

ACTIVITY MEASUREMENT OF SILICATE SLAGS EQUILIBRATED WITH MOLTEN SILICON ALLOYS

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Key words : Thermodynamics, Activity measurement, CaO-SiO₂-AlO_{1.5}-MgO slags,
Molten silicon, Ironmaking, Steelmaking

The activities of components in the CaO-SiO₂-AlO_{1.5}-MgO slags were directly measured by equilibrating the slags with silicon based alloys on the basis of a new integration method derived from the Gibbs-Duhem relation. For the CaO-SiO₂, CaO-SiO₂-AlO_{1.5} and CaO-SiO₂-MgO slags, the activity of SiO₂ was obtained from the distribution of each element between slag and metal using each thermodynamic property in molten silicon alloys, and the activities of other components in the slags were subsequently derived at 1823 or 1873 K. For the CaO-SiO₂-AlO_{1.5}-MgO slags, the activities of components other than SiO₂ on 10mass% MgO plane were obtained at 1873 K by using the activity of SiO₂ available in the literature. Therefore, it has been confirmed that the activities of components other than SiO₂ in multi-component silicate slag systems can be determined by this technique as long as the activity data of at least one component in the system is available.

I. INTRODUCTION

Silicate slags are known as fluxes for refining in steelmaking processes as well as by-products in ironmaking processes. Thermodynamic analysis requires a precise knowledge of the activity of each component in such slag systems over a wide range of liquid composition in order to solve the problems such as erosion of refractory, a composition control of inclusions in steels, etc.

Rein and Chipman^[1] determined the activities of SiO₂ in the ternary systems of CaO-SiO₂-AlO_{1.5} and CaO-SiO₂-MgO, and those at the 10, 20, 30 mass% MgO of the CaO-SiO₂-AlO_{1.5}-MgO quaternary system mainly at 1873 K by measuring the silicon distribution between the slags and Fe-Si-C alloys saturated with either graphite or silicon carbide under a CO atmosphere. In the ternary systems, they calculated the activities of other components from that of SiO₂ by Schuhmann's tangent intercept procedure. However, the activities of AlO_{1.5} and CaO in the SiO₂-rich region are not reported for the CaO-SiO₂-AlO_{1.5} system.

Kay and Taylor^{[2][3]} determined the activities of SiO₂ in the entire liquid region in the CaO-SiO₂-AlO_{1.5} system and those on the 11, 21 mass% AlO_{1.5} planes of the CaO-SiO₂-AlO_{1.5}-MgO system mainly at 1823 K by measuring the equilibrium CO pressure of the reaction SiO₂ + 3C = SiC + 2CO, and the value at 1873 K were also estimated by extrapolation. In the ternary system, the activities of other components were also derived by the Schuhmann's method.

However, this method essentially involves the errors caused by the accuracy in drawing tangent slopes of the iso-activity lines for SiO₂, and also requires the activity data of one component over a wide range of liquid composition together with the activity values of the

other components as integration limits. For quaternary or more complicated systems, it is difficult to apply this method and the direct measurement of the activities other than SiO₂, such as CaO, AlO_{1.5} and MgO, was difficult due to the thermodynamic fact that Ca, Al and Mg are less noble than Si in general.

Ohta and Suito^{[4][5]} determined the activity of SiO₂ and AlO_{1.5} on the liquidus lines at the 0, 10, 20, 30, 40 mass% AlO_{1.5} planes and the 0, 10, 20 mass% MgO planes of CaO-SiO₂-AlO_{1.5}-MgO slags at 1873 K by equilibrating the slags and Fe alloys in an AlO_{1.5} or CaO crucible. However, the reliable data are restricted to the liquidus composition and the activities in the liquid region had to be estimated by approximation.

Contrary to the approach of Rein et al.^[1] and Kay et al.^{[2][3]}, the feature of the present study is as follows. Firstly, the activity of SiO₂ was determined by applying a slag-metal technique using silicon based alloy and a newly proposed equation for integration derived from the Gibbs-Duhem relationship. Secondly, the activities of other components such as CaO, AlO_{1.5} and MgO were calculated at a definite composition on the basis of conventional equilibrium relations using the SiO₂ activity derived above or the one in literature and the thermodynamic properties of the silicon based alloys. Thus, the activities of CaO, AlO_{1.5} and MgO in the CaO-SiO₂, CaO-SiO₂-AlO_{1.5}, CaO-SiO₂-MgO and CaO-SiO₂-AlO_{1.5}-MgO (on 10mass% MgO plane) systems over a wide range of liquid composition were experimentally determined at 1823 and 1873 K.

II. EXPERIMENTAL

A. Experimental Procedure

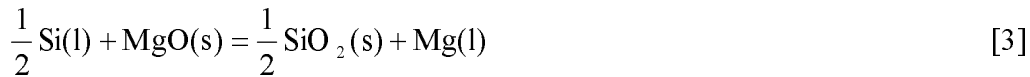
Silicate slags and silicon based alloys were equilibrated at 1823 and 1873 K within the accuracy of ± 2 K using a PID controlled electric resistance furnace. The slag was prepared from reagent grade Al₂O₃, SiO₂, MgO and CaO calcined from CaCO₃ in air. Sixteen grams of the slags and 8g of silicon based alloys with various Ca, Al and Mg contents in a graphite crucible were held in a graphite holder with a lid and equilibrated under deoxidized argon atmosphere for 18 h, and thereafter the sample was quenched and subjected to chemical analysis.

B. The Principle of the Measurement

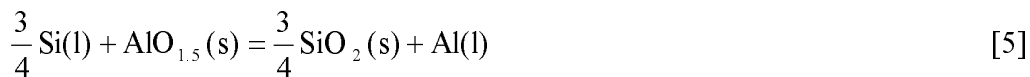
At equilibrium, the exchange reactions with respect to each component between molten slags and alloys may be written as follows:



$$\Delta G^\circ = -RT \ln \frac{a_{\text{SiO}_2}^{1/2} \cdot \gamma_{\text{Ca in Si}} \cdot X_{\text{Ca}}}{a_{\text{Si}}^{1/2} \cdot a_{\text{CaO}}} = 156,000 - 20.0T \text{(J/mol)}^{[6][8]} \quad [2]$$



$$\Delta G^\circ = -RT \ln \frac{a_{\text{SiO}_2}^{1/2} \cdot \gamma_{\text{Mg in Si}} \cdot X_{\text{Mg}}}{a_{\text{Si}}^{1/2} \cdot a_{\text{MgO}}} = 134,700 - 16.85T \text{(J/mol)}^{[6][7]} \quad [4]$$



$$\Delta G^\circ = -RT \ln \frac{a_{\text{SiO}_2}^{3/4} \cdot \gamma_{\text{Al in Si}} \cdot X_{\text{Al}}}{a_{\text{Si}}^{3/4} \cdot a_{\text{AlO}_{1.5}}} = 132,100 - 14.31T (\text{J/mol})^{[6][7]} \quad [6]$$

where γ_i is the activity coefficient of i in molten silicon based alloys relative to pure liquid i . The activity coefficients of Ca, Al and Mg in such alloys have been reported by Miki et al.^{[9][10]}, hence the activity of each oxide in the slag can be calculated by using the analyzed content of each component in the alloy, the activity of SiO_2 and the activity of Si. Also, the activities of SiO_2 and Si were derived from the experimental data as shown in the following sections C and D. for the binary and ternary systems. For the $\text{CaO-SiO}_2\text{-AlO}_{1.5}\text{-MgO}$ quaternary system, the SiO_2 activity data reported by Rein and Chipman^[11] were employed.

C. Estimation of the activity of SiO_2

The activities of SiO_2 in the slags were obtained as follows. The Gibbs-Duhem equation for a ternary system is expressed by the activity coefficients as Eq. [7].

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 + X_3 d \ln \gamma_3 = 0 \quad [7]$$

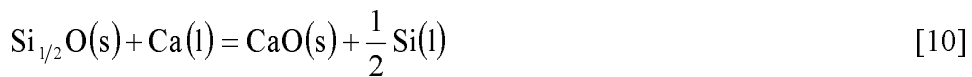
When $B = \gamma_2 / \gamma_1$, $C = \gamma_3 / \gamma_1$, and $k = X_3 / X_2$,

$$d \ln \gamma_1 = -X_2 d \ln B - kX_2 d \ln C \quad [8]$$

Accordingly, $\ln \gamma_1$ with a constant ratio of 2 and 3 components can be calculated by Eq. [9].

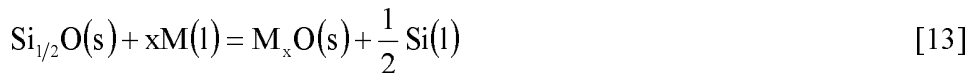
$$\ln \gamma_1 = \int_{X_2=X_2^i}^{X_2=X_2} -X_2 d \ln (B \cdot C^k) + \ln \gamma_1^{(X_2=X_2^i)} \quad [9]$$

In the case of the $\text{CaO-SiO}_2\text{-M}_x\text{O}$ system, components 1, 2 and 3 are designated to be $\text{Si}_{1/2}\text{O}$, CaO and M_xO ($M = \text{Al or Mg}$), respectively, in order that each activity coefficient may have the same order in Eqs. [11] and [14]. The values of B and C can be calculated by each exchange reaction between $\text{Si}_{1/2}\text{O}$ and other components, as shown by Eqs. [12] and [15].



$$K_{[10]} = \frac{\gamma_{\text{CaO}} \cdot X_{\text{CaO}} \cdot a_{\text{Si}}^{1/2}}{\gamma_{\text{Si}_{0.5}\text{O}} \cdot X_{\text{Si}_{0.5}\text{O}} \cdot a_{\text{Ca}}} \quad [11]$$

$$B = \frac{\gamma_{\text{CaO}}}{\gamma_{\text{Si}_{1/2}\text{O}}} = \frac{X_{\text{Si}_{1/2}\text{O}} \cdot \gamma_{\text{Ca}} \cdot X_{\text{Ca}}}{X_{\text{CaO}} \cdot \gamma_{\text{Si}}^{1/2} \cdot X_{\text{Si}}^{1/2}} \cdot K_{[10]} \quad [12]$$



$$K_{[13]} = \frac{\gamma_{\text{M}_x\text{O}} \cdot X_{\text{M}_x\text{O}} \cdot a_{\text{Si}}^{1/2}}{\gamma_{\text{Si}_{1/2}\text{O}} \cdot X_{\text{Si}_{1/2}\text{O}} \cdot a_{\text{M}}^x} \quad [14]$$

$$C = \frac{\gamma_{\text{M}_x\text{O}}}{\gamma_{\text{Si}_{1/2}\text{O}}} = \frac{X_{\text{Si}_{1/2}\text{O}} \cdot \gamma_{\text{M}}^x \cdot X_{\text{M}}^x}{X_{\text{M}_x\text{O}} \cdot a_{\text{Si}}^{1/2}} \cdot K_{[13]} \quad [15]$$

When the value of $\ln(B \cdot C^k)$ is calculated at each slag composition in the ternary systems, the activity of $\text{Si}_{1/2}\text{O}$, hence that of SiO_2 can be obtained by Eq. [9]. It can be derived more easily for the CaO-SiO_2 binary system because k in the equation becomes zero.

D. Estimation of the activity of Si

Using the activity coefficients of Ca, Al and Mg in molten silicon alloys, the activity of Si in the alloys can be obtained as follows. Suppose the ternary alloy consists of components 1, 2 and 3, and component 1 is Si, Eq. [7] can be rewritten as Eq. [16].

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 + k X_2 d \ln \gamma_3 = 0 \quad [16]$$

where $k = X_3/X_2$.

$$\ln \gamma_1 = \int_{X_2=0}^{X_2=X_2} -\frac{X_2}{X_1} d \ln(\gamma_2 \cdot \gamma_3^k) \quad [17]$$

Therefore, the activity of Si with a constant ratio of 2 and 3 components can be calculated by integration of Eq. [17]. For the binary alloys, the activity of Si can be obtained by an even simpler method.

In most of the experiments in the present study, the activity of Si was found to be equal to the molar fraction of Si since it was nearly unity.

III. RESULTS AND DISCUSSION

A. The CaO-SiO_2 system

The activities of both components for the CaO-SiO_2 slags at 1823 and 1873 K are shown in Fig. 1 as a function of SiO_2 content. Temperature dependence was found to be considerably small. Compared with the activity data investigated by various techniques, such as electrochemical cells^{[11]-[14]}, Knudsen effusion method^[15], gas-slag equilibrium method (the gas containing sulfur or SO_2)^{[16][17]}, measurements of CO pressure over slag-graphite-SiC system^[18] and equilibrium between slag and Fe-Si-C alloy^[1], etc., the present results were found to be among the fairly scattered data reported by others.

B. The $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ system

Iso-activity lines of SiO_2 for this system are drawn in Fig. 2. These contours are parallel to that of the SiO_2 -saturated liquidus down to low- SiO_2 content. The present results may be compared with those of Rein and Chipman^[1] and those of Kay and Taylor^[2] because their experimental temperatures are the same as the present work and the activity of SiO_2 was measured in this slag over a wide range of liquid composition together with the calculation of other component activities. Present results agree well with both data (Fig. 3) when SiO_2 content is less than 30 mol %

Iso-activity lines for CaO are drawn in Fig. 4. Although the curvatures of iso-activity contours agree well with those by Rein and Chipman^[1], the numerical values of the present results are about two thirds of their values.

Iso-activity lines for $\text{AlO}_{1.5}$ are drawn in Fig. 5. The curvatures of the lines also agree well with those by Rein and Chipman^[1]. However, the activity values are smaller than their results

when $\text{AlO}_{1.5}$ content is higher than 30 mol%. The discrepancies in both activities are considered to be due to the errors in their graphical treatment for the Gibbs-Duhem integration and those of the activity data at the integration limits.

C. The $\text{CaO-SiO}_2\text{-MgO}$ system

Iso-activity lines for SiO_2 , which are parallel to the SiO_2 -saturated liquidus, are shown in Fig. 6. The numerical values of the present work are in good agreement with those of Rein and Chipman^[1] in low-MgO area, while they are twice as large as those in the high-MgO area. (Fig. 7)

Iso-activity lines for CaO and MgO obtained in the present study are shown in Fig. 8, compared with their data. (Fig. 9) Although the curvatures of constant contours for CaO and MgO activities agree well with theirs, the CaO activities of the present work are about a half of their values, while the MgO activities are twice as large as theirs. This may be due to the inaccuracy in their graphical treatment of the Gibbs-Duhem integration with SiO_2 activities. These discrepancies would be large enough to cause considerable difference in estimating slag basicity or the erosion of refractories in steelmaking processes.

D. The $\text{CaO-SiO}_2\text{-AlO}_{1.5}\text{-MgO}$ system

The activity of each component was determined in the $\text{CaO-SiO}_2\text{-AlO}_{1.5}\text{-MgO}$ system on 10mass% MgO plane. For the present system, the activity data of SiO_2 reported by Rein et al and Chipman^[1] were used because it was difficult to employ the same method as binary and ternary systems considering the accuracy of calculation.

Iso-activity lines for CaO, $\text{AlO}_{1.5}$ are drawn in the $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ pseudo-ternary triangle as shown in Figs. 10 and 11, respectively. The results of the present slag showed little difference from those of the $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ slag system, which corresponds to the $\text{CaO-SiO}_2\text{-AlO}_{1.5}\text{-MgO}$ slag with 0mass% of MgO. Since there is some scatterings in MgO content after the experiments, the activity data of MgO were derived in terms of the activity coefficient at 10 mass% MgO as demonstrated in Figure 12. The activity coefficient increases with increasing slag basicity, and its value varies from 0.35 to 2 and the curvatures of iso-activity coefficient lines for MgO are similar to the activity curves for CaO at a constant MgO content of 10 mass %.

Since it is difficult to derive the activities of CaO, $\text{AlO}_{1.5}$ and MgO from those of SiO_2 using the Gibbs-Duhem, no other reliable data are available for such complicated slag systems that are of practical importance in iron- and steelmaking processes.

Accordingly, it has been confirmed that any activities in multi-component silicate slag systems can be determined by the technique developed in the present study as long as the activity datum of one component at a desired composition in the systems is available.

IV. CONCLUSIONS

By a slag-metal equilibration technique using silicon based alloy as the reference metal, the activities of each component in the CaO-SiO_2 , $\text{CaO-SiO}_2\text{-AlO}_{1.5}$, $\text{CaO-SiO}_2\text{-MgO}$, $\text{CaO-SiO}_2\text{-AlO}_{1.5}\text{-MgO}$ systems were directly determined at 1823 and 1873K. In the binary and ternary systems, the activity of SiO_2 was obtained by integrating equilibrium distribution data between silicon based alloys and slags, while the available data of SiO_2 activity were employed for the $\text{CaO-SiO}_2\text{-AlO}_{1.5}\text{-MgO}$ quaternary system. Then, the activities of other components were determined by using the conventional equilibrium relationship rather than Schuhmann's method.

It is the largest advantage of the present procedure that any activities in multi-component

silicate slag systems can be determined when the activity of one component at the desired composition is available.

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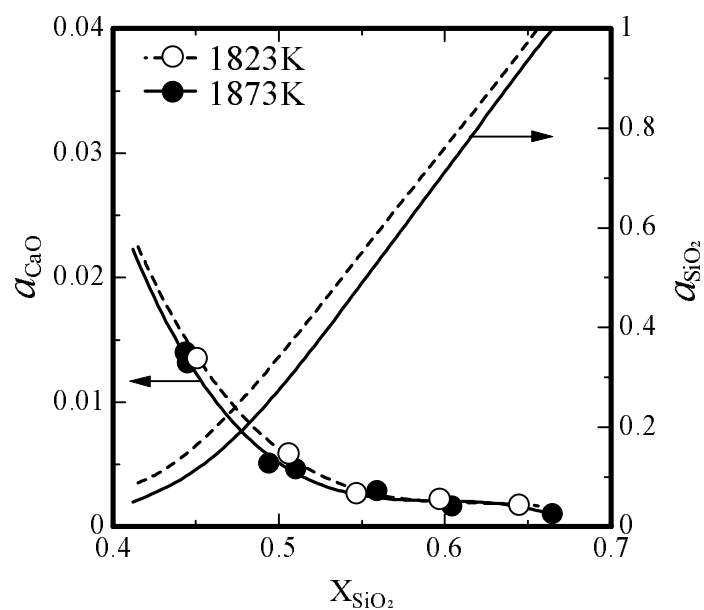


Fig.1 Relationship between slag composition and the activities of CaO and SiO₂ for the CaO-SiO₂ system at 1823 and 1873 K.

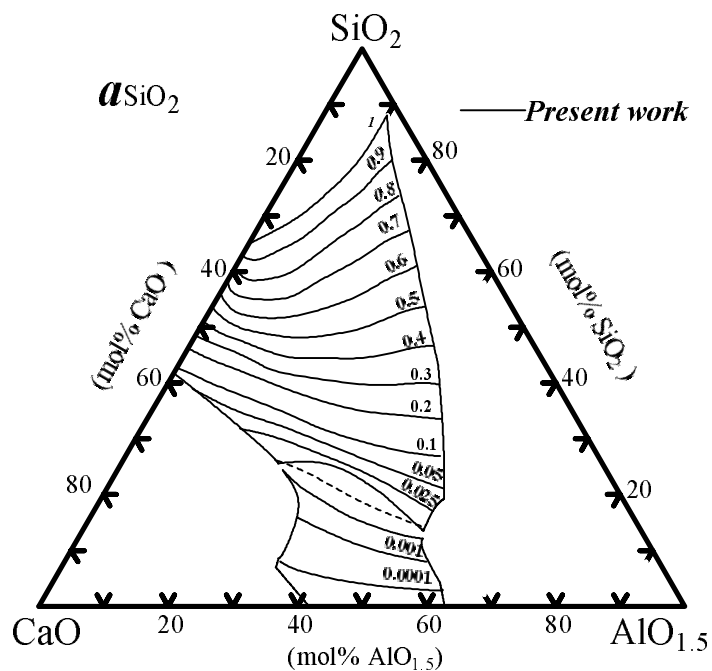


Fig.2 Iso-activity contours for SiO₂ in the CaO-SiO₂-AlO_{1.5} system at 1823 K.

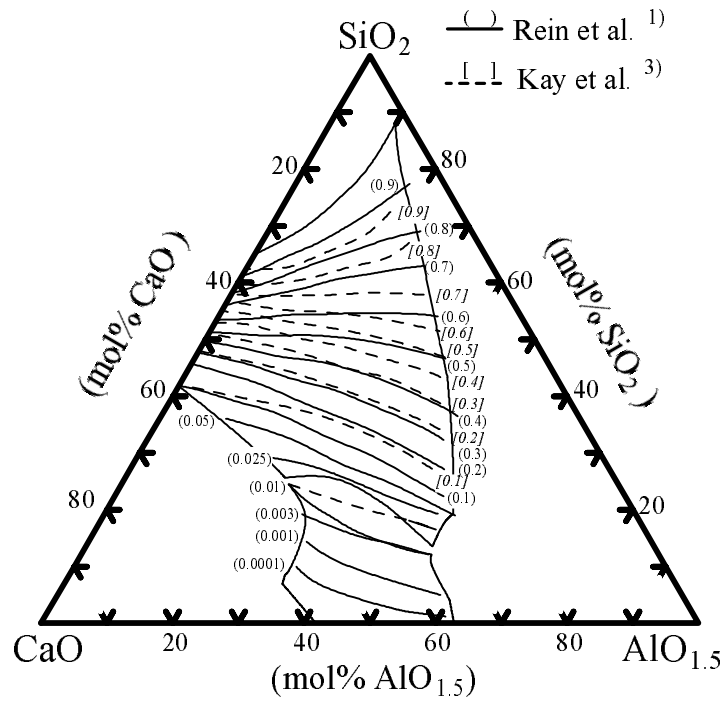


Fig.3 Iso-activity contours for SiO_2 in the $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ system at 1823 K after Rein et al.¹⁾ and Kay et al.³⁾

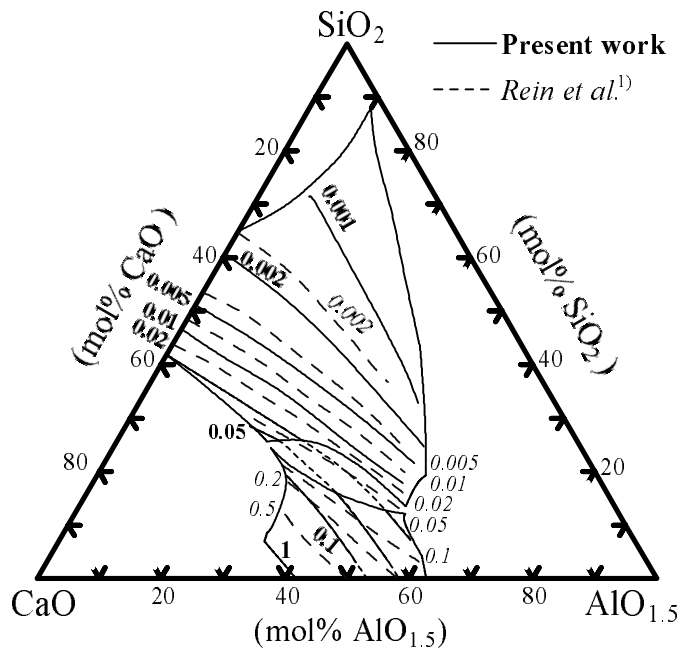


Fig.4 Iso-activity contours for CaO in the $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ system at 1823 K.

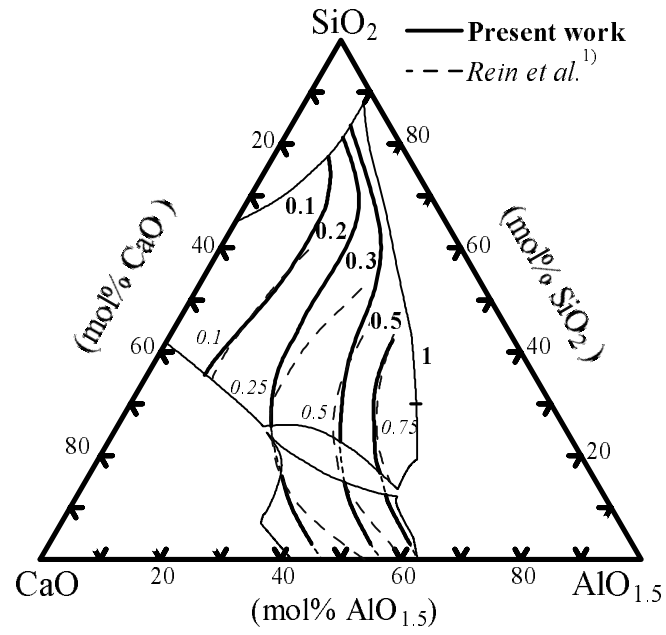


Fig.5 Iso-activity contours for $\text{AlO}_{1.5}$ in the $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ system at 1823 K.

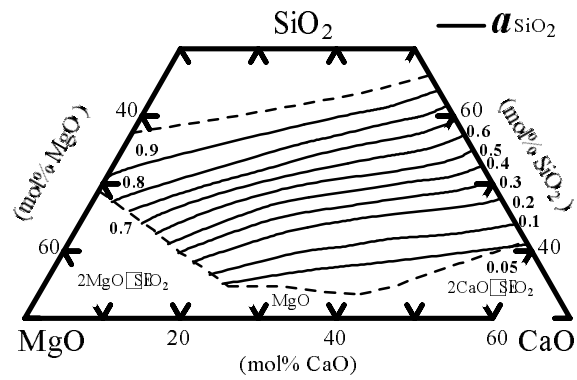


Fig.6 Iso-activity contours for SiO_2 in the $\text{CaO-SiO}_2\text{-MgO}$ system at 1873 K.

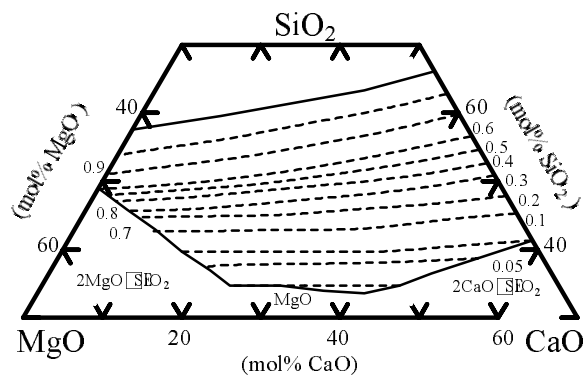


Fig.7 Iso-activity contours for SiO_2 in the $\text{CaO-SiO}_2\text{-MgO}$ system at 1873 K after Rein and Chipman¹⁾.

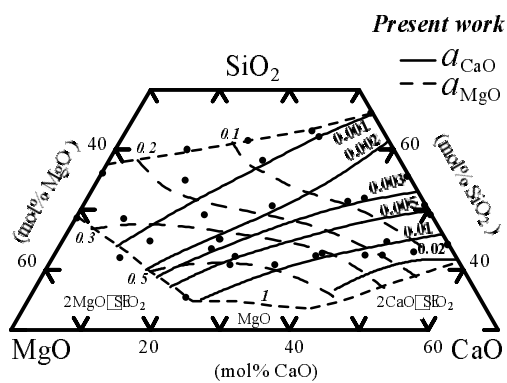


Fig.8 Iso-activity contours for CaO and MgO in the $\text{CaO-SiO}_2\text{-MgO}$ system at 1873 K.

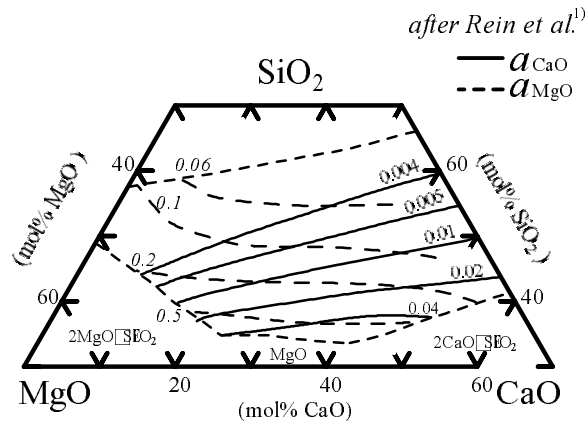


Fig.9 Iso-activity contours for CaO and MgO in the CaO-SiO₂-MgO system at 1873 K after Rein and Chipman¹⁾.

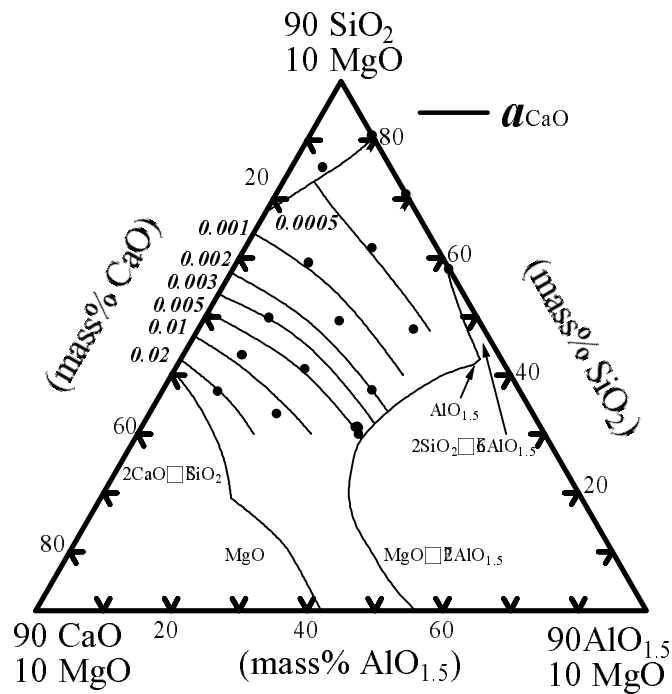


Fig.10 Iso-activity contours for CaO in the CaO-SiO₂-AlO_{1.5} pseudo-ternary system on the plane of 10 mass% MgO at 1873 K.

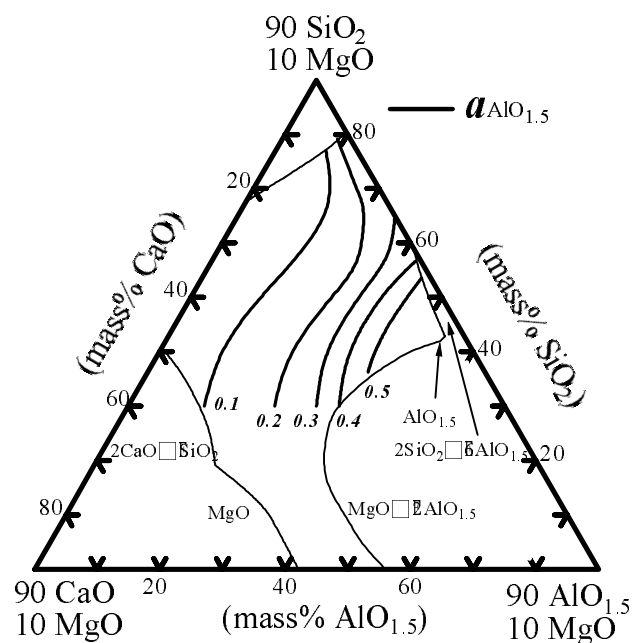


Fig. 11 Iso-activity contours for $\text{AlO}_{1.5}$ in the $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ pseudo-ternary system on the plane of 10 mass% MgO at 1873 K.

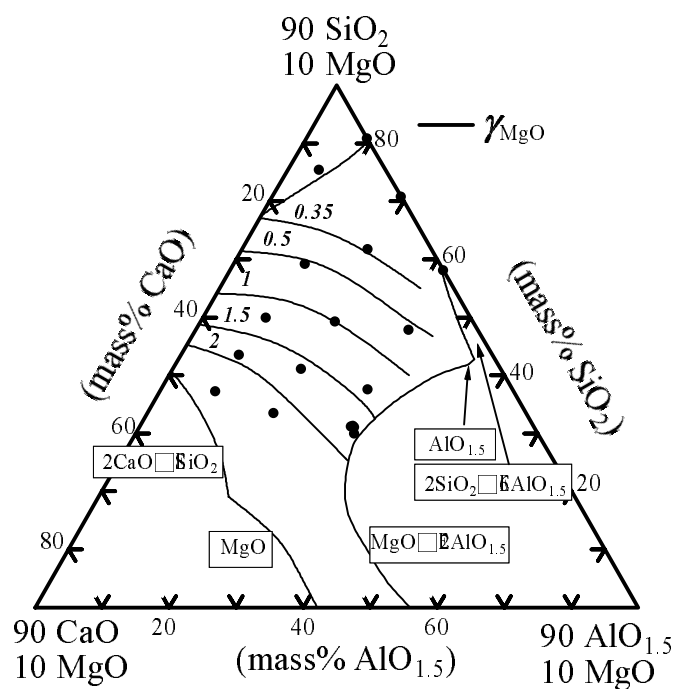


Fig. 12 Iso-activity coefficient contours for MgO in the $\text{CaO-SiO}_2\text{-AlO}_{1.5}$ pseudo-ternary system on the plane of 10 mass% MgO at 1873 K.