B phases are calculated and the existent forms are SiB_3 and Diamond_Si for Si-B phases in MG-Si melt.

Acknowledgments

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