Reassessment of Solid Solubilities and Thermodynamic Properties of Magnesium and Calcium in Silicon

Sakiko Kawanishi¹ and Takeshi Yoshikawa²

¹*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980–8577, Japan*

²*Institute of Industrial Science, The University of Tokyo, Tokyo 153–8505, Japan*

To obtain fundamental knowledge on the behavior of magnesium (Mg) and calcium (Ca) in solid silicon (Si) during solidification, the solid solubilities of Mg and Ca in Si were reinvestigated by temperature-gradient zone melting method. Solubilities were measured to be 0.0016–0.0041 mol% for Mg and 0.0006–0.0021 mol% for Ca at 1373–1623 K. The excess Gibbs energies of Mg and Ca in solid Si were determined from their solid solubilities as follows:

$$RT \ln \gamma_{\text{Mg(s) in solid Si}}^{\circ} = 193,000(\pm 52,000) - 69.8(\pm 34)T \text{ (J/mol)}$$

$$RT \ln \gamma_{\text{Ca(s) in solid Si}}^{\circ} = 140,000(\pm 35,000) - 72.6(\pm 23)T \text{ (J/mol)}$$

[doi:10.2320/matertrans.M2016323]

(Received September 14, 2016; Accepted December 5, 2016; Published January 20, 2017)

Keywords: silicon, magnesium, calcium, solid solubility, temperature-gradient zone melting

1. Introduction

High-purity silicon (Si) is in demand for the production of semiconductor Si, solar-grade Si and other chemical applications. Slag treatment is an efficient metallurgical refining process as it enables large-scale and reduced-time operation. During metallurgical grade Si production, oxidizing treatment is used to remove gangue components as slags from Si melts that are obtained by quartz reduction in the arc furnace. Slag treatment using calcium-oxide-based slags has been researched to remove boron and phosphorus from Si, and is aimed at solar-grade Si production^{1–4}. Because magnesium oxide and calcium oxide are major components of slag in both cases, the incorporation of magnesium (Mg) and calcium (Ca) into molten Si is thermodynamically inevitable^{2,3,5,6} and their behavior during solidification must be understood. Most metal elements have small segregation coefficients in Si, which allows their separation during solidification⁷. However, the segregation coefficients of Mg and Ca in Si have not been reported and so it is difficult to predict their behavior during Si solidification.

In addition to the segregation coefficients, the solid solubilities of Mg and Ca in Si are important to consider their incorporation into Si, and were only reported by Sigmund⁸. The author applied temperature-gradient zone melting⁹ to achieve equilibrium solidification of solid Si from liquid Ca–Si or Mg–Si alloys, and measured solubilities as high as 0.012 mol% at 1453 K for Ca and 0.025 mol% at 1473 K for Mg. However, such high contents of Ca or Mg were not found in Si grains after solidification.

In this work, the solid solubilities of Mg and Ca in Si were investigated again using temperature-gradient zone melting experiments at 1323–1623 K. Based on the measured solubilities, thermodynamic properties of Mg and Ca in solid Si were also determined.

2. Experimental

Figure 1 shows apparatus that is composed mainly of an induction furnace (280 kHz) that is equipped with a quartz reaction tube (60 mm OD, 54 mm ID, 400 mm length). A Ca (99% purity) or Mg (99%) film was inserted between two (111)-oriented Si wafers (10 × 5 × 0.6 mm, 10 Ω·cm), and the sample set was placed on a graphite susceptor in the reaction tube. After evacuation below 0.5 Pa with a rotary vacuum pump, the reaction tube was filled with hydrogen. The sample temperature was increased to 1323–1623 K for 1200–3600 s by inductively heating the susceptor. The temperature of the bottom surface was controlled by monitoring with a single-color pyrometer.

Fig. 1 Schematic image of temperature-gradient zone melting experiment.

As the sample was heated from the base by the susceptor, the temperature increased in a downward direction. After Ca or Mg forms a liquid zone by dissolving the contacted Si, the zone migrates downward in the lower Si wafer along the temperature gradient, which results in the crystallization of an equilibrium solid. When heat that is released at the top surface of the sample is assumed to be controlled by radiation, the temperature gradient in the solid Si is estimated to be 4.9×10^3 K/m at 1323 K and 1.1×10^4 K/m at 1623 K from the emissivity¹⁰⁾ and the heat conductivity¹¹⁾ of Si, respectively. The temperature difference in the crystallized Si is less than 6.6 K from the thickness of the Si wafer, and that in the liquid zone is assumed to be less than 2 K from its thickness (< 0.2 mm).

After the experiments, samples were subjected to electron probe micro analysis (EPMA) with an accelerating voltage of 15 kV, a sample current of 100–200 nA and a counting time of 100 s. The intensity of Ca K_{α} or Mg K_{α} radiation of the crystallized Si was determined by subtracting the background intensity obtained from the pure single crystalline Si. Thereafter, the Ca or Mg content was determined by applying a ZAF correction.

3. Results and Discussion

Figure 2 shows a sample cross-section after heat treatment with Ca addition by heating at 1323 K for 3600 s. Migration of a liquid Si–Ca zone from the original position “A” to position “B” was observed, which suggests a migration velocity of $\sim 4.6 \times 10^{-8}$ m/s. Measurements of Mg and Ca contents by EPMA were performed at more than 3 positions between A and B for each sample.

Measured solid solubilities of Ca and Mg in Si are shown in Figs. 3 and 4 along with reported data⁸⁾ for comparison. Solubilities ranged 0.0016–0.0041 mol% for Mg and 0.0006–0.0021 mol% for Ca at 1373–1623 K, and were below the detection limit at 1323 K. These data are smaller than the reported data. Sigmund determined the solubility in crystallized Si by wet analysis and found an inhomogeneous solubility. As shown in Fig. 2, inclusions were incorporated into crystallized Si in this work. Therefore, an analysis of the content in a certain specimen volume may overestimate the solubility.

The excess partial molar Gibbs energy of M (M = Mg or Ca) in solid Si was evaluated from the measured solid solubility. At equilibrium, the chemical potential of M in the solid Si is equal to that in the liquid Si–M alloy, which can be ex-

pressed by eqs. (1) and (2):

$$G_{M(s)}^{\circ} + RT \ln a_{M(s)} \text{ in solid Si} = G_{M(l)}^{\circ} + RT \ln a_{M(l)} \text{ in the melt} \quad (1)$$

$$RT \ln \gamma_{M(s)} \text{ in solid Si} = \Delta G_M^{\text{fus.}} + RT \ln a_{M(l)} \text{ in the melt} - RT \ln X_M \text{ in solid Si} \quad (2)$$

Here, $RT \ln \gamma_{M(s)} \text{ in solid Si}$ is the excess partial molar Gibbs energy of Mg or Ca in solid Si, and $\Delta G_M^{\text{fus.}}$ represents the Gibbs energy of fusion of Mg or Ca¹²⁾. The Mg or Ca activity in the liquid phase along the liquidus ($a_{M(l)} \text{ in the melt}$) was taken from the reported excess Gibbs energy for the liquid Si–Mg or Si–Ca melt^{13,14)}. $X_M \text{ in solid Si}$ is the solid solubility as measured in this study. The temperature dependence of $RT \ln \gamma_{M(s)} \text{ in solid Si}$ is shown in Fig. 5. Using least-squares regression, the excess partial molar Gibbs energies of Mg and Ca in the solid Si at infinite dilution were determined as shown in eqs. (3) and (4):

$$RT \ln \gamma_{Mg(s)}^{\circ} \text{ in solid Si} = 193,000(\pm 52,000) - 69.8(\pm 34)T \text{ (J/mol)} \quad (3)$$

$$RT \ln \gamma_{Ca(s)}^{\circ} \text{ in solid Si} = 140,000(\pm 35,000) - 72.6(\pm 23)T \text{ (J/mol)} \quad (4)$$

Here, hexagonal close-packed Mg and face-centered cubic

Fig. 2 Cross-section of the sample (Ca, 1323 K, 3600 s).

Fig. 3 Solid solubilities of Mg in Si.

Fig. 4 Solid solubilities of Ca in Si.

Fig. 5 Excess partial molar Gibbs energy of Mg and Ca in solid Si.

Ca were selected as standard states, respectively.

The temperature dependence of the solid solubilities of Mg and Ca were derived by inserting eqs. (3) and (4) into eq. (2) as shown by the broken curves of Figs. 3 and 4. A retrograde solubility was determined for Mg and Ca, and the maximum solubilities were 0.0040 mol% at 1560 K for Mg and 0.0014 mol% at 1580 K for Ca.

The segregation coefficient, k , was estimated. When the solid and liquid Si are equilibrated for small contents of Mg or Ca, eq. (2) can be rearranged as:

$$RT \ln \gamma_{M(s)}^{\circ} \text{ in solid Si} = \Delta G_M^{\text{fus.}} + RT \ln \gamma_{M(l)}^{\circ} \text{ in liquid Si} + RT \ln X_M \text{ in liquid Si} - RT \ln X_M \text{ in solid Si} \quad (5)$$

$$RT \ln k = RT \ln \frac{X_M \text{ in solid Si}}{X_M \text{ in liquid Si}} = \Delta G_M^{\text{fus.}} + RT \ln \gamma_{M(l)}^{\circ} \text{ in liquid Si} - RT \ln \gamma_{M(s)}^{\circ} \text{ in solid Si} \quad (6)$$

Extrapolating eqs. (3) and (4) to the melting temperature and using the excess partial molar Gibbs energy in the liquid Si at infinite dilution, $RT \ln \gamma_{M(l)}^{\circ} \text{ in liquid Si}$, the segregation coefficient, can be obtained from the Gibbs energy of the liquid Si–Mg or Si–Ca alloy and was found to be 0.00021 for Mg and 0.00029 for Ca. As is known for other metal elements¹⁵⁾, Mg and Ca show strong segregation tendencies in Si.

4. Conclusions

To determine the solid solubilities of Mg and Ca in solid Si, temperature-gradient zone melting experiments were performed at 1323–1623 K. The following results were obtained:

- (1) Solubilities were measured as 0.0016–0.0041 mol% for Mg and 0.0006–0.0021 mol% for Ca at 1373–1623 K.
- (2) The excess Gibbs energies of Mg and Ca in solid Si were determined from the measured solid solubilities as follows:

$$RT \ln \gamma_{Mg(s)}^{\circ} \text{ in solid Si} = 193,000(\pm 52,000) - 69.8(\pm 34)T \text{ (J/mol)}$$

$$RT \ln \gamma_{Ca(s)}^{\circ} \text{ in solid Si} = 140,000(\pm 35,000) - 72.6(\pm 23)T \text{ (J/mol)}$$

- (3) The temperature dependence of the solid solubilities was estimated, and the maximum solubility was 0.0040 mol% at 1560 K for Mg and 0.0014 mol% at 1580 K for Ca.

Acknowledgement

The authors are grateful to Prof. Hiroyuki Shibata and Mr. Masanori Tashiro for their help with conducting solubility measurement by electron probe micro-analyzer analysis.

REFERENCES

- 1) K. Suzuki, T. Sugiyama, K. Takano and N. Sano: *J. Jpn. Inst. Metals* **54** (1990) 168–172.
- 2) H. Fujiwara, J.Y. Liang, K. Takeuchi and E. Ichise: *Mater. Trans., JIM* **37** (1996) 923–926.
- 3) H. Fujiwara, J.Y. Liang, K. Miyata, E. Ichise and R. Otsuka: *J. Jpn. Inst. Metals* **60** (1996) 65–71.
- 4) L.A.V. Teixeira and K. Morita: *ISIJ Int.* **49** (2009) 783–787.
- 5) K. Morita, K. Kume and N. Sano: *ISIJ Int.* **40** (2000) 554–560.
- 6) K. Kume, K. Morita, T. Miki and N. Sano: *ISIJ Int.* **40** (2000) 561–566.
- 7) K. Morita and T. Miki: *Intermetallics* **11** (2003) 1111–1117.
- 8) H. Sigmund: *J. Electrochem. Soc.* **129** (1982) 2809–2812.
- 9) W.G. Pfann: *JOM* **203** (1955) 961–964.
- 10) B. Sopori, W. Chen, J. Madjdpur and N.M. Ravindra: *J. Electron. Mater.* **28** (1999) 1385–1389.
- 11) H. Kobatake, H. Fukuyama, T. Tsukada and S. Awaji: *Meas. Sci. Technol.* **21** (2010) 025901.
- 12) A.T. Dinsdale: *Calphad* **15** (1991) 317–425.
- 13) H. Feufel, T. Gödecke, H.L. Lukas and F. Sommer: *J. Alloy. Compd.* **247** (1997) 31–42.
- 14) J.C. Anglezio, C. Servant and I. Ansara: *Calphad* **18** (1994) 273–309.
- 15) F.A. Trumbore: *Bell Syst. Tech. J.* **39** (1960) 205–233.