Solubility of Calcium and Oxygen in Molten Iron Equilibrated with Slag in CaO, Al₂O₃ or CaO-stabilized ZrO₂ Crucible at 1 873 K

Ichiro SEKI,1) Kazuhiro NAGATA,2) Tetsuya ASHINO1) and Jun TANABE3)

1) Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577 Japan. E-mail: seki.ichiro@imr.tohoku.ac.jp, ayustet@imr.tohoku.ac.jp
2) Department of Conservation, Tokyo University of the Arts, 12-8, Ueno Park, Taito-ku, Tokyo, 110-8714 Japan. E-mail: nagata@mtl.titech.ac.jp
3) Department of Mechanical Engineering, Faculty of Engineering, Nippon Institute of Technology, 4-1, Gakuen-dai, Miyashiro-cho, Minamisaitama-gun, Saitama, 345-8501 Japan. E-mail: tanabe@nit.ac.jp

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The solubility of calcium and oxygen in molten iron equilibrated with CaO–Al₂O₃–ZrO₂ molten slag in CaO, Al₂O₃ or 5.5 mass% CaO-stabilized ZrO₂ crucible at 1 873 K was measured by means of the slag-metal equilibrium partition method under Ar gas atmosphere. From the results by XRD and the phase diagram of CaO–Al₂O₃–ZrO₂ system, the slag in a CaO crucible was in equilibrium with CaO·ZrO₂ and CaO and the slag composition was 57.36 mass% CaO-34.86% Al₂O₃-7.78% ZrO₂. The slag in an Al₂O₃ crucible was in equilibrium with CaO·2Al₂O₃ and ZrO₂–CaO solid solution (Css) and the slag composition was 27.08 mass% CaO-53.42% Al₂O₃-19.50% ZrO₂. The slag in a CaO-stabilized ZrO₂ crucible was in equilibrium with ZrO₂–CaO solid solution (Css) and CaO·ZrO₂ and the slag composition was 30.38 mass% CaO-51.56% Al₂O₃-18.06% ZrO₂. The average concentrations of oxygen and calcium in molten iron in equilibrium with slag and compounds were 251 ppm and 3 ppm in a CaO crucible, 33 ppm and 4 ppm in an Al₂O₃ crucible and 21 ppm and 5 ppm in a CaO-stabilized ZrO₂ crucible, respectively. The logarithm of equilibrium constant, logK, for the reaction of CaO(s) = Ca+O is –4.38 and the interaction parameter of e CaO is 31.8. The value is satisfied the thermodynamic phase stability.

KEY WORDS: molten iron; solubility; calcium; oxygen; CaO; Al₂O₃; CaO-stabilized ZrO₂.

1. Introduction

Calcium, aluminum and zirconium are highly reactive metals with oxygen and are used as deoxidizers not only for steelmaking but also for refining processes of some nonferrous metals with high affinity of oxygen. Then, CaO–Al₂O₃–ZrO₂ molten slag is produced as a result of deoxidation of metals. The solubility of calcium and oxygen in molten iron deoxidized with metallic calcium in lime, alumina or magnesia crucibles was investigated by several researchers until 1999 and summarized by Hino and Ito.1) They determined the recommendable thermodynamic values of the interaction parameters of elements in molten iron and the equilibrium constants of the decomposition of metal oxides and sulfides. The solubility of calcium and oxygen in molten iron was measured under Ar or H₂ gas without molten slag.2–4) Because the partial pressure of calcium vapor on liquid calcium is 1.8 atm at 1 873 K, calcium is difficult to dissolve into immiscible molten iron with calcium5) and is easy to vaporize from the free surface of molten iron. Suito et al.6) measured aluminum, calcium and oxygen concentrations in molten iron deoxidized by aluminum in Al₂O₃ crucibles with and without CaO–Al₂O₃ slag. They showed that the concentration of oxygen in molten iron without slag was lower than that with slag. This means that it could be difficult to attain the equilibrium between molten iron, gas and crucible phases.

The equilibration of soluble calcium and oxygen in molten iron with CaO in solid or molten slag is expressed as CaO(s) = Ca+O. The solubility product of soluble calcium and oxygen can be determined from temperature and the activity of lime. In the case that CaO–Al₂O₃–ZrO₂ molten slag covers molten iron in lime, alumina and CaO-stabilized zirconia crucibles, the activity of CaO is fixed at a constant temperature. According to the ternary phase diagram of CaO–Al₂O₃–ZrO₂ system as shown in Fig. 1 determined by Murakami et al.,7) the slag in a CaO crucible is equilibrated with CaO and CaO·ZrO₂ compound, that in an Al₂O₃ crucible is equilibrated with CaO·2Al₂O₃ compound and ZrO₂–CaO solid solution (Css) and that in a CaO-stabilized ZrO₂ crucible is equilibrated with ZrO₂–CaO solid solution (Css) and CaO·ZrO₂ compound. Nagata et al.8) measured the activity of CaO in CaO–Al₂O₃ system and Tanabe et al.9) measured it in CaO–ZrO₂ system by means of an electrochemical method. Tanabe et al.10) measured the activity of Al₂O₃ in CaO–Al₂O₃–ZrO₂ molten slag in equilibrium with molten iron in a CaO-stabilized ZrO₂ crucible at 1 873 K. Seki et al.11) also measured the activity of ZrO₂ in CaO–Al₂O₃–ZrO₂ molten slag in equilibrium with molten iron in an Al₂O₃ crucible at 1 873 K.

In the present study, the solubility of calcium and oxygen in molten iron in equilibrium with CaO–Al₂O₃–ZrO₂ molten
slag in CaO, Al₂O₃ or CaO-stabilized ZrO₂ crucible at 1873 K has been measured. The interaction parameters of soluble calcium and oxygen and the equilibrium constant of the reaction of CaO = Ca + O have been also determined and the interaction parameters including literature data have been examined from the view point of thermodynamic phase stability.

2. Experiments

The slag was prepared from the mixture of CaCO₃, Al₂O₃, and ZrO₂ powders (> 99.9 mass%). The initial composition of slag is listed in Table 1. Each composition of slag was determined to be in equilibrium with other two compounds in the CaO–Al₂O₃–ZrO₂ system in a CaO, Al₂O₃ or 5.5 mass% CaO-stabilized ZrO₂ crucible at 1873 K, respectively. Electrolytic iron including oxygen of 300–1000 ppm was used. 3 g of slag and 7 g of iron were melted in a crucible, as listed in Table 1. The crucible was heated in a reaction chamber of graphite tube which was set in a vertical resistance furnace with MoSi₂ heating elements, as shown in Fig. 2. The temperature was measured with a Pt/Pt-13%Rh thermocouple and controlled to be at 1873 ± 2 K in the range of 40 mm length. The lower part of the reaction tube was dipped in water bath in order to quench sample. When the reaction chamber was made in vacuum after setting sample, the lower edge of reaction tube was closed by a rubber plate without sucking water. The rubber plate was taken out after filling the reaction chamber with Ar gas. During heating furnace, the temperature of water was kept at room temperature of about 283 K at which water vapor was 0.13 Pa. Slag covered molten iron and prevented it from reaction with water.

After making the reaction chamber in vacuum during 1200 s, dried and deoxidized Ar gas was blown into a crucible with the flow rate of 2 Nm³/s. The oxygen partial pressure in Ar gas was measured with an oxygen sensor composed of a CaO-stabilized ZrO₂ tube with 13 mm diameter and 50 mm length as a solid electrolyte and the mixed powder of Cr and Cr₂O₃ as a reference electrode. The sensor was installed near the outlet of gas in the upper part of reaction chamber, as shown in Fig. 2. The oxygen partial pressure in Ar gas was 8.3 × 10⁻²⁷ Pa at 1100 K.

After the samples were kept in melt at 1873 K for 1200 s, 0.05 g of calcium blocks as deoxidizer sealed in an iron capsule were added to molten iron. The samples were kept in melt at 1873 K for 1200 s, 0.05 g of calcium blocks as deoxidizer sealed in an iron capsule were added to molten iron. The samples were kept in melt at 1873 K for 1200 s, 0.05 g of calcium blocks as deoxidizer sealed in an iron capsule were added to molten iron.

![Fig. 1. Slag compositions in equilibrium with oxide compounds in CaO, Al₂O₃ and CaO-stabilized ZrO₂ crucibles, respectively, on the phase diagram of CaO–Al₂O₃–ZrO₂ system at 1873 K.](image1)

![Fig. 2. Schematic diagram of the experimental apparatus.](image2)

| Run No. | Crucible                  | Initial composition of slag/mol% | Weight of slag/g | Weight of Ca/g | Capsule | Electrolytic | Total    |
|---------|---------------------------|----------------------------------|-----------------|----------------|---------|--------------|----------|
| 1       | Al₂O₃                     | 41.45 44.97 13.59                | 2.996           | 0.057          | 0.488   | 7.207        | 7.695    |
| 2       | CaO-stabilized ZrO₂       | 45.37 42.36 12.28                | 3.006           | 0.044          | 0.606   | 7.348        | 7.954    |
| 3       | CaO                        | 71.63 23.95 4.42                 | 2.703           | 0.055          | 0.398   | 7.094        | 7.492    |
| 4       | CaO-stabilized ZrO₂       | 45.37 42.36 12.28                | 3.000           | 0.009          | 0.398   | 7.596        | 7.994    |
| 5       | CaO                        | 71.63 23.95 4.42                 | 2.706           | 0.051          | 0.493   | 7.093        | 7.586    |
capsule was dropped into molten iron through slag layer using an alumina tube with about 1 m length. Calcium vapor generated during deoxidizing molten iron. After 3 600 s, the sample was dropped into water and quenched. In order to confirm the equilibration, the holding time was changed during 1 800 s and 10 800 s.

The ICP-OES (IRIS Advantage-Duo/Thermo Fisher Scientific, Inc.) was used to measure the concentrations of aluminum, calcium and zirconium in a quenched iron sample. The spectral lines for analysis were 396.152 nm for Al I, 393.368 nm for Ca II and 339.198 nm for Zr I. 0.5 to 0.8 g of iron sample was exactly weighed into a PTFE vessel and dissolved with the solution composed of 2 ml of 12 N HCl (electronics industry grade), 2 ml of 14 N HNO₃ (same grade) and 10 ml of deionized water (Millipore Corp.) at 420 K using a heating plate. After cooling the solution to room temperature, the solution was exactly diluted with 50 ml of water. The amounts of Al, Zr and Ca in the solution were determined by the ICP-OES with the sensitivity of 0.0001 mass% Al, 0.0003 mass% Zr and 0.0005 mass% Ca. A blank test was examined using the solution without sample. In order to calibrate the concentrations, three standard solutions of 1 g·dm⁻³ were produced of aluminum (99.99%), calcium carbonate (CaCO₃) (99.99%) and zirconium (99.999%) in an appropriate acid, respectively. For the analysis of oxygen in iron, the LECO TC-436 (LECO Corp.) with the sensitivity of 0.0001 mass% is employed. 0.5 to 0.6 g of iron sample was put into a graphite crucible and was heated at 2 363 K in helium atmosphere. Oxygen in a sample was extracted and reacted with graphite to produce carbon dioxide gas. The amount of carbon dioxide gas was measured by means of an infrared absorption method and the amount of oxygen in iron sample was determined. The reference materials made by LECO Corp. were employed for the calibration of oxygen in iron sample.

3. Results

3.1. Slag Compositions

Figure 3(a), 3(b) and 3(c) show the diffraction spectrums of XRD on oxide compounds which were equilibrated with molten slag and precipitated from slag during cooling in Al₂O₃, CaO-stabilized ZrO₂ and CaO crucibles, respectively. In a CaO crucible, 3CaO·Al₂O₃ and CaO·ZrO₂ are detected as well as CaO. The intensity of XRD peaks of 3CaO·Al₂O₃ is stronger than the others. From the CaO–Al₂O₃–ZrO₂ phase diagram as shown in Fig. 1, 3CaO·Al₂O₃ decomposes at 1 873 K and the molten slag is equilibrated with CaO·ZrO₂ and CaO. The composition of slag is 71.63 mol% CaO-23.95 mol% Al₂O₃-4.42 mol% ZrO₂. In an Al₂O₃ crucible, a solid solution of ZrO₂ with CaO (Css) and CaO·Al₂O₃ are detected. The intensities of peaks of a solid solution of ZrO₂ with CaO (Css) and CaO·Al₂O₃ are stronger than CaO·2Al₂O₃. Thus, the slag is equilibrated with a

![Fig. 3. Diffraction spectrums of XRD on oxide compounds in quenched slag in a) Al₂O₃, b) CaO-saturated ZrO₂ and c) CaO crucibles, respectively.](image-url)
solid solution of ZrO₂ with CaO (Css) and CaO-2Al₂O₃. The slag composition is 41.45 mol% CaO-44.97 mol% Al₂O₃-13.59 mol% ZrO₂. In a CaO-stabilized ZrO₂ crucible, a solid solution of ZrO₂ with CaO (Css), CaO-ZrO₂ and CaO-Al₂O₃ are detected. The intensity of peak of CaO-ZrO₂ is much smaller than the others. The molten slag is in equilibrium with a solid solution of ZrO₂ with CaO (Css) and CaO-ZrO₂. The compositions of slag is 45.37 mol% CaO-42.36 mol% Al₂O₃-12.28 mol% ZrO₂.

3.2. Concentrations of Elements in Iron Samples

The concentrations of oxygen and calcium in molten iron decreased and became almost constant after 3 600 s after adding calcium, as shown in Fig. 4. Table 2 shows the concentrations of calcium, aluminum, zirconium and oxygen in iron samples in CaO, Al₂O₃ and CaO-stabilized ZrO₂ crucibles at 1 873 K, respectively. 7 iron samples were obtained. Each element in a sample was analyzed one to four times and the concentrations were averaged.

Figure 5 shows the present results of logarithm-logarithm plots of calcium and oxygen concentrations in molten iron in equilibrium with CaO–Al₂O₃–ZrO₂ slag and compounds in CaO, Al₂O₃ and CaO-stabilized ZrO₂ crucibles at 1 873 K. Open triangles, circles and squares represent the concentrations in CaO, Al₂O₃ and CaO-stabilized ZrO₂ crucibles, respectively.

![Graph](image)

**Table 2.** Concentrations of oxygen, calcium, aluminum and zirconium in molten iron in equilibrium with slag.

| Run No. | Concentration of elements in molten iron/mass% | Crucible | Equilibrated composition of slag/mol% | Compounds in equilibrium with slag |
|---------|---------------------------------------------|----------|-------------------------------------|----------------------------------|
| O       | Ca                                         | Al       | Zr                                  |                                  |
| 1       | 0.0044 0.0004 0.0017 0.0032                 |          | Al₂O₃ 41.45 44.97 13.59 ZrO₂–CaO (Css) and 2CaO-Al₂O₃ |
| Av.     | 0.0040 0.0004 0.0016 0.0032                 |          |                                    |                                  |
| 2       | 0.0031 0.0005 0.1140 0.0070                 | CaO-stabilized ZrO₂ 45.37 42.36 12.28 ZrO₂–CaO (Css) and CaO-ZrO₂ |
|          | 0.0021 0.0003 0.1130 0.0057                 |          |                                    |                                  |
|          | 0.0834                                       |          |                                    |                                  |
|          | 0.0683                                       |          |                                    |                                  |
| Av.     | 0.0026 0.0004 0.0947 0.0063                 |          |                                    |                                  |
| 3       | 0.0015 <0.0005 0.0044 <0.0003               |          |                                    |                                  |
|          | 0.0013 0.0010 0.0043 <0.0003                 |          |                                    |                                  |
| Av.     | 0.0014 0.0008 0.0044 0.0003                  |          |                                    |                                  |
| 4       | 0.0020 <0.0005 0.0033 <0.0003               |          |                                    |                                  |
|          | 0.0020                                       |          |                                    |                                  |
| Av.     | 0.0020 0.0005 0.0033 0.0003                  | CaO-stabilized ZrO₂ 45.37 42.36 12.28 ZrO₂–CaO (Css) and CaO-ZrO₂ |
| 5       | 0.0031 0.0003 0.0889 0.0065                 |          |                                    |                                  |
|          | 0.0027 0.0003 0.0838 0.0064                 |          |                                    |                                  |
|          | 0.0788                                       |          |                                    |                                  |
|          | 0.0782                                       |          |                                    |                                  |
| Av.     | 0.0029 0.0003 0.0824 0.0064                  |          |                                    |                                  |
| 6       | 0.0268 0.0002 0.0003 0.0032                 | CaO 71.63 23.95 4.42 CaO-ZrO₂ and CaO |
|          | 0.0250 0.0002 0.0002 0.0031                 |          |                                    |                                  |
| Av.     | 0.0259 0.0002 0.0003 0.0032                  |          |                                    |                                  |
| 7       | 0.0249 0.0005 0.0003 0.0032                 |          |                                    |                                  |
|          | 0.0238 0.0002 0.0002 0.0031                 |          |                                    |                                  |
| Av.     | 0.0244 0.0004 0.0003 0.0032                  |          |                                    |                                  |
4. Discussions

4.1. Comparison of the Concentrations of Calcium and Oxygen in Molten Iron with Literatures

Miyashita et al.\(^4\) showed that when molten iron in a MgO or Al\(_2\)O\(_3\) crucible without slag in Ar gas was deoxidized by calcium, oxygen concentration in molten iron was rapidly decreased to be constant, while slag concentration initially increased and gradually decreased. Suito et al.\(^5\) showed that the deoxidation of molten iron by aluminum in Al\(_2\)O\(_3\) and CaO crucibles with CaO–Al\(_2\)O\(_3\) slag made the almost same oxygen concentration in iron in both crucibles, even though oxygen concentration in a CaO crucible should be higher than that in an Al\(_2\)O\(_3\) crucible, because the activity of CaO is unity in a CaO crucible and is 0.25 in equilibrium with CaO–2Al\(_2\)O\(_3\) in an Al\(_2\)O\(_3\) crucible.\(^6\)

These results show that calcium added into molten iron rapidly reacts with oxygen to produce CaO and gradually vaporizes from the free surface of molten iron. The solid particles of CaO float and adhere on the wall of crucible, while CaO in a crucible hardly decomposes to calcium and oxygen because of the positive interfacial energy and the small contact area between molten iron and the wall of oxide crucible. Therefore, the concentrations of oxygen and calcium in molten iron with the free surface hardly attain the equilibrium with CaO in a crucible and tend to become lower.

As shown in Fig. 5, the concentrations of calcium and oxygen in a CaO crucible are larger than those in an Al\(_2\)O\(_3\) and CaO-stabilized ZrO\(_2\) crucibles. The reason is that the activity of CaO in slag in an Al\(_2\)O\(_3\) crucible is 0.03 within crucibles with CaO–Al\(_2\)O\(_3\) slag made the almost same oxygen equilibrium with CaO in a crucible and tend to become lower.

As shown in Fig. 5, the concentrations of calcium and oxygen in a CaO crucible are larger than those in an Al\(_2\)O\(_3\) and CaO-stabilized ZrO\(_2\) crucibles. The reason is that the activity of CaO in slag in an Al\(_2\)O\(_3\) crucible is 0.25 in equilibrium with CaO–2Al\(_2\)O\(_3\) in an Al\(_2\)O\(_3\) crucible.\(^7\)

Fig. 5. Relation between the concentrations of calcium and oxygen in molten iron in equilibrium with slag in CaO (△), Al\(_2\)O\(_3\) (○) and CaO-stabilized ZrO\(_2\) (□) crucibles at 1 873 K. The solid lines were calculated from K and the interaction parameters by the least square method.

Table 3. Calculated activity of calcium and oxygen in molten iron and CaO in slag at 1 873 K.

| Run No. | Crucible           | Calculated activity | Ca   | O   | CaO  |
|--------|--------------------|---------------------|------|-----|------|
|        |                    |                     |      |     |      |
| 1      | Al\(_2\)O\(_3\)     | 5.36 \times 10\(^{-4}\) | 3.96 \times 10\(^{-4}\) | 0.037 |
| 2      | CaO-stabilized ZrO\(_2\) | 4.82 \times 10\(^{-4}\) | 1.97 \times 10\(^{-3}\) | 0.023 |
| Av.    |                    |                     | 0.030 |
| 3      | CaO-stabilized ZrO\(_2\) | 8.31 \times 10\(^{-4}\) | 1.41 \times 10\(^{-4}\) | 0.028 |
| 4      | CaO-stabilized ZrO\(_2\) | 5.79 \times 10\(^{-4}\) | 2.01 \times 10\(^{-4}\) | 0.028 |
| 5      | CaO-stabilized ZrO\(_2\) | 3.70 \times 10\(^{-4}\) | 2.27 \times 10\(^{-3}\) | 0.020 |
| Av.    |                    |                     | 0.025 |
| 6      | CaO                | 1.33 \times 10\(^{-3}\) | 2.54 \times 10\(^{-2}\) | 0.81 |
| 7      | CaO                | 2.08 \times 10\(^{-3}\) | 2.40 \times 10\(^{-2}\) | 1.20 |
| Av.    |                    |                     | 1.00  |
been calculated from the determined values and well represent the experimental values.

4.3. Criterion of the Interaction Parameter of e_{Ca} from the Thermodynamic Phase Stability

The interaction parameter between calcium and oxygen in molten iron can be examined using the criterion of thermodynamic phase stability. Prigogine et al.\(^1\) thermodynamically established that the necessary and enough conditions of ternary phase stability (1-2-3 system) are expressed as

\[ \mu_1 \geq 0, \mu_2 \geq 0 \] ............................................... (6)

and

\[ \mu_1 + \mu_2 - \mu_i^2 \geq 0 \] ........................................ (7)

where

\[ \mu_i = (\partial \mu_i / \partial n_i)_{n_j} \].......................... (8)

\[ \mu_i \] is chemical potential of \( i \) element and expressed as

\[ \mu_i = \mu_i^0 + RT \ln f_i \] ....................................... (9)

\( n_j \) is mol of element \( j \).

\[ [\text{mass}\% i] = 100n_i / (M_1 n_1 + M_2 n_2 + M_3 n_3) (i = 1, 2, 3) \] ............................................. (10)

From Eq. (6),

\[ \mu_i = (\partial \mu_i / \partial n_i)_{n_j} n_i \] .......................... (11)

As

\[ \log f_i / [\text{mass}\% i] = e_i^i, \]

\[ e_i^i \geq -1 / 2.303 \] [mass\% \( i \)] ........................... (11)

From Eq. (7),

\[ |e_i^i| \leq \sqrt{\frac{M_i}{M_j}} \cdot \left( e_i^i + 1/2.303 [\text{mass}\% j] \right) + 1/230.1 \cdots (12) \]

where [mass\% \( i \)] is the maximum concentration of \( i \) element that Eq. (2) is valid. From the ISIJ recommended data,\(^1\) as

\[ [\text{mass}\% Ca] < 0.0174 \] and \[ [\text{mass}\% O] < 0.003, e_{Ca}^{Ca} \geq -25.0, e_0^{O} \geq -144.7 \] and \[ -38.0 \leq e_0^{Ca} \leq 38.0 \]. The data of \( e_{Ca}^{Ca} \) of \(-0.002\) and \( e_0^{O} \) of \(-0.17\) are satisfied the criterion, while the absolute value of \(-515\) of \( e_0^{Ca} \) recommended by ISIJ is much larger than the criterion range. In the present work, [mass\% Ca] \( < 0.0010 \) and [mass\% O] \( < 0.0044 \). Then, \( e_0^{Ca} \geq -434, e_0^{O} \geq -98.7 \) and \( 131 \leq e_0^{Ca} \leq 131 \). \( e_0^{Ca} \) of 31.8 is satisfied the criterion range. The values of \( e_0^{Al}, e_{Ca}^{Al} \) and \( e_0^{Si} \) are satisfied the criterion.

4. Conclusions

The concentrations of calcium, oxygen, aluminum and zirconium dissolved in molten iron in equilibrium with CaO–Al2O3–ZrO2 slag and two compounds were measured at 1873 K. The values of logK and \( e_{0}^{Ca} \) are \(-4.38\) and 31.8, respectively, and are satisfied the criterion of thermodynamic phase stability.

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