

Experimental Study on the Activities of Al and Ca in Ferrosilicon



SILVIA TOMÉ-TORQUEMADA, BJÖRN GLASER, KJETIL HILDAL, and DU SICHEN

Experiments were carried out to determine the activities of Al and Ca in liquid ferrosilicon (with about 50 wt pct Si) at 1823 K (1550 °C) in their dilution ranges. Liquid FeSi50 and SiO₂-Al₂O₃-CaO slag were stirred mechanically in a graphite crucible to enhance the transfer of Al and Ca between the two phases. The stirring time for the two phases to reach equilibrium was studied. It was found that a time of 45 minutes was long enough to reach the slag-metal equilibrium. The activities of Al and Ca in the ferrosilicon alloy were calculated based on the compositions of the two liquid phases. The activity coefficients obtained for Al and Ca in the liquid FeSi50 at 1823 K (1550 °C) were found to be nearly constant in the composition range studied.

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I. INTRODUCTION

THE largest application of ferrosilicon is in the alloying of steel and cast iron. In cast iron, ferrosilicon is used, together with some other elements, as a nodularizer to change the graphite shape from flakes to spheres during solidification. Nodular graphite improves the properties of the cast iron. Ferrosilicon, as a source of Si, is also used to increase the elasticity, annealing resistance, and tensile yield in steels.^[1-3] Due to the increasing demand on steel quality, the purity of the additives is becoming an important matter in steelmaking. More attention is being paid to control the impurities of the ferrosilicon in ppm levels.^[1,4] Aluminum and calcium are some of the main impurities found in industrial ferrosilicon. As both elements have a higher oxygen affinity than silicon, they can be removed through a liquid silicon oxidative refining process in which oxygen can be introduced as gaseous oxygen through a porous bottom plug and/or as an oxidizing slag.^[5,6]

In order to establish a predictive process control of the refining of the ferrosilicon, the thermodynamic data for Al and Ca in liquid ferrosilicon are essential.

Dumay and Allibert^[7] equilibrated several FeSi65 alloys with SiO₂-Al₂O₃-CaO slags at 1623 K, 1723 K, and 1823 K (1350 °C, 1450 °C, and 1550 °C) in

SiC-coated crucibles under Ar atmosphere. The activity coefficients for Al and Ca in FeSi65 were also calculated to be $\gamma_{\text{Al}}^{\circ} = 0.65 \pm 0.2$ and $\gamma_{\text{Ca}}^{\circ} = 0.003 \pm 0.001$, respectively.

Tuset^[5] equilibrated FeSi75 alloys with SiO₂-Al₂O₃-CaO slags at 1773 K and 1873 K (1500 °C and 1600 °C). Based on the experimental results, the activity coefficients obtained for Al and Ca in FeSi75 are $\gamma_{\text{Al}}^{\circ} = 0.45$ and $\gamma_{\text{Ca}}^{\circ} = 2.1 \times 10^{-3}$, respectively.

Dumay *et al.*^[8] determined the activities of Al, Ca, and Si in liquid Fe-Si-Al-Ca alloys using a Knudsen mass spectrometric technique. The composition range studied was 0-55 wt pct Fe, 0-0.5 wt pct Al, and 0-0.5 wt pct Ca. The range of temperature varied between 1523 K and 1923 K (1250 °C and 1650 °C). The authors reported the following activity coefficient values: $\gamma_{\text{Al}}^{\circ} = 0.67$ and $\gamma_{\text{Ca}}^{\circ} = 3 \times 10^{-3}$ for FeSi65 at 1723 K (1450 °C) and $\gamma_{\text{Al}}^{\circ} = 0.84$ for FeSi45 at 1723 K (1450 °C).

Ageev *et al.*^[9] studied the equilibrium distribution of aluminum between FeSi75 and different SiO₂-Al₂O₃-CaO slags in the temperature range between 1723 K (1450 °C) and 1973 K (1700 °C) in covered graphite crucibles. The experimental duration was 0.5 to 2 hours depending on the temperature. It was concluded that for slags containing up to 30 wt pct Al₂O₃, the amount of Al dissolved in the FeSi75 depends greatly on the SiO₂ content of the slag (higher Al in the alloy for lower SiO₂ concentrations in the slag).

To the best of our knowledge, there are no available experimental thermodynamic data for FeSi50. Although the activities of Al and Ca could be calculated using thermodynamic software, the experimental measurements provide the equilibrium concentrations of the elements in the liquid metal. These experimental data

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will help the ferrosilicon industries use the thermodynamic software more efficiently and optimize their process. The data can also be valuable in the improvement of the thermodynamic databases. In view of the importance of the experimental data for the ferrosilicon industry, the present work focuses on the determination of the activities of Ca and Al in the liquid FeSi50 alloys, with dilute Ca and Al.

II. EXPERIMENTAL

A. Experimental setup

The experimental setup is illustrated in Figure 1. The details of the setup have been described in a previous publication.^[10] An electrical tube furnace with Kanthal super heating elements and an alumina reaction tube were used. The reaction tube was sealed at its ends with o-rings, with a water-cooled cap, made of aluminum, on the bottom and a water-cooled quenching chamber, made of brass, on the top. A 2404 Eurotherm controller was used to control the furnace temperature through a type B thermocouple (70 pct Pt/30 pct Rh-94 pct Pt/6 pct Rh) mounted in the wall of the furnace. Another type B thermocouple, with its tip positioned just below the sample holder (as seen in Figure 1), was used to measure the sample temperature.

The reaction gas entered the bottom of the furnace and exited through the upper part of the furnace. Two additional gas inlets were allocated in the quenching chamber to introduce Ar of high flow for fast quenching of the sample. A graphite holder attached to a steel tube was used to hold the crucible in the hot zone of the furnace. The steel support tube was fastened to a motorized lift that enabled lowering the sample from the quenching chamber to the hot zone of the furnace and rapidly moving the sample from the hot zone of the furnace to the quenching chamber.

Mechanical stirring was used in order to reduce the time to reach equilibrium between the metal and slag phase. The graphite impeller used to stir the metal–slag mixture was connected to a graphite extension rod that was threaded into a stainless steel impeller shaft. The upper end of the impeller shaft was connected to a Eurostar variable-speed stirring motor that was fastened to the motorized lift and could therefore move in the longitudinal axis of the furnace.

Figure 2 shows a more detailed view of the sample holder assembly. The assembly, completely made of graphite, consisted of a holding crucible, a working crucible wherein the sample was kept, a support cap, a support ring, and a support tube. The support tube was fastened into the lower end of the stainless steel support by means of a threaded stainless steel adaptor. The support cap was mounted on the support tube using a threaded supporting ring. The holding crucible was attached to the support cap with threaded graphite pins. The working crucible had a quatrefoil profile made by boring four 18-mm holes into a graphite cylinder of 38 mm in diameter. The working crucible was placed inside the holding crucible and the lower part of the impeller

used for stirring was located 5 mm above the base of the working crucible during stirring.

B. Material Preparation

The FeSi utilized in this study was FeSi50 provided by Elkem Technology and the composition was 52.2 wt pct Si, 47.12 wt pct Fe, 0.57 wt pct Al, and 0.11 wt pct Ca. Different compositions of SiO₂-Al₂O₃-CaO slags were used in this study. The oxide powders (SiO₂ 99.5 pct purity provided by Alfa Aesar, Al₂O₃ 99.7 pct purity provided by Sigma-Aldrich, and CaO 98 pct purity provided by Alfa Aesar) were first dried at 1173 K (900 °C) to remove the moisture and absorbed gases. Once dried, the oxides were mixed in an agate mortar and pellets with the desired composition were pressed. The pellets were placed inside a graphite crucible with walls coated with ZrO₂ (provided by ZYP coatings) in order to reduce the oxidation of the crucible. The coated crucible, with the slag pellets inside, was heated to 1923 K (1650 °C) in an induction furnace in air atmosphere. When the slag was completely molten, slag was quenched in air, crushed into small pieces, and stored in a desiccator until use. The pre-molten slags were analyzed with x-ray fluorescence (XRF) prior to the experiments.

C. Procedure

In a typical run, 90 grams of FeSi50 was placed in the working crucible. This crucible was then placed into the holding crucible and the whole sample holder assembly previously described was fastened to the steel support tube. Note that the sample holder assembly was kept in the quenching chamber until the target temperature of the furnace was reached.

After the whole system was sealed, the alumina tube was evacuated and filled with the reaction gases (2 pct CO–98 pct Ar gas mixture). A total gas flow rate of 0.05L/min was maintained throughout the whole experiment. The furnace was heated up with a heating rate of 1.5 to 2 K/min. Once the target temperature of the furnace was reached, the sample was lowered slowly to the resting position that was at about 1423 K (1150 °C). In this way, the crucible could be preheated without melting the sample so that the thermal shock of the reaction alumina tube was minimized. The sample was kept at this temperature for 15 minutes before being lowered all the way down to the final position in the hot zone of the furnace. Preliminary experiments indicated that the ferrosilicon would be completely molten after 10 minutes. Thereafter, the FeSi was rapidly raised to the water-cooled quenching chamber with the motorized lift and a high flow of Ar gas initiated in the water-cooled quenching chamber to favor the quenching of the sample. Once the crucible had cooled down, the graphite assembly was removed from the quenching chamber and the crushed pre-molten slag was added to the working crucible, on top of the FeSi. The slag-to-ferrosilicon mass ratio was 1:2. The crucible was placed into the holding crucible again and the whole graphite sample holder assembly was fastened to the steel tube following

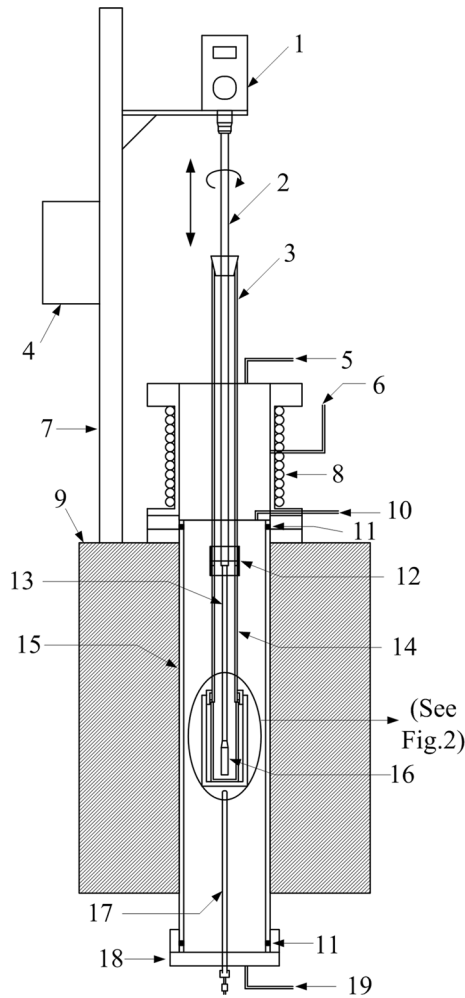


Fig. 1—Experimental setup showing the constituent parts: 1. Stirring motor; 2. Stainless steel impeller shaft; 3. Steel support tube; 4. Lifting motor; 5. Gas outlet; 6. Gas inlet; 7. Lift tracks; 8. Water-cooled quenching chamber; 9. Furnace body; 10. Gas outlet; 11. O-ring seal; 12. Stainless steel coupling; 13. Graphite extension rod; 14. Graphite support tube; 15. Alumina reaction tube; 16. Graphite impeller; 17. Thermocouple; 18. Water-cooled cap; 19. Gas inlet.

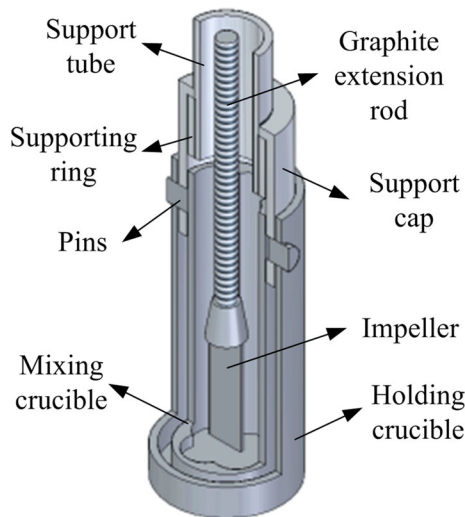


Fig. 2—Isometric view of the graphite assembly.

the same procedure as before. The crucible was lowered slowly with the motorized lift to the resting position at 1423 K (1150 °C) and kept there for 15 minutes before lowering it down to the hot zone of the furnace. It took approximately 8 minutes to melt the slag and ferrosilicon. After the melting period, the graphite impeller was lowered into the liquid bath and stirring was started. To ensure the moment when slag and ferrosilicon were molten, the impeller was pushed down until it was possible to touch the bottom of the crucible. The impeller was then moved up so that it was located 5 mm above the base of the working crucible while stirring. The stirring speed was set to 100 rpm, which was determined by a previous work.^[10] Increasing the stirring speed above 100 rpm had negligible effect on the reaction rate. Stirring times varied from 90 seconds to 1 hour. At the end of each run, the assembly was lifted to the water-cooled quenching chamber and quenched. Once the crucible was cooled down, it was removed from the quenching chamber. The weight of the samples was measured before and after to check if there was a considerable SiO formation. The ferrosilicon and slag were carefully separated and cleaned, and special attention was paid to remove all possible slag pieces from the ferrosilicon samples.

D. Analyses

Chemical analyses of the samples were conducted at Elkem Technology analytical laboratory. The aluminum, calcium, and iron contents of the ferrosilicon and the slag were analyzed using atomic adsorption spectroscopy (AAS) with a Varian AA280FS atomic adsorption spectrometer. To prepare the solution for AAS analysis, the FeSi sample was crushed. HNO₃ was added to a suitable amount of sample, which was followed by HF addition until the sample was completely dissolved. Finally HClO₄ was added. Thereafter, the sample was heated until it becomes dry in a platinum beaker. The salts obtained were then dissolved in HCl and transferred to a 100-mL flask prior to analysis. The slag was milled to powder and then 0.1 grams of the powder was put into a platinum crucible together with LiBO₂. The sample was heated to 1223 K (950 °C), and once cooled, it was dissolved in diluted HNO₃ and transferred to a 100-mL flask. The carbon content in the FeSi was analyzed with LECO combustion analysis.

III. RESULTS

To obtain the time required for the slag to reach equilibrium with the ferrosilicon melt, the first series of experiments were carried out using the same slag composition but with different time durations. In all these experiments, an initial slag composition of 49.8 wt pct SiO₂, 21.7 wt pct Al₂O₃, and 28.5 wt pct CaO was used and the metal-to-slag ratio of 2:1 was employed. Figure 3(a) shows the variation of the Al and Ca contents in the ferrosilicon as a function of the stirring time at 1823 K (1550 °C). Both the aluminum and

calcium contents in the metal decrease exponentially. No significant change in the concentration is observed after 45 minutes of stirring in the case of both Al and Ca, thereby indicating that slag and metal have reached thermodynamic equilibrium after 45 minutes. As shown in Figure 3(b), no large variation in the CaO content in the slag was found with stirring time. The Al₂O₃ content, however, slightly increased with time until it becomes almost constant after 30 minutes. Note that due to the relatively large amount of the slag, the slag composition is not expected to change with time as shown in Figure 3(b). Hence, in the rest of the experiments, which focused on thermodynamic equilibrium, a stirring time of 60 minutes was employed.

Table I presents the compositions of the slag and metal after equilibration along with the experimental conditions. FeO contents in all the slag samples and C content in the FeSi samples after equilibration were analyzed. The FeO contents were found to be lower than 0.27 wt pct. In case of extremely low FeO contents, they are not included in the table and are not considered in any calculation. The C content in the FeSi was also very low, being below 0.024 wt pct. This finding is in agreement with the previous work.^[11]

IV. DISCUSSION

A. Equilibrium

Figure 3(a) shows evidently that the equilibrium between the metal and slag phase has reached after 45 minutes. This is in very good accordance with a previous work performed in the current laboratory.^[10,12] The results indicate that mechanical stirring reduces considerably the equilibration time.

The oxygen potential plays a crucial role in the equilibrium of the present system. Thermodynamic calculations reveal that the equilibrium of graphite with a gas mixture of 2 pct CO–98 pct Ar would result in an oxygen potential pressure 1.22×10^{-19} atm,^[13] which is about two orders of magnitude lower than the slag–silicon equilibrium. Note that both the crucible and the crucible holder used in the experiments (Figure 1) have relatively large heights. As is common knowledge, since very low gas flow rate was used the mass transfer of oxygen in the reaction crucible would be mainly due to gas diffusion, which is an extremely slow process at such low oxygen concentration. Hence, the oxygen potential at the slag–metal interface is expected to be controlled by silicon activity in the melt. In fact, the slight increase of alumina content in the slag in the initial stage of the process and the almost constant value after 30 minutes further confirms this aspect. If the oxygen potential in the gas phase outside the holder is dominating, a decrease of alumina content in the later stage in the slag should definitely be noticed. As a matter of fact, the thermodynamic calculation in the later discussion confirms again this argument.

The use of graphite crucible would lead to the formation of silicon carbide. However, the solubility of carbon in the liquid ferrosilicon is very low. The

extremely low carbon concentration in the melt would have negligible effect on silicon activity.

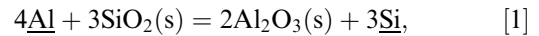
To examine the reproducibility of the experiments, some experiments were repeated. This is exemplified by the two runs with a stirring time of 5 minutes in Figure 3. The differences between the two runs are within the uncertainty level of the chemical analyses.

B. Effect of Slag Composition

The aluminum content in FeSi after equilibration at 1823 K (1550 °C) is plotted as a function of the Al₂O₃ composition in the slag after the experiment in Figure 4. In general, the final Al content in the metal increases with the increasing alumina content in the slag. However, for alumina concentrations below 25 wt pct, the effect of the alumina content is not as profound as for higher alumina content. The increasing trend of Al with Al₂O₃ in the slag is in agreement with those reported by Dumay and Allibert,^[7] Tuset,^[5] and Ageev *et al.*^[9] where the higher the final alumina content in the slag, the higher the Al content in the ferrosilicon.

C. Activity of Al in FeSi50 at 1823 K (1550 °C)

One way to describe the reaction between aluminum dissolved in ferrosilicon and the slag is given below.



where the underlined elements are dissolved in the liquid metal phase.

The standard Gibbs energy for Eq. [1], ΔG_1° , can be found in the literature^[13]:

$$\Delta G_1^\circ = -505340 + 37.1 \times T \text{ J/mol}, \quad [2]$$

where the temperature is in Kelvin. The standard states for Eq. [1] are pure solid for Al₂O₃ and SiO₂ and pure liquid for Al and Si. The equilibrium constant for Eq. [1] can be expressed as

$$k_1 = \frac{a_{\text{Al}_2\text{O}_3}^2 \times a_{\text{Si}}^3}{a_{\text{SiO}_2}^3 \times a_{\text{Al}}^4}, \quad [3]$$

where $a_{\text{Al}_2\text{O}_3}$ and a_{SiO_2} are the activities of solid alumina and solid silica, and a_{Si} and a_{Al} are the activities of liquid silicon and liquid aluminum, respectively.

The activities of the oxides ($a_{\text{Al}_2\text{O}_3}$ and a_{SiO_2}) together with the activity of silicon can be calculated using FactSage^[14] or Thermo-Calc.^[15] Once these activities are known, the activity of aluminum can then be calculated from Eq. [3]. Activities of Al calculated using both software are presented in Table II along with the activity data calculated using both FactSage^[14] and Thermo-Calc.^[15] FTlite database was used in FactSage^[14] to calculate the Si activity and TCFE8 (Steels/Fe Alloys v8.0) in Thermo-Calc.^[15] For the calculation of the activities of the oxides, FToxid was used in FactSage^[14] and TCOX5 (Metal Oxide Solutions v5.1) in Thermo-Calc.^[15]

As shown in Table II, there are some discrepancies in the oxides and silicon activities calculated using the two

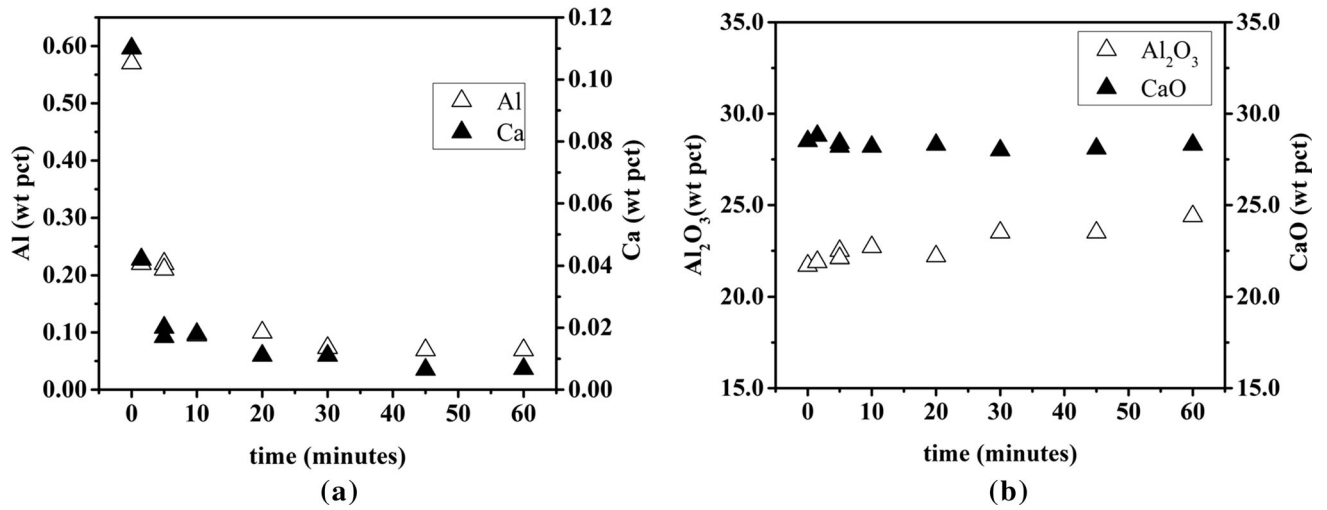


Fig. 3—Effect of stirring time for an initial slag composition of 49.8 wt pct SiO₂, 21.7 wt pct Al₂O₃, and 28.5 wt pct CaO at 1823 K (1550 °C) on (a) Al and Ca contents in the FeSi and (b) Al₂O₃ and CaO contents in the slag.

Table I. Slag Compositions Before and After Equilibration and Al, Ca, and Si Contents in FeSi50 After Equilibration at 1823 K (1550 °C)

| Test No. | Initial Slag Composition | | | Slag Composition After Equilibration | | | Al, Ca, and Si in FeSi After Equilibration | | |
|----------|---------------------------|---|--------------|--------------------------------------|---|--------------|--|-------------|-------------|
| | SiO ₂ (Wt Pct) | Al ₂ O ₃ (Wt Pct) | CaO (Wt Pct) | SiO ₂ (Wt Pct) | Al ₂ O ₃ (Wt Pct) | CaO (Wt Pct) | Al (Wt Pct) | Ca (Wt Pct) | Si (Wt Pct) |
| 1 | 49.8 | 21.7 | 28.5 | 47.3 | 24.4 | 28.3 | 0.069 | 0.0067 | 51.2 |
| 2 | 48.5 | 19.9 | 31.6 | 47.4 | 21.4 | 31.2 | 0.059 | 0.0088 | 51.5 |
| 3 | 34.2 | 37.6 | 28.2 | 31.5 | 39.3 | 29.2 | 0.350 | 0.0125 | 52.1 |
| 4 | 30.4 | 35.9 | 33.7 | 30.3 | 35.3 | 34.4 | 0.385 | 0.0320 | 52.9 |
| 5 | 56.3 | 10.3 | 33.4 | 54.0 | 11.9 | 34.1 | 0.023 | 0.0088 | 52.9 |
| 6 | 49.8 | 17.2 | 33.0 | 44.7 | 21.0 | 34.3 | 0.079 | 0.0125 | 52.1 |
| 7 | 41.6 | 26.6 | 31.8 | 36.7 | 29.1 | 34.2 | 0.205 | 0.0180 | 53.3 |

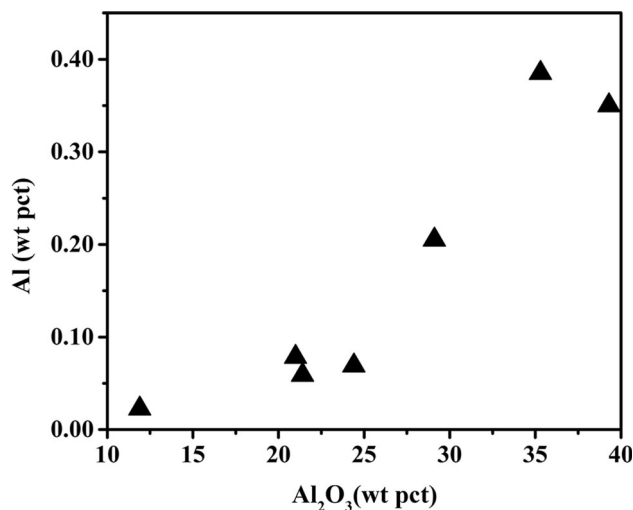


Fig. 4—Al content in the FeSi as a function of the final alumina content in the slag at 1823 K (1550 °C).

software. On the other hand, the differences in the evaluated activities of Al using the two software are not substantial. It should be noted that the accuracy in the

aluminum activity values depends on the accuracy of the calculated silica, alumina, and silicon activities and the standard Gibbs energy for Eq. [2]. Listing the calculated results from both software in the table is to present a perspective picture to the readers.

The activity coefficient ($\gamma_{\text{Al}}^{\circ}$) can be calculated by the following equation:

$$a_{\text{Al}} = x_{\text{Al}} \times \gamma_{\text{Al}}^{\circ} \quad [4]$$

The activity of aluminum at 1823 K (1550 °C) is plotted as a function of Al content in ferrosilicon in Figures 5(a) and (b) using the data from FactSage^[14] and Thermo-Calc^[15] respectively.

As shown in Eq. [4], the slope of the fitting line is the activity coefficient of Al in FeSi50 at 1823 K (1550 °C). While the regression using the data from FactSage^[14] results in a value of $\gamma_{\text{Al}}^{\circ} = 0.62$, the regression based on Thermo-Calc^[15] results in a slightly lower value, viz. $\gamma_{\text{Al}}^{\circ} = 0.55$.

The results obtained in this work show good agreement with those obtained by Dumay and Allibert^[7] for FeSi65 ($\gamma_{\text{Al}}^{\circ} = 0.65 \pm 0.2$) where the same Reference 14 was used for the calculation of the activities of Si, SiO₂, and Al₂O₃. The results are also in agreement with the

Table II. Comparison of the Activities of Aluminum in FeSi50 at 1823 K (1550 °C) When the Activities of SiO₂, Al₂O₃, and Si Are Calculated Using FactSage^[14] and Thermo-Calc^[15]

| Test No. | Final Slag Composition | | | | Activities ^[14] | | | Activities ^[15] | | | a _{Al} (Activities of Oxides and Si Calculated with Thermo-Calc ^[15]) |
|----------|---------------------------|---|--------------|--|----------------------------|--------------------------------|-------|----------------------------|--------------------------------|-------|--|
| | SiO ₂ (Wt Pct) | Al ₂ O ₃ (Wt Pct) | CaO (Wt Pct) | | SiO ₂ | Al ₂ O ₃ | Si | SiO ₂ | Al ₂ O ₃ | Si | |
| 1 | 47.3 | 24.4 | 28.3 | | 0.295 | 0.178 | 0.663 | 0.301 | 0.315 | 0.613 | 7.00 × 10 ⁻⁴ |
| 2 | 47.4 | 21.4 | 31.2 | | 0.269 | 0.108 | 0.669 | 0.273 | 0.220 | 0.618 | 6.33 × 10 ⁻⁴ |
| 3 | 31.5 | 39.3 | 29.2 | | 0.088 | 0.614 | 0.686 | 0.110 | 0.701 | 0.632 | 2.27 × 10 ⁻³ |
| 4 | 30.3 | 35.3 | 34.4 | | 0.048 | 0.418 | 0.693 | 0.065 | 0.513 | 0.639 | 2.92 × 10 ⁻³ |
| 5 | 54.0 | 11.9 | 34.1 | | 0.400 | 0.010 | 0.693 | 0.406 | 0.027 | 0.639 | 1.68 × 10 ⁻⁴ |
| 6 | 44.7 | 21.0 | 34.3 | | 0.196 | 0.102 | 0.680 | 0.196 | 0.215 | 0.628 | 8.12 × 10 ⁻⁴ |
| 7 | 36.7 | 29.1 | 34.2 | | 0.098 | 0.278 | 0.706 | 0.109 | 0.425 | 0.650 | 1.82 × 10 ⁻³ |

expression proposed by Dumay *et al.*^[8] for different ferrosilicon alloys ($\gamma_{Al} = 0.45 + 1.03 \times (1 - x_{Si})$). For the particular case of ferrosilicon used in this study, $\gamma_{Al} = 0.77 \pm 0.23$ at 1723 K (1450 °C). On the other hand, the results differ from the ones obtained for FeSi75 at 1873 K (1600 °C) by Tuset^[5] ($\gamma_{Al} = 0.45$). Tuset^[5] calculated the silicon activities in the ferrosilicon from a different Reference 11 and used the activity values of the oxides from the work of Rein and Chipman.^[16] The difference in the activity coefficient value can be due to the different references used for the calculation of the activities.

It should be mentioned that the above comparison should be used with precaution, since the ferrosilicon alloys have different Si contents from the present work (50 wt pct). Also, the temperatures are somewhat different.

D. Activity of Ca in FeSi50 at 1823 K (1550 °C)

Similar calculations can be done to calculate the activity of Ca. In this case, the reaction between calcium dissolved in ferrosilicon and the slag is given below.



where the underlined elements are dissolved in the liquid metal phase. The standard Gibbs energy for Eq. [5], ΔG_5° , can be found in the literature^[13]:

$$\Delta G_5^\circ = -323900 + 11.6 \times T \text{ J/mol}, \quad [6]$$

where the temperature is given in Kelvin. The standard states for Eq. [5] are pure solid for CaO and SiO₂ and pure liquid for Ca and Si. The equilibrium constant for Eq. [5] can be written as

$$k_5 = \frac{a_{\text{CaO}}^2 \times a_{\text{Si}}}{a_{\text{SiO}_2} \times a_{\text{Ca}}^2}, \quad [7]$$

where a_{CaO} and a_{SiO_2} are the activities of solid calcium oxide and solid silicon oxide and a_{Si} and a_{Ca} are the activities of liquid silicon and liquid calcium, respectively.

The activities of the oxides (a_{CaO} and a_{SiO_2}) together with the activity of silicon can be calculated using FactSage^[14] or Thermo-Calc.^[15] Once these activities are known, the activity of calcium can then be calculated from Eq. [7]. Activities calculated using both software are listed in Table III. To calculate the activity of Si, FTlite database was used in FactSage^[14] and TCFE8 in Thermo-Calc.^[15] For the activities of the oxides, FToxid was used in FactSage^[14] and TCOX5 in Thermo-Calc.^[15] The table indicates that the results are somehow affected when using different software for the calculation of the SiO₂, CaO, and Si activities.

The activity of calcium at 1823 K (1550 °C) is plotted as a function of the Ca content in Figures 6(a) and (b) using the data from FactSage^[14] and Thermo-Calc,^[15] respectively. The slope of the fitting line is the activity coefficient of Ca, γ_{Ca} , in FeSi50 at 1823 K (1550 °C) according to Eq. [8].

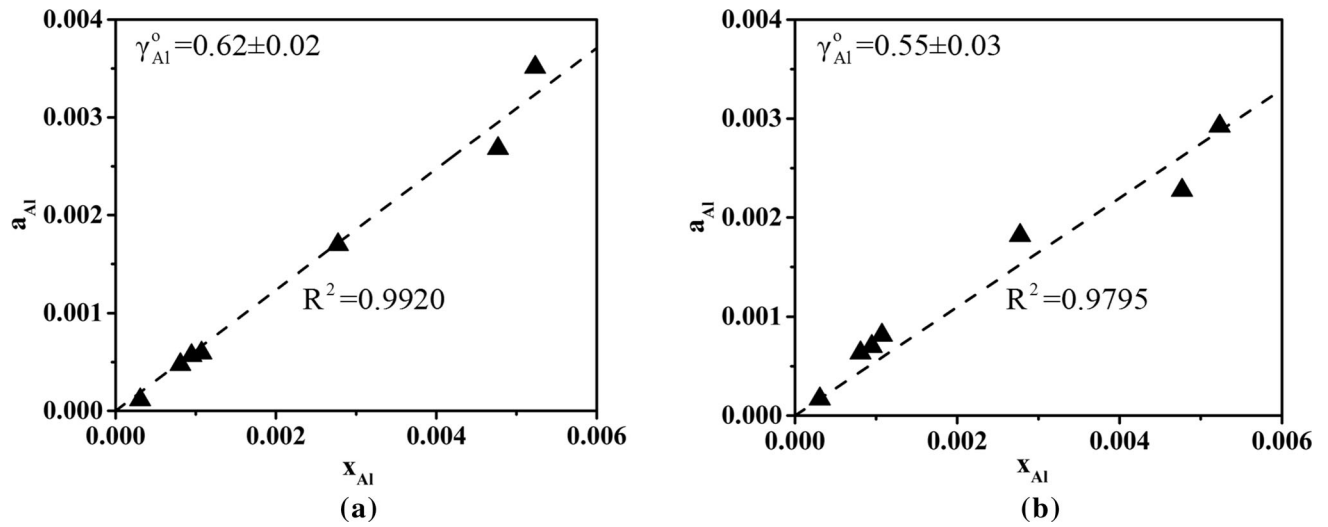


Fig. 5—Activity of Al as a function of the mole fraction of aluminum in FeSi50 at 1823 K (1550 °C). (a) Activities calculated with FactSage^[14] and (b) activities calculated with Thermo-Calc.^[15]

Table III. Comparison of the Activities of Calcium in FeSi50 at 1823 K (1550 °C) When the Activities of SiO₂, CaO, and Si Are Calculated Using FactSage^[14] and Thermo-Calc^[15]

| Test No. | Final Slag composition | | | Activities ^[14] | | | a _{Ca} (Activities of Oxides and Si Calculated with FactSage ^[14]) | Activities ^[15] | | | a _{Ca} (Activities of Oxides and Si Calculated with Thermo-Calc ^[15]) |
|----------|---------------------------|---|--------------|----------------------------|-------------------------|-------|---|----------------------------|-------------------------|-------|--|
| | SiO ₂ (Wt Pct) | Al ₂ O ₃ (Wt Pct) | CaO (Wt Pct) | SiO ₂ | CaO | Si | | SiO ₂ | CaO | Si | |
| 1 | 47.3 | 24.4 | 28.3 | 0.295 | 3.26 × 10 ⁻³ | 0.663 | 2.3 × 10 ⁻⁷ | 0.301 | 2.26 × 10 ⁻³ | 0.613 | 1.5 × 10 ⁻⁷ |
| 2 | 47.4 | 21.4 | 31.2 | 0.269 | 4.62 × 10 ⁻³ | 0.669 | 3.3 × 10 ⁻⁷ | 0.273 | 3.04 × 10 ⁻³ | 0.618 | 2.1 × 10 ⁻⁷ |
| 3 | 31.5 | 39.3 | 29.2 | 0.088 | 7.25 × 10 ⁻³ | 0.686 | 9.3 × 10 ⁻⁷ | 0.110 | 5.15 × 10 ⁻³ | 0.632 | 5.7 × 10 ⁻⁷ |
| 4 | 30.3 | 35.3 | 34.4 | 0.048 | 1.61 × 10 ⁻² | 0.693 | 2.8 × 10 ⁻⁶ | 0.065 | 1.02 × 10 ⁻² | 0.639 | 1.5 × 10 ⁻⁶ |
| 5 | 54.0 | 11.9 | 34.1 | 0.400 | 4.92 × 10 ⁻³ | 0.693 | 3.0 × 10 ⁻⁷ | 0.406 | 3.01 × 10 ⁻³ | 0.639 | 1.7 × 10 ⁻⁷ |
| 6 | 44.7 | 21.0 | 34.3 | 0.196 | 7.15 × 10 ⁻³ | 0.680 | 6.1 × 10 ⁻⁷ | 0.196 | 4.75 × 10 ⁻³ | 0.628 | 3.9 × 10 ⁻⁷ |
| 7 | 36.7 | 29.1 | 34.2 | 0.098 | 1.03 × 10 ⁻² | 0.706 | 1.3 × 10 ⁻⁶ | 0.109 | 6.95 × 10 ⁻³ | 0.650 | 7.8 × 10 ⁻⁷ |

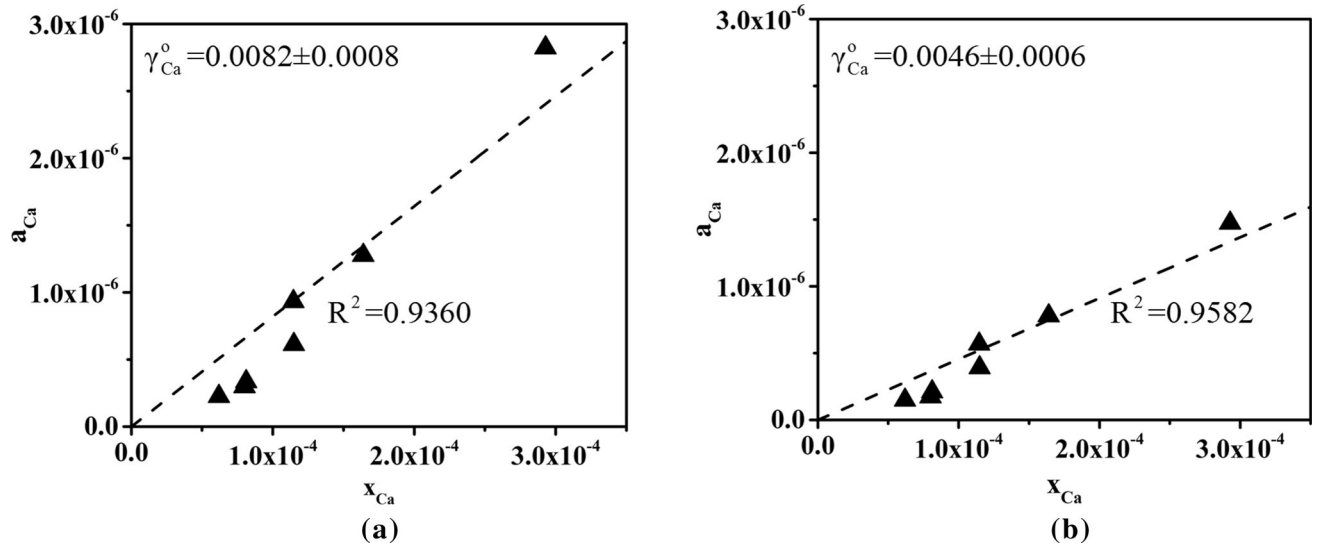


Fig. 6—Activity of Ca as a function of the mole fraction of calcium in FeSi50 at 1823 K (1550 °C). (a) Activities calculated with FactSage^[14] and (b) activities calculated with Thermo-Calc.^[15]

$$a_{\text{Ca}} = x_{\text{Ca}} \times \gamma_{\text{Ca}}^{\circ} \quad [8]$$

As shown in Figure 6, there is an appreciable difference in the activity coefficient of calcium in FeSi50 when different software are used for the calculation of the activities of silica, calcia, and silicon. The calculated activity coefficients of calcium are also quite different: in the case of FactSage^[14] $\gamma_{\text{Ca}}^{\circ} = 0.0082$, and in the case of Thermo-Calc^[15] $\gamma_{\text{Ca}}^{\circ} = 0.0046$. Since the activity of silicon in the metal phase does not differ a lot, the main reason would be the difference in CaO activities. To clarify this situation, the activities of CaO should be restudied. While this clarification is out of the scope of the present work, it is hoped that presenting the raw data would help the required future investigation.

It should be mentioned that the linear relationships in Figure 6 should be used with precaution when the calcium content is higher than the present composition range. As observed in Figure 6, the relationship between the activity of Ca and its mole fraction has already shown some curvature regardless of the software used for the calculation of the silicon and oxide activities.

Results from this work show good agreement with the expression proposed by Dumay *et al.*^[8] ($\ln \gamma_{\text{Ca}} = 1.167 - 8.807 \times x_{\text{Si}}$) for different ferrosilicon alloys at 1723 K (1450 °C). The value obtained from this expression for the ferrosilicon used is $\gamma_{\text{Ca}}^{\circ} = 0.008 \pm 0.002$. Dumay *et al.*^[8] used the same software^[14] to calculate the activities of Si, SiO₂, and CaO. Results from this work based on the activities calculated using FactSage^[14] differ slightly from the results obtained by Dumay and Allibert^[7] ($\gamma_{\text{Ca}} = 0.003 \pm 0.001$). However, it should be mentioned that Dumay and Allibert^[7] encountered large scatter in their results concerning Ca. As in the case of aluminum activity, the present results of Ca do not agree with the value reported by Tuset^[5] ($\gamma_{\text{Ca}} = 0.0021$). Again, the use of thermodynamic activities of the oxides could be one of the reasons leading to the disagreement.

V. SUMMARY

To gain a better control of the removal of Ca and Al from a FeSi50 alloy in the ferrosilicon refining process, experiments were performed to determine the thermodynamic activities of these elements in the liquid alloy. By stirring the slag–ferrosilicon system in a graphite crucible, equilibrium was reached after 45 minutes. The contents of both Al and Ca were in their dilution ranges, relevant to the refining process. Al in the FeSi was found to increase with the increase of alumina in the SiO₂–Al₂O₃–CaO slag. The activity coefficients in the infinite dilution range for aluminum and calcium in FeSi50 at 1823 K (1550 °C) were calculated based on the experimental data and the activities of Al₂O₃, SiO₂, CaO, and Si calculated using software. While the uses of FactSage^[14] and Thermo-Calc^[15] resulted in only a small difference in the activities of Al, a considerable

discrepancy was noticed in the case of Ca activities. Since the two software calculated similar activities of Si in the ferrosilicon alloys, the main reason for the discrepancy could be due to the data for oxide activities. Further study is needed to clarify this situation.

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