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Phase Equilibria in the Ni–Si–B System*

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A thermodynamic study has been carried out on the Ni–Si–B ternary system, which is an important system in view of the development of Ni-base filler metals. A regular solution approximation based on the sublattice model was adopted to describe the Gibbs energy for the individual phases in the binary and ternary systems. Thermodynamic parameters for each phase have been evaluated using the available experimental information on phase boundaries and other related thermodynamic properties. Thermal analysis experiments have also been conducted on several ternary alloys to re-examine the available ternary experimental data on phase boundaries. The set of evaluated parameters in this study enables reproducible calculations of the liquidus and solidus temperatures and vertical section diagrams satisfactorily.

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1. Introduction

Ni-base brazing filler metals are widely used in the fields of aircraft, various engines, and nuclear engineering due to their high strength at high temperatures, corrosion resistance and oxidation resistance. At present, the study on the development of Ni-base filler metals is done by trial and error. The melting point has to be measured for many alloy specimens in spite of only a few candidate alloys out of them are used for brazing processes. Therefore, the prediction of liquidus and solidus temperatures and phase equilibria is significantly useful in the design of candidate alloy composition. The CALPHAD (CALculation of PHAse Diagrams) approach[1)] of phase equilibria calculation using thermodynamic descriptions from databases provides a powerful tool for obtaining such information.

In the present study, a thermodynamic analysis of the phase equilibria in the Ni–Si–B system, which is an important system of Ni-base brazing filler metals, has been carried out. And also thermal analysis experiments have been conducted on several ternary alloys in order to re-examine the available experimental data on phase boundaries.

2. Experimental Procedures

The phase boundaries of the ternary system were determined by differential scanning calorimetry (DSC). The starting materials are powders of Ni(99.9%), Si(99.9%), and B(99%). The alloys were prepared by arc melting of cold-pressed pellets in an atmosphere of argon. A titanium button was melted to getter the residual oxygen in the chamber, prior to melting the actual charges. The arc-melted alloys were re-melted in vacuum by induction heating in order to ensure homogeneity. The as-cast alloys were encapsulated in quartz tubes under vacuum and then annealed at 850°C for 18 days before water quenching. No chemical analysis for the alloys was conducted, since the weight losses in preparing alloys were generally less than 1%. The prepared alloy compositions are shown in Table 1. Thermal analysis (DSC) was carried out using a Rigaku ThermoPlus DSC8270 (Rigaku Corp., Tokyo, Japan). A cylindrical specimen was heated and cooled in Al_2O_3 crucible at a rate of 5°C/min under a purified argon-flow atmosphere with α-Al_2O_3 as the standard materials. However, in order to avoid experimental error caused by supercooling, the peak temperature values during heating were adopted in a thermodynamic analysis. The peak temperatures in heating processes are shown in Table 1.

In addition, in order to confirm the eutectic temperature of the Si–B system, two alloys of the Si–B binary system were

Table 1 Experimental results for phase boundaries of the Si–B binary and the Ni–Si–B ternary alloys determined by DSC.

Alloy composition (mol%)			Peak temperature (°C)		
Ni	Si	B			
Si–B alloys					
	95.0	5.0	1388	1411	
	88.0	12.0	1388	1421	
Ni–Si–B alloys					
85.0	5.0	10.0	1062	1261	
80.0	10.0	10.0	993	1039	1170
77.5	12.5	10.0	993	1077	
75.0	15.0	10.0	992	1048	
70.0	20.0	10.0	1000	1070	1162
65.0	25.0	10.0	994	1123	1164
60.0	30.0	10.0	999	1037	1177
66.7	28.3	5.0	1154	1159	1206
66.7	23.3	10.0	999	1113	1167
66.7	18.3	15.0	997	1122	
66.7	13.3	20.0	990	999	1089
66.7	8.3	25.0	991	998	1033
66.7	3.3	30.0	991	998	1081
75.0	20.0	5.0	991	1016	1157
75.0	10.0	15.0	992	1038	
75.0	5.0	20.0	992	1104	

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prepared and thermal analysis for two as-cast alloys was also conducted.

3. Thermodynamic Description

There are two ternary compounds in the Ni–Si–B ternary system, namely Ni_6Si_2B and $Ni_{4.29}Si_2B_{1.43}$,[2,3] and these compounds were treated as stoichiometric ones in the present study due to negligible homogeneity ranges. In view of negligible solid solubility of the third element,[2,3] all binary intermetallic compounds were treated as pure binary phases.

The Gibbs energies of the ternary liquid phase and the terminal solid solutions were described by the conventional regular solution model as follows:

$$\begin{aligned} G_{\mathrm{m}}^{\phi} = {} & x_{\mathrm{B}}{}^{0}G_{\mathrm{B}}^{\phi} + x_{\mathrm{Ni}}{}^{0}G_{\mathrm{Ni}}^{\phi} + x_{\mathrm{Si}}{}^{0}G_{\mathrm{Si}}^{\phi} + RT(x_{\mathrm{B}}\ln x_{\mathrm{B}} + x_{\mathrm{Ni}}\ln x_{\mathrm{Ni}} + x_{\mathrm{Si}}\ln x_{\mathrm{Si}}) \\ & + x_{\mathrm{B}}x_{\mathrm{Ni}}L_{\mathrm{B,Ni}}^{\phi} + x_{\mathrm{Ni}}x_{\mathrm{Si}}L_{\mathrm{Ni,Si}}^{\phi} + x_{\mathrm{B}}x_{\mathrm{Si}}L_{\mathrm{B,Si}}^{\phi} + x_{\mathrm{B}}x_{\mathrm{Ni}}x_{\mathrm{Si}}L_{\mathrm{B,Ni,Si}}^{\phi}. \end{aligned} \tag{1}$$

where ${}^{0}G_{i}^{\phi}$, called the lattice stability, denotes the Gibbs energy of the element i in the ϕ phase state. The descriptions of the lattice stability parameters were taken from the SGTE (Scientific Group Thermodata Europe) data file.[4] R is the gas constant, and x_{B}, x_{Ni}, and x_{Si} are the mole fraction of B, Ni, and Si, respectively. The parameters denoted $L_{i,j}^{\phi}$ and $L_{\mathrm{B,Ni,Si}}^{\phi}$ are the interaction parameters of binary systems and ternary system, respectively. The Gibbs energies of ternary compound phases, $Ni_aSi_bB_c$, were described as follows:

$$G_{\mathrm{m}}^{\mathrm{Ni}_a\mathrm{Si}_b\mathrm{B}_c} = \frac{a}{a+b+c}\cdot{}^{0}G_{\mathrm{Ni}}^{\mathrm{fcc}} + \frac{b}{a+b+c}\cdot{}^{0}G_{\mathrm{Si}}^{\mathrm{diamond}} + \frac{c}{a+b+c}\cdot{}^{0}G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}} + \Delta G_{\mathrm{Ni}_a\mathrm{Si}_b\mathrm{B}_c}^{f}. \tag{2}$$

where $\Delta G_{\mathrm{Ni}_a\mathrm{Si}_b\mathrm{B}_c}^{f}$ is the Gibbs energy of formation per mole of atoms of the compound that can be expressed by the following equation:

$$\Delta G_{\mathrm{Ni}_a\mathrm{Si}_b\mathrm{B}_c}^{f} = A + B\cdot T. \tag{3}$$

4. Optimization of Parameters and Calculation of Phase Diagrams in the Ni–Si–B Ternary System

In the present modeling, the thermodynamic parameters in the Ni–Si system and the liquid and Ni_3B phases for the Ni–B system were taken from Tokunaga *et al.*,[5] Campbell and Kattner,[6] respectively, and some modifications of thermodynamics description in the Ni–B system were made based on experimental data on enthalpies of formation for Ni_2B reported by Sato and Kleppa,[7] for NiB by Meschel and Kleppa.[8]

In the Si–B binary system, a thermodynamic analysis has been carried out by Tokunaga *et al.*[9] using the available experimental data compiled by Olesinski and Abbaschian.[10] Recently, Zaitsev and Kodentsov[11] have investigated the thermodynamic properties in the Si–B system by Knudsen mass spectrometry and established the phase diagram. According to their results, the eutectic temperature was found to be 1362°C and lower than the reported value[10] by 23°C. On the other hand, the eutectic temperature was 1388°C in the present thermal analysis. Therefore a thermodynamic re-evaluation of the Si–B system has carried out using the present results and the thermochemical properties by Zaitsev and Kodentsov[11] as well as the already available data. The optimized parameters are listed in Table 2. The calculated phase diagram of the Si–B system is shown in Fig. 1 and the calculated eutectic temperature agrees well with the present results.

Table 2 Evaluated thermodynamic parameters in the Ni–Si–B system.

System	Phase	Thermodynamic parameters, J/mol
Si–B	Liquid	$L_{\mathrm{B,Si}}^{\mathrm{liquid}} = -68220.33 + 41.76042T + (x_{\mathrm{B}} - x_{\mathrm{Si}})\cdot(10902.63 - 11.10014T) + (x_{\mathrm{B}} - x_{\mathrm{Si}})^2\cdot(39692.79 - 17.31724T)$
	(Si)	$G_{\mathrm{B}}^{(\mathrm{Si})} = 50000 + G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}}$
		$L_{\mathrm{B,Si}}^{(\mathrm{Si})} = -5144.67$
	SiB_3	$G_{\mathrm{Si:B}}^{\mathrm{SiB_3}} = 1/4\cdot(-72884.29 + 25.72064T + G_{\mathrm{Si}}^{\mathrm{diamond}} + 3\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}})$
	SiB_6	$G_{\mathrm{Si:B}}^{\mathrm{SiB_6}} = 1/7\cdot(-142768.22 + 49.60747T + G_{\mathrm{Si}}^{\mathrm{diamond}} + 6\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}})$
	SiB_n	$G_{\mathrm{Si:B}}^{\mathrm{SiB}_n} = -12193.76 + 4.11924T + 0.041\cdot G_{\mathrm{Si}}^{\mathrm{diamond}} + 0.959\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}}$
	(B)	$G_{\mathrm{Si}}^{(\mathrm{B})} = 50000 + G_{\mathrm{Si}}^{\mathrm{diamond}}$
		$L_{\mathrm{B,Si}}^{(\mathrm{B})} = -35253.31$
Ni–B	(Ni)	$L_{\mathrm{B,Ni}}^{(\mathrm{Ni})} = -41420$
	Ni_2B	$G_{\mathrm{Ni:B}}^{\mathrm{Ni_2B}} = -26702.78 + 4.07298T + 0.667\cdot G_{\mathrm{Ni}}^{\mathrm{fcc}} + 0.333\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}}$
	o-Ni_4B_3	$G_{\mathrm{Ni:B}}^{\mathrm{o\text{-}Ni_4B_3}} = -23747.78 + 2.35549T + 0.586\cdot G_{\mathrm{Ni}}^{\mathrm{fcc}} + 0.414\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}}$
	m-Ni_4B_3	$G_{\mathrm{Ni:B}}^{\mathrm{m\text{-}Ni_4B_3}} = -22952.21 + 1.93373T + 0.564\cdot G_{\mathrm{Ni}}^{\mathrm{fcc}} + 0.436\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}}$
	NiB	$G_{\mathrm{Ni:B}}^{\mathrm{NiB}} = -20865.70 + 1.67458T + 0.5\cdot G_{\mathrm{Ni}}^{\mathrm{fcc}} + 0.5\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}}$
Ni–Si–B	Liquid	$L_{\mathrm{B,Ni,Si}}^{\mathrm{liquid}} = 50000\cdot x_{\mathrm{B}} - 80000\cdot x_{\mathrm{Ni}} + 50000\cdot x_{\mathrm{Si}}$
	Ni_6Si_2B	$G_{\mathrm{Ni:Si:B}}^{\mathrm{Ni_6Si_2B}} = 1/9\cdot(-478009.54 + 66.79389T + 6\cdot G_{\mathrm{Ni}}^{\mathrm{fcc}} + 2\cdot G_{\mathrm{Si}}^{\mathrm{diamond}} + G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}})$
	$Ni_{4.29}Si_2B_{1.43}$	$G_{\mathrm{Ni:Si:B}}^{\mathrm{Ni_{4.29}Si_2B_{1.43}}} = 1/7.72\cdot(-447174.56 + 88.75740T + 4.29\cdot G_{\mathrm{Ni}}^{\mathrm{fcc}} + 2\cdot G_{\mathrm{Si}}^{\mathrm{diamond}} + 1.43\cdot G_{\mathrm{B}}^{\mathrm{beta\_rhombohedral}})$

Experimental information in the Ni–Si–B ternary system is very limited. The liquidus surface has been studied by thermal analysis and metallographical observation.[12,13] The isothermal sections have been reported at 800°C[2] and 850°C.[3] A thermodynamic analysis have been carried out in the composition range below 35 mol%Si and B by Jansson and Ågren[14] and the parameters in their analysis reproduced the reported experimental data almost satisfactorily. However, the Gibbs energy of the liquid phase was described by a sublattice model.[15] This model is not capable of treating the liquid phase with more than 50 mol%B, because all the interstitial sites are occupied at this point.

In the present analysis, the thermodynamic parameters for the liquid phase were mainly based on the liquidus data shown in Table 1. The parameters of the ternary compounds were evaluated using the reported data on isothermal section at 850°C[3] and liquidus surface projection.[13] The optimized parameters are shown in Table 2.

The calculated liquidus surface projection in the composition range of 0 to 50 mol%Si and 0 to 50 mol%B is shown in Fig. 2. The calculated isopletic sections at 10 mol%B, 75 mol%Ni, and 66.7 mol%Ni are compared with the DSC data obtained by the present work in Figs. 3(a) to (c). The experimental data reported by Lebaili and Hamar-Thibault[13] also shown in Fig. 3. According to the results, the calculated phase boundaries agree well with the present experimental ones.

The calculated isothermal section at 850°C is shown in Fig. 4 together with the experimental results reported by Lugscheider *et al.*[3] As SiB_n phase has not been identified in their diagram, the calculated results related to SiB_n phase are not consistent with the experimental diagram. Furthermore, the phase equilibrium between Ni_5Si_2 (γ), Ni_3B, and Ni_6Si_2B observed by Lugscheider *et al.*[3] was not reproduced in the calculated diagram. As this phase relation was confirmed in the present study by XRD analysis, it is considered that the evaluation of phase stability for binary compounds is not sufficient. Except for above inconsistency, the calculated result reproduced the feature of the ternary Ni–Si–B phase diagram satisfactorily.

5. Conclusions

A thermodynamic analysis of the Ni–Si–B ternary system was carried out by combining the experimental results on the phase boundaries by DSC and already available experimental

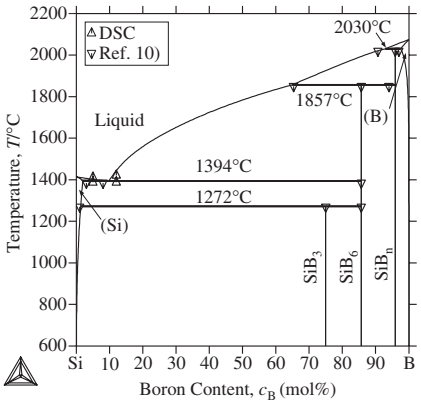

Fig. 1 Calculated phase diagram in the Si–B system.

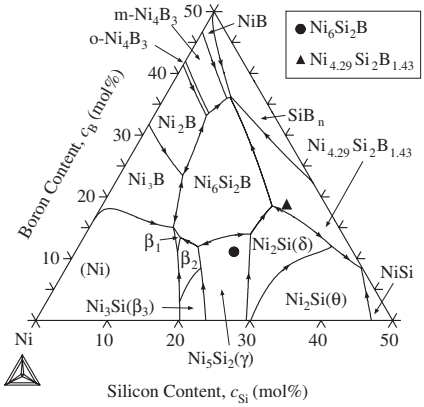

Fig. 2 Calculated liquidus surface projection of Ni-rich portion in the Ni–Si–B system.

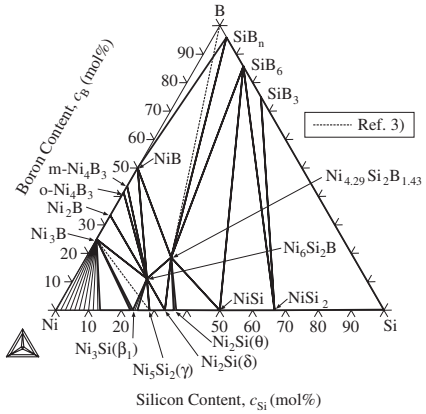

Fig. 4 Calculated isothermal section diagram at 850°C in the Ni–Si–B system.

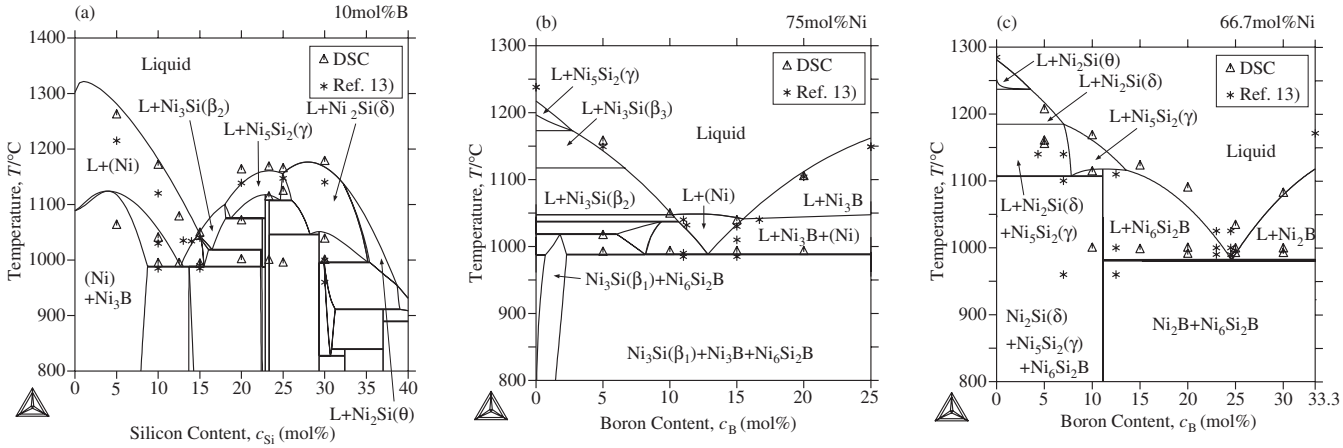

Fig. 3 Calculated vertical section diagrams with experimental values at (a) 10 mol%B, (b) 75 mol%Ni, and (c) 66.7 mol%Ni.

data. The results obtained are as follows:

(1) The optimized parameters in the Si–B system reproduced the present DSC data and the already available data satisfactorily.

(2) The calculated results of the Ni–Si–B system reproduced the experimental results on the phase boundaries by DSC measurement and already available phase boundaries satisfactorily, except for the phase equilibrium between Ni_5Si_2 (γ), Ni_3B, and Ni_6Si_2B at 850°C.

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