Thermodynamic Activities and Distributions of Calcium and Magnesium Between Silicon and CaO-MgO-SiO₂ Slags at 1873 K (1600 °C)

LARS KLEMET JAKOBSSON and MERETE TANGSTAD

The distributions of calcium and magnesium between silicon and CaO-MgO-SiO₂ slags have been determined in the present study at 1873 K (1600 °C). The distribution equilibria were used to estimate the activities of the slag components in the binary CaO-SiO₂ and MgO-SiO₂ systems. These activities were used to determine the Henrian activity coefficients of calcium and magnesium in liquid silicon at 1873 K (1600 °C). The distribution equilibria were also used to estimate the activity of SiO₂ in the ternary CaO-MgO-SiO₂ system. Finally, the activities of CaO and MgO were estimated in the ternary CaO-MgO-SiO₂ system using the determined Henrian activity coefficients in liquid silicon together with the distribution equilibria and the estimated activities of SiO₂.

DOI: 10.1007/s11663-014-0268-8

© The Author(s) 2015. This article is published with open access at Springerlink.com

I. INTRODUCTION

SLAG refining is used to purify metallurgical grade silicon after it is tapped from the reduction furnace. The combined knowledge of activities of slag components, dilute elements in silicon and the equilibrium concentration of slag-forming elements in silicon allows a thermodynamically consistent description of the refining process. This work has focused on the ternary CaO-MgO-SiO₂ system, which is an important system for refining of silicon. The knowledge of activities of CaO, MgO, and SiO₂ in the ternary CaO-MgO-SiO₂ system is also important for other high temperature processes involving this slag, most notably in iron and steelmaking. Thermodynamic properties of dilute elements in silicon are important for refining processes of both metallurgical and solar-grade silicon. The distributions of calcium and magnesium between silicon and CaO-MgO-SiO₂ slags, have been investigated in the present study at 1873 K (1600 °C). These distributions were used to estimate the activities of all the oxides in the slag and the Henrian activity coefficients of calcium and magnesium in silicon at 1873 K (1600 °C).

II. EXPERIMENTAL

Graphite crucibles containing 15 g slag and 15 g silicon were heated to 1873 K (1600 °C) under argon atmosphere. The system was held at this temperature for 0.6 to 18 hours before it was cooled to room temperature. It typically took

2 minutes to cool the crucible down to the melting point of silicon, where the cooling followed an exponential trend toward room temperature. The crucible was completely removed by grinding before slag and silicon were carefully separated. The silicon pieces were closely inspected and any remaining slag was removed by further grinding. Any remaining silicon on the slag pieces was also removed in the same way. Both silicon and slag were then crushed in a tungsten carbide crusher. The crusher was cleaned by crushing 99.9999999 pct pure silicon three times before the silicon samples were crushed. XRF was used to determine the slag composition after the experiments while ICP-MS was used to determine the calcium and magnesium concentrations in silicon. The silicon was analyzed in three replicate splits, and the three analyses were used to calculate 95 pct confidence intervals of the measured concentration. These intervals are given together with the tabulated values of the measured concentrations of calcium and magnesium in silicon, and they are also indicated as error bars in the figures showing the results of the binary slag systems. More details about the experimental and analytical procedure are given in a previous paper.^[1] The holding time required for boron to reach equilibrium in the previous paper was also chosen in the present work even if it may have reached equilibrium faster with respect to calcium and magnesium since they are major components in the slag. Some of the experiments with the shortest holding times in the binary CaO-SiO₂ and MgO-SiO₂ systems were, therefore, disregarded when evaluating the results.

III. RESULTS

A. The Binary CaO-SiO₂ System

The results from the binary CaO-SiO₂ system are listed in Table I and shown in Figure 1. Experiments CS1 and

LARS KLEMET JAKOBSSON, Postdoctoral Research Fellow, and MERETE TANGSTAD, Professor, are with the Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology, Trondheim, Norway. Contact e-mail: lars.k.jakobsson@ntnu.no

Manuscript submitted September 29, 2014.

Article published online January 31, 2015.

Table I. Slag Compositions in the Binary CaO-SiO₂ System as Measured After the Experiments and Calcium Concentration in Silicon in Equilibrium with These Slags

	Holding Time (h)	SiO ₂ (mass pct)	CaO (mass pct)	Ca (mg/kg)
CS1	0.6	63.2	36.3	355 ± 173
CS2	3	62.3	37.4	393 ± 162
CS3	6	60.3	39.4	840 ± 276
CS4	9	57.7	42.1	630 ± 117
CS5	6	62.1	37.7	644 ± 214
CS6	6	53.8	45.9	1061 ± 151*
CS7	6	48.6	51.1	3723 ± 634*
CS8	3	47.7	51.9	3903 ± 144*
CS9	6	46.3	53.4	4504 ± 1192
CS10	3	44.3	55.3	7422 ± 1348
CS11	6	43.1	56.6	14,141 ± 469*
CS12**	18	68.4	31.2	372 ± 63
CS13†	6	42.6	56.8	17,638 ± 1450
FS5	6	48.2	51.3	3006 ± 217

*Average concentration from two separate analyses with confidence intervals based on the pooled standard deviation.

**System held in a silica crucible.

†Starting with silicon alloyed with 5 mass pct calcium.

CS2 were excluded from the evaluation of the data because the system was not in equilibrium with respect to boron in the previous study,^[1] and may therefore also not be in equilibrium with respect to calcium. The calcium concentration in silicon is seen to increase significantly with increasing concentration of CaO in the slag. This is caused by an increasing activity of CaO and a decreasing activity of SiO₂ where the equilibrium

is displaced to the right giving a higher concentration of calcium in silicon. One experiment was performed where silicon was alloyed with 5 mass pct calcium, where calcium was added as calcium disilicide and melted in the crucible together with pure silicon before slag was added. The calcium concentration found in silicon after this experiment was also in line with the other results. Silicon from three of the experiments in the binary system was also analyzed by ICP-OES. The measured concentrations were 0.08 mass pct for CS3, 0.38 mass pct for CS7, and 1.3 mass pct for CS11. These values are seen in Figure 1 to be in good agreement with the values found by ICP-MS.

The results in the present work are compared with previous works in Figure 2 where it is seen that the calcium concentration in the present work is somewhat lower than in previous works^[2–4] for slags with high CaO content. An estimate by Schei *et al.*^[5] at 1823 K (1550 °C) is also included in the figure, and this estimate is seen to be in closest agreement with the present work. This estimate was made by converting values measured in equilibrium with an alloy of 75 mass pct Si and 25 mass pct Fe to values for pure silicon using the activity of silicon in the alloy and the Henrian activity coefficient of calcium in the alloy and in pure silicon. The calcium concentration in silicon from the study by Wang *et al.*^[4] (0.22 mass pct) in equilibrium with the slag with the highest SiO₂ content (74.2 mass pct) is far outside the liquid region and orders of magnitude higher

than for slags at SiO₂ saturation. For these two reasons, this value was disregarded.

The region close to SiO₂ saturation is compared with previous works^[2–8] in Figure 3, and the present work is seen to be higher than most other works at SiO₂ saturation. Only in the study by Miki *et al.*^[8] they found a higher concentration than in the present work. It is seen that the value closest to SiO₂ saturation from the study by Wang *et al.*^[4] is significantly higher than in any other studies. It should also be noted that the slags in the study by Weiss and Schwerdtfeger^[7] at 1773 K (1500 °C) with 1 hour holding time was probably not in equilibrium with the SiO₂ crucible since the compositions are relatively far from the liquidus line.

The binary section of the surface fit of the calcium concentration across the entire CaO-MgO-SiO₂ system is also shown in Figures 2 and 3 together with the 95 pct confidence bands of the surface fit. Details on how the surface fit was obtained will be discussed later in this article.

B. The Binary MgO-SiO₂ System

The results in the binary MgO-SiO₂ system are shown together with the previous measurements by Morita *et al.*^[2] in Figure 4. The concentrations found in the present work are also listed in Table II. Experiments MS1, MS2, and MS3 were excluded from the evaluation of the data because the system was not in equilibrium with respect to boron in the previous study,^[1] and may therefore also not be in equilibrium with respect to magnesium. Most of the values found in the present work are seen to be somewhat lower than the two measurements by Morita *et al.* The binary section of the surface fit of the magnesium concentration in silicon in the ternary CaO-MgO-SiO₂ system with 95 pct confidence bands is also shown together with the measured values. The concentration of magnesium in silicon is controlled by the following equilibrium:

Fig. 1—Concentration of calcium in silicon in equilibrium with binary CaO-SiO₂ slags at 1873 K (1600 °C). Holding time in hours is indicated beside the data points.

Fig. 2—Calcium concentration in silicon in equilibrium with CaO-SiO₂ slags compared with previous works conducted in a major part of the liquid region. The liquidus line after Jung *et al.* [10] at 1873 K (1600 °C) is also in the figure indicated as vertical lines.

Fig. 3—Measured calcium concentration in equilibrium with SiO₂-rich CaO-SiO₂ slags. The liquidus line for SiO₂ saturation at 1873 K (1600 °C) from Fig. 2 is also indicated. (* studies conducted in a silica crucible).

C. The Ternary CaO-MgO-SiO₂ System

The measured concentration of calcium and magnesium in silicon in equilibrium with ternary CaO-MgO-SiO₂ slags are given in Table III. The measured concentrations of calcium and magnesium in the ternary system are shown in Figures 5(a) and (b), respectively. Some iso-concentration lines from the surface fit to the experimental data are also shown in the figures. Morita *et al.* [2] have previously measured the concentrations of calcium and magnesium in silicon in equilibrium with this ternary slag system at 1873 K (1600 °C). The calcium concentration on the most CaO-rich side of the ternary CaO-MgO-SiO₂ system was found to be somewhat lower in the present work, in the same way as has already been seen in the binary CaO-SiO₂ system. A somewhat lower concentration was also found in the present work as compared to in the work by Morita *et al.*, for the rest of the ternary system. For magnesium, the concentration in the ternary system is also a little lower than found by Morita *et al.* in the same way as already seen in the binary MgO-SiO₂ system.

IV. DISCUSSION

The concentration of calcium and magnesium across the entire CaO-MgO-SiO₂ system can be approximated by a surface fit to the experimentally measured values. The surface fit of the concentration of both calcium and magnesium was chosen to be expressed by:

$$\ln w_{\text{Me}} = a + b/(1 + \exp(c \cdot x_{\text{SiO}_2})) + d \cdot x_{\text{CaO}} + e \cdot x_{\text{CaO}}^2 + f \cdot x_{\text{SiO}_2} \cdot x_{\text{CaO}}, \quad [3]$$

where w_{Me} is the weight fraction of calcium or magnesium in liquid silicon and x is the mole fraction of CaO and SiO₂ in the slag. The MATLAB Surface Fitting Tool was used to fit Eq. [3] to the measured data, and

Fig. 4—Magnesium concentration in silicon in equilibrium with MgO-SiO₂ slags at 1873 K (1600 °C). The liquidus line at 1873 K (1600 °C) from Jung *et al.* [10] is also indicated as vertical lines.

Table II. Slag Compositions in the Binary MgO-SiO₂ System as Measured After the Experiments and Magnesium Concentration in Silicon in Equilibrium with These Slags

	Holding Time (h)	SiO ₂ (mass pct)	MgO (mass pct)	CaO (mass pct)	Mg (mg/kg)
MS1	1	65.3	34.0	0.41	466 ± 173
MS2	2	64.1	35.2	0.42	586 ± 234
MS3	3	63.8	35.4	0.42	747 ± 76
MS4	6	62.7	36.6	0.43	1044 ± 175
MS5	9	58.6	40.6	0.5	1533 ± 318
MS6	6	58.9	40.5	0.43	1059 ± 212*
MS7	6	60.4	38.6	0.58	818 ± 50**
MS8	12	62.2	37	0.58	791 ± 75

All experiments except MS6 performed with 5 g slag and 5 g silicon.

*Mean concentration from two separate analyses with confidence interval based on the pooled standard deviation.

**Mean concentration from three separate analyses with confidence interval based on the standard deviation between the three analyses.

Table III. Slag Compositions in the Ternary CaO-MgO-SiO₂ System as Measured After the Experiments and Calcium and Magnesium Concentrations in Silicon in Equilibrium with These Slags

	SiO ₂ (mass pct)	CaO (mass pct)	MgO (mass pct)	Ca (mg/kg)	Mg (mg/kg)
CMS1	54.5	38.6	6.7	734 ± 125	293 ± 69
CMS2	49.6	37.0	13.2	1726 ± 191	1354 ± 204
CMS3	46.8	36.7	16.3	3231 ± 436	2846 ± 383
CMS4	45.1	41.0	13.6	6264 ± 511	3862 ± 316
CMS5	43.7	52.0	4.1	13,076 ± 1389	1690 ± 321
CMS6	53.9	16.8	29.1	265 ± 26	1551 ± 216
CMS7	44.5	46.2	9.0	8208 ± 986	3632 ± 328
CMS8	49.8	32.0	18.0	1710 ± 247	2032 ± 40*
CMS9	46.9	44.8	8.0	3139 ± 1059	975 ± 129
CMS10	47.6	25.8	26.4	2010 ± 107	5113 ± 487
CMS11	50.1	18.0	31.7	656 ± 127	3433 ± 420
CMS12	52.7	9.3	37.7	155 ± 55	2090 ± 234
CMS13	46.5	34.4	18.9	5691 ± 703	5373 ± 326
CMS14	45.4	33.7	20.7	6215 ± 826	7445 ± 794
CMS15	57.8	32.6	9.4	346 ± 19	282 ± 29
CMS16	61.8	28.3	9.6	342 ± 28	324 ± 42
CMS17	58.6	22.0	19.2	327 ± 96	733 ± 223*
CMS18	57.0	23.2	19.6	397 ± 69	775 ± 142
CMS19	58.9	11.3	29.6	92 ± 2	905 ± 51
CMS20	61.3	10.0	28.4	138 ± 4*	721 ± 166

*Based on two replicate splits, where one of the replicate splits was deemed as an outlier. Excluded outliers: 2882 (mg/kg) Mg from CMS8, 1848 (mg/kg) Mg from CMS17 and 873 (mg/kg) Ca from CMS20.

the parameter values for calcium and magnesium are given in Table IV. The expression for the second term in the fit, which contains the exponential function, was chosen because the calcium and magnesium concentrations in silicon, from a thermodynamic point of view, should be monotonically increasing with the decreasing SiO₂-concentration. Except from this, the form of the function was chosen to give a good fit to the data with a minimal number of terms. Equation [3] gave a very good fit to the measured concentrations with $R^2 = 0.98$ for calcium and $R^2 = 0.97$ for magnesium. The function does not contain any inflection points within the range of interest, and does hence give a smooth change of values within this range. The confidence bands shown in Figures 2, 3 and 4 are the pointwise 95 pct confidence bands of these surface fits.

A. Determination of Activities in the Ternary CaO-MgO-SiO₂ System

The concentrations of calcium and magnesium in silicon are so low that it is reasonable to assume that silicon will behave as a Raoultian solvent. Morita *et al.*^[2] have shown that under these conditions, the activity of SiO₂ can be determined using the concentration of calcium in silicon and the Gibbs–Duhem equation. An outline of this method is given below.

The Gibbs–Duhem equation for the ternary CaO-MgO-SiO₂ system gives:

$$x_{\text{SiO}_2} d \ln \gamma_{\text{SiO}_2} + x_{\text{CaO}} d \ln \gamma_{\text{CaO}} + x_{\text{MgO}} d \ln \gamma_{\text{MgO}} = 0. \quad [4]$$

By introducing

$$B = \gamma_{\text{CaO}}^2 / \gamma_{\text{SiO}_2}, \quad [5]$$

Fig. 5—Measured concentration of (a) calcium and (b) magnesium in the ternary CaO-MgO-SiO₂ system at 1873 K (1600 °C). Iso-concentration lines from the surface fits are also indicated. The liquidus lines from a recent thermodynamic optimization^[10] are indicated as bold solid lines and the liquidus lines from the Slag Atlas^[25] are indicated as bold-dashed lines. (* mean value of two experiments, ** mean value of three experiments).

$$C = \gamma_{\text{MgO}}^2 / \gamma_{\text{SiO}_2}, \quad [6]$$

we get

$$x_{\text{SiO}_2} d \ln \gamma_{\text{SiO}_2} + x_{\text{CaO}} d \ln (B \gamma_{\text{SiO}_2})^{1/2} + x_{\text{MgO}} d \ln (C \gamma_{\text{SiO}_2})^{1/2} = 0. \quad [7]$$

By introducing the ratio

$$k = x_{\text{MgO}} / x_{\text{CaO}}. \quad [8]$$

Equation [7] becomes

Table IV. Obtained Parameter Values for the Surface Fits to Eq. [3] for Calcium and Magnesium in the Ternary CaO-MgO-SiO₂ System

	Ca	Mg
a	−7.22866	−10.2973
b	3511.11	20,568.3
c	18.5540	22.7121
d	17.3019	16.2950
e	−11.2707	−7.69311
f	−30.5502	−10.1856

$$\begin{aligned} & x_{\text{SiO}_2} d \ln \gamma_{\text{SiO}_2} + x_{\text{CaO}} d \ln (B \gamma_{\text{SiO}_2})^{1/2} \\ & + k \cdot x_{\text{CaO}} d \ln (C \gamma_{\text{SiO}_2})^{1/2} = 0 \\ \Rightarrow & x_{\text{SiO}_2} d \ln \gamma_{\text{SiO}_2} + 1/2 \cdot x_{\text{CaO}} d \ln (B \cdot C^k) \\ & + (1+k)/2 \cdot x_{\text{CaO}} d \ln \gamma_{\text{SiO}_2} = 0 \\ \Rightarrow & (2x_{\text{SiO}_2} + x_{\text{MgO}} + x_{\text{CaO}}) d \ln \gamma_{\text{SiO}_2} = -x_{\text{CaO}} d \ln (B \cdot C^k) \\ \Rightarrow & d \ln \gamma_{\text{SiO}_2} = \frac{-x_{\text{CaO}}}{1 + x_{\text{SiO}_2}} d \ln B C^k. \end{aligned} \quad [9]$$

Integrating this equation gives:

$$\ln \gamma_{\text{SiO}_2} \Big|_{x_{\text{CaO}}} = \int_{x_{\text{CaO}}^0}^{x_{\text{CaO}}} \frac{-x_{\text{CaO}}}{1 + x_{\text{SiO}_2}} d \ln (B \cdot C^k) + \ln \gamma_{\text{SiO}_2}^0 \Big|_{x_{\text{CaO}}^0}. \quad [10]$$

The integral can be evaluated by replacing γ_{CaO} , γ_{MgO} and γ_{SiO_2} in the variables B and C with quantities that were measured in the present work. This is achieved using with the equilibrium constant for Reaction [1]:

$$K_1 = \frac{x_{\text{CaO}}^2 \gamma_{\text{CaO}}^2 \cdot x_{\text{Si}}}{x_{\text{SiO}_2} \gamma_{\text{SiO}_2} \cdot x_{\text{Ca}}^2 \gamma_{\text{Ca}}^2}, \quad [11]$$

where the silicon follows Raoult's law. Using the first-order interaction parameter formalism for calcium in silicon from Wagner,^[9] we have

$$\ln \gamma_{\text{Ca}} = \ln \gamma_{\text{Ca}}^0 + \varepsilon_{\text{Ca}}^{\text{Ca}}. \quad [12]$$

By rearranging Eq. [11] and inserting it into Eq. [5] we get:

$$B = \frac{K_1 \cdot x_{\text{SiO}_2} \cdot x_{\text{Ca}}^2 (\gamma_{\text{Ca}}^0 \exp(\varepsilon_{\text{Ca}}^{\text{Ca}} x_{\text{Ca}}))^2}{x_{\text{CaO}}^2 \cdot x_{\text{Si}}} \quad [13]$$

and hence

$$d \ln B = d \ln \left(\frac{x_{\text{SiO}_2} \cdot x_{\text{Ca}}^2 \exp(2\varepsilon_{\text{Ca}}^{\text{Ca}} x_{\text{Ca}})}{x_{\text{CaO}}^2 \cdot x_{\text{Si}}} \right), \quad [14]$$

where K_1 and γ_{Ca}^0 are eliminated because they are constant. The parameter C can in an equivalent way be found using the equilibrium constant for Reaction [2].

$$d \ln C = d \ln \left(\frac{x_{\text{SiO}_2} \cdot x_{\text{Mg}}^2 \exp \left(2\varepsilon_{\text{Mg}}^{\text{Mg}} x_{\text{Mg}} \right)}{x_{\text{MgO}}^2 \cdot x_{\text{Si}}} \right). \quad [15]$$

The surface fits were used together with the liquidus line for SiO₂ saturation at 1873 K (1600 °C) to determine the activity of SiO₂ across the entire liquid region at 1873 K (1600 °C) down to $x_{\text{SiO}_2} = 0.4$. There was no experimental data from the present work in the region with lower SiO₂ content than this, and extrapolation was not attempted because of the large change of calcium and magnesium concentration in silicon in this region. The liquidus line from the thermodynamic optimization of this system by Jung *et al.*^[10] was used for the calculations. The ternary integral was used for values of k given by Eq. [8] in the range from 0.4 to 2.5. Outside this range, the measured concentration of either calcium or magnesium was limited. Therefore, the determined activity of SiO₂ was interpolated between the binary systems and the given range of k in the ternary system.

B. Activity of SiO₂ in the Binary CaO-SiO₂ System

The self-interaction coefficient of calcium in silicon ($\varepsilon_{\text{Ca}}^{\text{Ca}}$) has been determined by Miki *et al.*^[11] between 1723 K and 1823 K (1450 °C and 1550 °C), and by linear extrapolation it can be estimated to be 7.58 at 1873 K (1600 °C). Using this value, integration from silica saturation in the binary CaO-SiO₂ system with the surface fit for calcium in silicon gives $a_{\text{SiO}_2} = 0.0724$ at Ca₂SiO₄ saturation while assuming $\varepsilon_{\text{Ca}}^{\text{Ca}}$ to be zero gives $a_{\text{SiO}_2} = 0.0770$. The self-interaction coefficient of calcium as measured by Miki *et al.* does in other words only give a decrease of the activity of SiO₂ by 6.0 pct as relative to no self-interaction. The value found when including the self-interaction coefficient may be considered more accurate even if there is not a big difference in the results by disregarding the self-interaction coefficient. Therefore, the activities determined with the self-interaction coefficient were used in the present work. The liquidus line at 1873 K (1600 °C) from the thermodynamic optimization of the ternary CaO-MgO-SiO₂ system by Jung *et al.*^[10] was used as start and endpoints for the integral given by Eq. [10].

The activity of SiO₂ found in the present work is compared with previous works^[2,12–20] in Figure 6 and it is seen to be in relatively good agreement with them. Only the temperature at or closest to 1873 K (1600 °C) was included in the figure for studies conducted at several temperatures. The thermochemical software FactSage was used to calculate liquidus lines and thermodynamic activities from the optimization by Jung *et al.*^[10] The activity of SiO₂ from this optimization is also shown in Figure 6.

The calcium concentration in silicon in equilibrium with CaO-SiO₂ slags was found to be somewhat lower than in the study by Morita *et al.*^[2] Hence, by Gibbs-Duhem integration the activity of SiO₂ was found to be somewhat higher in the present study.

In three studies, reverse cell EMF measurements were used to determine the activity of SiO₂ in binary CaO-SiO₂ slags. Chang and Derge^[12] used SiC-C electrode

pairs to measure the activity of SiO₂ from 1773 K to 1873 K (1500 °C to 1600 °C) in 25 °C intervals, and their activities of SiO₂ are among the highest values found in previous works. A discontinuity in the trend around CaSiO₃ indicates that their cell may not have been completely stable across the entire region investigated. Sakagami^[13] also used SiC-C electrode pairs to determine the activity of SiO₂ at 1823 K, 1848 K, and 1873 K (1550 °C, 1575 °C, and 1600 °C). The activities are in the middle range of values found in previous works but also their data show a discontinuity around CaSiO₃. Omori and Sanbongi^[14] determined the activity of SiO₂ at 1903 K (1630 °C). The cell construction was different than in the two other works using FeSi electrodes and a reference slag. The activity was found to be lower than in any other works, but they also had a discontinuity in the trend around CaSiO₃. The activities of CaO were also estimated by Gibbs-Duhem integration but the estimates were incorrect because of erroneous thermochemical data at that time.

Rein and Chipman^[15] determined the activity SiO₂ by equilibrating CaO-SiO₂ slags with carbon saturated or silicon-carbide saturated iron at 1823 K and 1873 K (1550 °C and 1600 °C). The activities were determined using the activities of silicon in the Fe-Si-C alloys. They also calculated the activity of CaO by Gibbs-Duhem integration of the activity of SiO₂. This work was the final work after many years of research where the previous works (starting with Reference 21) gave wrong activities due to erroneous thermochemical data for SiO₂.^[22]

Kay and Taylor^[16] measured the CO pressure above liquid CaO-SiO₂ slags held in graphite crucibles at 1723 K, 1773 K, and 1823 K (1450 °C, 1500 °C, and 1550 °C). The equilibrium SiO₂ + 3C = SiC + 2CO was then used to calculate the activity of SiO₂. At that time, as mentioned above, the literature value for the Gibbs energy of SiO₂ was erroneous, but they determined the correct Gibbs energy change for the reaction and used this value for the calculations. They also determined the activity of CaO by Gibbs-Duhem integration from Ca₂SiO₄ saturation in addition to a few values at CaSiO₃ saturation at 1723 K and 1773 K (1450 °C and 1500 °C).

Yang *et al.*^[17] used a Knudsen cell to determine the activity of SiO₂ in CaO-SiO₂ slags at 1910 K (1637 °C). They used pure SiO₂ as reference, held the samples in platinum crucibles, and measured the SiO and O₂ pressures. From these pressures, they could calculate the activity of SiO₂, and the activity of SiO₂ was found to be somewhat higher than in the present work and other previous works.

In summary, the activity of SiO₂ determined in the present study is among the highest values for low SiO₂ content and in the mid-range of previous works for high SiO₂ content. It is in best agreement with the activity found by Chang and Derge.^[12]

C. Activity of CaO in the Binary CaO-SiO₂ System

The activity of CaO at Ca₂SiO₄ saturation can be calculated using thermochemical data together with the determined activity of SiO₂. The NIST-JANAF

Fig. 6—Activity of $\text{SiO}_2(\text{s})$ in the binary CaO-SiO_2 system compared with previous works. (* activity determined by Gibbs–Duhem integration of the activity of CaO).

tables^[23] gives $\Delta G_{\text{SiO}_2(\text{s})}^\circ = -575.914 \text{ kJ/mol}$ and $\Delta G_{\text{CaO}(\text{s})}^\circ = -426.199 \text{ kJ/mol}$. From Barin,^[24] we have $\Delta G_{\text{Ca}_2\text{SiO}_4(\text{s})}^\circ = -1573.218 \text{ kJ/mol}$ from elements at 1873 K (1600 °C). Thereby, using the equilibrium

we have the equilibrium constant $K_2 = 9.10 \cdot 10^{-5}$, and we get

$$a_{\text{CaO}(\text{s})} = (K_2/a_{\text{SiO}_2(\text{s})})^{1/2} = 3.55 \cdot 10^{-2}. \quad [17]$$

The activity of CaO at Ca_2SiO_4 saturation will decrease by 3.1 pct if the self-interaction coefficient measured by Miki *et al.*^[11] is disregarded when determining the activity of SiO_2 .

The activity of CaO across the liquid region can now be determined by Gibbs–Duhem integration from Ca_2SiO_4 saturation. The activity of CaO at SiO_2 saturation was in this way found to be 0.00260 when using the self-interaction coefficient by Miki *et al.*^[11] The activity of CaO found in the present work is compared with previous works in Figure 7. For works conducted at several temperatures, only the temperature closest to 1873 K (1600 °C) was included.

In the present work, a different approach was used for determination of the activity of CaO than in the study by Morita *et al.*^[2] The Gibbs energy of Ca_2SiO_4 was used at Ca_2SiO_4 saturation for determination of the activity of CaO while Morita *et al.* used the previously determined Henrian activity coefficient of calcium in silicon found by Miki *et al.*^[11] to calculate the activity of CaO at SiO_2 saturation. The advantage of using the Gibbs energy of Ca_2SiO_4 is that the Henrian activity coefficient of calcium in silicon is not needed. Rein and Chipman^[15] also determined the activity of CaO by Gibbs–Duhem integration using the Gibbs energy of Ca_2SiO_4 .

Three studies have been conducted to determine the activity of CaO in CaO-SiO_2 slags directly without using Gibbs–Duhem integration. Carter and Macfarlane^[18] conducted a study where they equilibrated slags with

Fig. 7—Activity of $\text{CaO}(\text{s})$ in the binary CaO-SiO_2 system compared with previous works.

$\text{CO-CO}_2\text{-SO}_2$ gas mixtures at 1773 K (1500 °C). The concentration of sulfur in slags was measured after the experiments and used together with the activity coefficient of CaS to calculate the activity of CaO . Sharma and Richardson^[19] did a similar study as Carter and Macfarlane at 1773 K and 1823 K (1500 °C and 1550 °C) but used a mixture of N_2 , H_2S , H_2 , and CO_2 gas. They also included the variation of the activity coefficient of CaS with slag composition. This study may, therefore, be considered more accurate than the study by Carter and Macfarlane even if they are relatively good agreement with each other. Only four data points were obtained in their study at 1823 K (1550 °C), and therefore their data at 1773 K (1500 °C) is also included in Figure 7. Sawamura^[20] determined the activity of CaO in CaO-SiO_2 slags at 1873 K (1600 °C) by double-cell EMF measurements using tungsten electrodes where one cell contained a reference slag. Their results agree well with the two works that uses the activity coefficient of CaS . The activity of CaO found by a thermodynamic optimization of the system by Jung *et al.*^[10] is also shown in Figure 7, and it is seen to be in relatively good agreement with the work by Rein and Chipman.^[15]

The present work is seen to be in best agreement with the work by Rein and Chipman^[15] and the thermodynamic optimization of the system by Jung *et al.*,^[10] which are the highest values across most of the liquid region.

D. The Henrian Activity Coefficient of Calcium in Silicon

The Henrian activity coefficient of calcium in silicon can be calculated using the determined activities of CaO and SiO_2 . The reaction

has a Gibbs energy of -869.028 kJ/mol .^[23] Hence, the equilibrium constant from Eq. [11] gives:

$$\ln \gamma_{\text{Ca}}^0 = \ln \left(\frac{K_1 \cdot a_{\text{CaO}}^2 \cdot x_{\text{Si}}}{a_{\text{SiO}_2} \cdot x_{\text{Ca}}^2 \exp(2\varepsilon_{\text{Ca}}^{\text{Ca}} x_{\text{Ca}})} \right)^{1/2} = -6.99 \pm 0.15, \quad [19]$$

where the uncertainty is expressed as a 95 pct confidence interval based on the confidence interval of the surface fit for $\ln w_{\text{Ca}}$ in the middle of the liquid region of the binary CaO-SiO₂ system. If the self-interaction coefficient given by Miki *et al.*^[11] is disregarded we get $\ln \gamma_{\text{Ca}}^0 = -6.97$, which is well within the given uncertainty range. It should be noted that the Henrian activity coefficient of calcium was not needed for determination of the activities of CaO and SiO₂.

The Henrian activity coefficient of calcium in liquid silicon found in the present work is compared with previous works in Figure 8. Pinto and Takano^[6] measured the distribution of calcium between silicon and a SiO₂ saturated CaO-SiO₂ slag at 1823 K and 1923 K (1550 °C and 1650 °C) under argon atmosphere in an induction furnace. In their study, Gibbs energies for CaO and SiO₂ from the NIST-JANAF tables^[23] were used together with the liquidus line from the Slag Atlas.^[25] The activity of CaO at SiO₂ saturation was determined from the study by Sharma and Richardson^[19] using a temperature coefficient derived from the study by Rein and Chipman.^[15]

Margarita *et al.*^[26] also conducted a study where they equilibrated CaO-SiO₂ slags with silicon for 12 to 48 hours in graphite crucibles. Values found in literature (source not indicated) for the activity of CaO and SiO₂ were used together with the calcium concentration in silicon to calculate the Henrian activity coefficient. They also checked the results by measuring the partial pressure of calcium using effusion cell coupled with mass spectroscopy. However, details of the experimental procedure were not given in their paper.

Miki *et al.*^[8,11] did two studies of the Henrian activity coefficient of calcium in silicon from 1723 K to 1823 K (1450 °C to 1550 °C). In the first study,^[8] they equilibrated silicon with SiO₂ saturated CaO-SiO₂ slags and calculated the activity coefficient in a similar way as the other studies. The activity of CaO at SiO₂ saturation was taken from a thermodynamic optimization by Eriksson *et al.*^[27] In the second study,^[11] they equilibrated silicon with lead at 1723 K (1450 °C). Based on the distribution of calcium between lead and silicon they found the self-interaction coefficient of calcium in silicon to be 9.90. Then they used a Knudsen effusion cell

coupled with mass spectroscopy to determine the temperature dependence of the self-interaction coefficient of calcium from 1723 K to 1823 K (1450 °C to 1550 °C). They could also re-evaluate the temperature dependence of the Henrian activity coefficient of calcium in silicon from the results with the effusion cell. Both for the equilibration with lead and the Knudsen effusion they used the result at 1723 K (1450 °C) from the first study as a reference point for the Henrian activity coefficient of calcium. The results obtained by the Knudsen effusion method is less scattered than the results they found in their first study, and the activity coefficient from this study is seen to be somewhat larger than in the other studies. They did, however, use a somewhat different Gibbs energy of CaO than suggested in the most recent literature.^[28] The Gibbs energy they used was from a single study by Wakasugi and Sano.^[29] By recalculating the activity coefficient using the Gibbs energy of CaO from the NIST-JANAF tables, the activity coefficient becomes lower than found in other studies as can be seen in Figure 8.

A study where a SiO₂-saturated CaO-SiO₂ slag was equilibrated with silicon is also given in the book by Schei *et al.*^[5] In this study, a different temperature dependence was found than the other studies. The values are in good agreement with other works with values between the works by Margarita *et al.*^[26] and the value found by Pinto and Takano.^[6] The value at 1873 K (1600 °C) from the present work is seen to be between the values given by Schei *et al.* and the values found by Pinto and Takano.

The Henrian activity coefficient of calcium in silicon from a recent thermodynamic optimization of the system by Heyrman and Chartrand^[30] is also shown in the figure, and it is seen to be in close agreement with the recalculated value from Miki *et al.*^[11]

For all studies, the activity of CaO is one of the main sources of uncertainty besides the measured calcium concentration in silicon, and the calculated activity coefficient will depend somewhat on the literature selected. The literature values for the activity of CaO are compared in Figure 7.

E. Activities in the Binary MgO-SiO₂ System

The activity of SiO₂ in the binary MgO-SiO₂ system was found in the same way as in the binary CaO-SiO₂ system using the surface fit for the concentration of magnesium in silicon for the entire CaO-MgO-SiO₂ system.

Miki *et al.*^[11] also investigated the self-interaction coefficient of magnesium in silicon ($\epsilon_{\text{Mg}}^{\text{Mg}}$) and found it to be 6.02 at 1723 K (1450 °C). If the same temperature dependence as for the self-interaction coefficient of calcium in silicon is assumed, $\epsilon_{\text{Mg}}^{\text{Mg}}$ will be almost half of $\epsilon_{\text{Ca}}^{\text{Ca}}$ at 1873 K (1600 °C). Using this estimate the self-interaction coefficient was found to decrease the calculated activity of SiO₂ at Mg₂SiO₄ saturation by approximately 0.1 pct as compared to when assuming no self-interaction. Since the influence was so small, magnesium was assumed to behave as a Henrian solute in silicon in equilibrium with the binary MgO-SiO₂ system.

Fig. 8—Henrian activity coefficient of calcium in silicon compared with previous works.

At Mg_2SiO_4 saturation, the Gibbs energy of Mg_2SiO_4 was used together with the determined activity of SiO_2 to determine the activity of MgO in the same way as for CaO at Ca_2SiO_4 saturation. From Barin,^[24] the Gibbs energy of Mg_2SiO_4 is -1326.229 kJ/mol (from elements) at 1873 K (1600 °C), and from the NIST-JANAF tables,^[23] the Gibbs energy of MgO is -345.887 kJ/mol. The determined activities of MgO and SiO_2 are compared with previous works in Figure 9.

The work by Rein and Chipman^[15] described above also included the binary MgO-SiO_2 system where they employed the same procedure as in the binary CaO-SiO_2 system. Kambayashi and Kato^[31] determined the activity of MgO and SiO_2 using mass spectroscopy combined with a platinum effusion cell. They measured the intensities of Mg(g) and SiO(g) , and could then determine the activities by Gibbs–Duhem integration. Zaitsev *et al.*^[32] used the same method but with tantalum, niobium, and molybdenum as combined reductants and effusion cells. The activities of SiO_2 found in previous works are in relatively close agreement except the work by Morita *et al.* where the activity of SiO_2 was found to be somewhat higher. The activity found in the present work is seen to be even higher than found by Morita *et al.* except from at the highest MgO concentration.

As can be seen in Figure 4, the amount of data is somewhat limited in the present work. The activity of SiO_2 would be 22 pct lower at Mg_2SiO_4 saturation if a simple linear fit is used on these measurements. In this case, the determined activity of SiO_2 would be somewhat lower than found in previous works. The activity of MgO would on the other hand be 13 pct higher at Mg_2SiO_4 saturation when using this linear fit. Using a separate fit for the binary system would however give activities that are inconsistent with the ternary CaO-MgO-SiO_2 system. The comparison with a linear fit was only to demonstrate the uncertainty of the activities in the binary MgO-SiO_2 system determined in the present work.

Fig. 9—Activity of MgO(s) and $\text{SiO}_2\text{(s)}$ in the binary MgO-SiO_2 system compared with previous works.

F. The Henrian Activity Coefficient of Magnesium in Silicon

The Henrian activity coefficient of magnesium in silicon was determined in the same way as the Henrian activity coefficient of calcium. In the same way as in the binary CaO-SiO_2 system, the Henrian activity coefficient of magnesium in silicon was not needed for determination of the activities of MgO and SiO_2 . From the NIST-JANAF tables,^[23] the Gibbs energy for the reaction

is -784.402 kJ/mol at 1873 K (1600 °C). Using this value together with the given Gibbs energy for SiO_2 , we get

$$\ln \gamma_{\text{Mg}}^0 = \ln \left(\frac{K_3 \cdot a_{\text{MgO}}^2 \cdot x_{\text{Si}}}{a_{\text{SiO}_2} \cdot x_{\text{Mg}}^2} \right)^{1/2} = -1.71 \pm 0.16, \quad [21]$$

where the uncertainty is expressed as a 95 pct confidence interval based on the confidence interval of the surface fit for $\ln w_{\text{Mg}}$ in the middle of the liquid region of the binary MgO-SiO_2 system. Miki *et al.*^[8] determined the Henrian activity coefficient of magnesium in the range from 1698 K to 1798 K (1425 °C to 1525 °C). They also investigated the concentration dependence of the activity coefficient at 1723 K (1450 °C)^[11] and found it to be so small that they kept the Henrian activity coefficient from the first study unchanged. An extrapolation of the Henrian activity coefficient in their study gives $\ln \gamma_{\text{Mg}}^0 = -1.52$ at 1873 K (1600 °C), which is a little lower than found in the present study. A recent thermodynamic optimization of the system by Jung *et al.*^[33] gives $\ln \gamma_{\text{Mg}}^0 = -1.74$ at 1873 K (1600 °C), which is in very close agreement with the present work.

The determined activities of MgO and SiO_2 in the binary MgO-SiO_2 system are, as discussed in the previous section, based on a somewhat limited number of measurements. A linear fit to the data would give different activities of MgO and SiO_2 , and the activities from a linear fit gives $\ln \gamma_{\text{Mg}}^0 = -1.64$. This value is, however, seen to be well within the given uncertainty range of the determined Henrian activity coefficient given above.

G. Activities in the Ternary CaO-MgO-SiO_2 System

The activity of SiO_2 in the ternary CaO-MgO-SiO_2 system was determined by Gibbs–Duhem integration using the surface fits for calcium and magnesium through Eq. [10]. No interaction between calcium and magnesium in liquid silicon was assumed, while the self-interaction coefficient for calcium estimated from the work by Miki *et al.*^[11] [7.58 at 1873 K (1600 °C)] was used. The estimated self-interaction coefficient of magnesium in silicon was found to influence the determined activity of SiO_2 even less in the ternary system than in the binary MgO-SiO_2 system. Magnesium was, therefore, also in the ternary system assumed to behave as a Henrian solute in silicon. In the same way as in the binary systems, the integration to obtain the activity of

Fig. 10—Activities of (a) $\text{SiO}_2(\text{s})$, (b) $\text{CaO}(\text{s})$, and (c) $\text{MgO}(\text{s})$ at 1873 K (1600 °C) in the ternary CaO-MgO-SiO_2 system compared with previous works. The liquidus line from a Jung *et al.*^[10] is indicated as a bold solid line and the liquidus lines from the Slag Atlas^[25] are indicated as bold-dashed lines.

SiO_2 is independent of the Henrian activity coefficients of calcium and magnesium in silicon.

The activity obtained in the present work is compared with previous works in Figure 10(a). The activity of SiO_2 is seen to be in relatively good agreement with previous works in most of the liquid region. Some difference between different works is seen in the MgO -rich part of the system. Morita *et al.*^[2] found somewhat higher activities of SiO_2 in this part of the system than obtained in the present work, while somewhat lower activities were found in other works. The activity of SiO_2 in both the work by Morita *et al.*^[2] and Rein and Chipman^[15] was determined by Gibbs–Duhem integration, and the liquidus line at SiO_2 saturation was used as a starting point for the integration. The liquidus line used in the present work is from a recent thermodynamic optimization of the system.^[10] This line is seen in Figure 10(a) to be somewhat different from the liquidus line from the Slag Atlas,^[25] which is similar to the liquidus lines used by Morita *et al.* and Rein and Chipman. The iso-activity lines of SiO_2 close to the liquidus line for SiO_2 saturation should to some extent follow the curvature of the liquidus line of SiO_2 . Because of this, the curvature of the iso-activity lines for high SiO_2 content is seen to be somewhat different from previous experimental works. The iso-activity lines for SiO_2 from the thermodynamic optimization by Jung *et al.*^[10] is also shown in the figure, and it is seen to be in relatively good agreement with the present work and previous experimental works.

The activities of CaO and MgO could be determined using the Henrian activity coefficients of calcium and magnesium determined from the binary silicate systems. For this calculation, the Henrian activity coefficients were used together with the determined activity of SiO_2 and the concentrations of calcium and magnesium in silicon. For calcium, the self-interaction coefficient in silicon estimated from Miki *et al.*^[11] [7.58 at 1873 K (1600 °C)] was also used. No self-interaction of magnesium or interaction between calcium and magnesium was assumed. The determined activities of CaO and MgO in the ternary system are compared with previous works in Figures 10(b) and (c), respectively.

The activity of CaO is seen to be somewhat higher than in the work by Morita *et al.*^[34] while it is lower than in the work by Rein and Chipman^[15] in the ternary region. The activities of CaO found in the present work are in relatively good agreement with the thermodynamic optimization of the system by Jung *et al.*^[10] where the activities are identical in several regions of the system. The activity of MgO is seen to be somewhat lower than in the work by Morita *et al.*^[34] while it is higher than in the work by Rein and Chipman except for in the most CaO -rich region. Also in this system, the

present work is in relatively good agreement with Jung *et al.*^[10] except for the region with the highest MgO content where the activity of MgO in the present work was found to be somewhat higher and more in agreement with the work by Morita *et al.* The iso-activity lines for the lowest activities of MgO found in the present work are also seen to have a somewhat different curvature than found in the work by Jung *et al.*

V. CONCLUSIONS

The distributions of calcium and magnesium between silicon and CaO-MgO-SiO₂ slags have been measured at 1873 K (1600 °C). Activities of CaO, MgO, and SiO₂ in the binary CaO-SiO₂, binary MgO-SiO₂, and ternary CaO-MgO-SiO₂ systems have been estimated using the Gibbs–Duhem equation on the measured calcium and magnesium concentrations in silicon, and they are in good agreement with previous works. The Henrian activity coefficients of calcium and magnesium in silicon at 1873 K (1600 °C) have also been determined. Altogether, a self-consistent set of thermodynamic properties was obtained for the equilibrium between silicon and CaO-MgO-SiO₂ slags at 1873 K (1600 °C).

ACKNOWLEDGMENTS

This work has been financed through the Research Council of Norway. The large number of analytical determinations by Syverin Lierhagen is highly appreciated.

OPEN ACCESS

This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

REFERENCES

1. L.K. Jakobsson and M. Tangstad: *Metall. Mater. Trans. B*, 2014, vol. 45B, pp. 1644–55.
2. K. Morita, K. Kume, and N. Sano: *ISIJ Int.*, 2000, vol. 40 (6), pp. 554–60.
3. L.A.V. Teixeira, Y. Tokuda, T. Yoko, and K. Morita: *ISIJ Int.*, 2009, vol. 49 (6), pp. 777–82.
4. X.G. Wang, W.Z. Ding, K. Tang, G.C. Jiang, and K.D. Xu: *Trans. Nonferr. Met. Soc. China*, 2001, vol. 11 (4), pp. 535–39.
5. A. Schei, J.K. Tuset, and H. Tveit: *Production of High Silicon Alloys*, Akademika Publishing, Trondheim, 1998.
6. E.C. de Oliveira Pinto and C. Takano: *Metall. Mater. Trans. B*, 2000, vol. 31B, pp. 1267–72.
7. T. Weiss and K. Schwerdtfeger: *Metall. Mater. Trans. B*, 1994, vol. 25B, pp. 497–504.
8. T. Miki, K. Morita, and N. Sano: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 1043–49.
9. C. Wagner: *Thermodynamics of Alloys*, Addison-Wesley, Reading, MA, 1952.
10. I.-H. Jung, S.A. Decterov, and A.D. Pelton: *J. Eur. Ceram. Soc.*, 2005, vol. 25 (4), pp. 313–33.
11. T. Miki, K. Morita, and N. Sano: *JIM Mater. Trans.*, 1999, vol. 40 (10), pp. 1108–16.
12. L.C. Chang and G. Derge: *Met. Technol.*, 1946, vol. 13, pp. 1–27.
13. R. Sakagami: *Tetsu to Hagane*, 1953, vol. 39 (6), pp. 587–95.
14. J. Omori and K. Sanbongi: *J. Jpn. Inst. Met.*, 1961, vol. 25 (2), pp. 139–43.
15. R.H. Rein and J. Chipman: *Trans. Metall. Soc. AIME*, 1965, vol. 233 (2), pp. 415–25.
16. D.A.R. Kay and J. Taylor: *Trans. Faraday Soc.*, 1960, vol. 56, pp. 1372–86.
17. L. Yang, C.L. McCabe, and R. Miller: *The Physical Chemistry of Steelmaking*, Wiley, New York, 1958, pp. 63–64.
18. P.T. Carter and T.G. Macfarlane: *J. Iron Steel Inst.*, 1957, vol. 185, pp. 62–66.
19. R.A. Sharma and F.D. Richardson: *J. Iron Steel Inst.*, 1962, vol. 200 (5), pp. 373–79.
20. K. Sawamura: *Tetsu to Hagane*, 1961, vol. 47 (14), pp. 1873–78.
21. J.C. Fulton and J. Chipman: *Trans. Am. Inst. Min. Metall. Eng.*, 1954, vol. 200 (10), pp. 1136–46.
22. J. Chipman: *J. Am. Chem. Soc.*, 1961, vol. 83 (7), pp. 1762–63.
23. M.W. Chase: *Journal of Physical and Chemical Reference Data*, Monograph 9, 1998.
24. I. Barin: *Thermochemical Data of Pure Substances*, Part 2, VCH, Weinheim, 1995.
25. V.D. Eisenhüttenleute, ed.: *Slag Atlas*, Verlag Stahleisen GmbH, Düsseldorf, 1995.
26. T. Margaria, M. Rebiere, F. Traversaz, and C. Dumay: *Silicon for the Chemical Industry III*, 1996, pp. 21–31.
27. G. Eriksson, P. Wu, M. Blander, and A.D. Pelton: *Can. Metall. Q.*, 1994, vol. 33 (1), pp. 13–21.
28. K.T. Jacob and V. Varghese: *Metall. Mater. Trans. B*, 1996, vol. 27B, pp. 647–51.
29. T. Wakasugi and N. Sano: *Metall. Trans. B*, 1989, vol. 20B, pp. 431–33.
30. M. Heyrman and P. Chartrand: *J. Phase Equilib. Diffus.*, 2006, vol. 27 (3), pp. 220–30.
31. S. Kambayashi and E. Kato: *J. Chem. Thermodyn.*, 1983, vol. 15 (8), pp. 701–07.
32. A.I. Zaitsev, N.A. Arutyunyan, N.G. Shaposhnikov, N.E. Zaitseva, and V.T. Burtsev: *Russ. J. Phys. Chem.*, 2006, vol. 80 (3), pp. 335–44.
33. I.-H. Jung, D.-H. Kang, W.-J. Park, N.J. Kim, and S. Ahn: *CALPHAD*, 2007, vol. 31 (2), pp. 192–200.
34. K. Morita, K. Kume, and N. Sano: *Scand. J. Metall.*, 2000, vol. 31 (3), pp. 178–83.