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Evaluation of Viscosity of Molten SiO$_2$–CaO–MgO–Al$_2$O$_3$ Slags in Blast Furnace Operation

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The viscosity of molten SiO$_2$–CaO–MgO–Al$_2$O$_3$ slag was measured using a rotating cylinder method at high CaO and Al$_2$O$_3$ concentration regions to search for a slag with low melting temperature and low viscosity. The experimental results showed that the viscosity of molten 35mass%Al$_2$O$_3$–43.1mass%CaO–7.5mass%MgO–14.4mass%SiO$_2$ slag at 1 673 K was lower than 0.6 Pa·s that satisfies the fluidity in blast furnace operation.

The experimental results were compared with the calculated results of the viscosity model derived by the authors. The viscosity of molten SiO$_2$–CaO–MgO–Al$_2$O$_3$ system can be evaluated from our model in wide Al$_2$O$_3$ concentration range.

KEY WORDS: blast furnace; low temperature; molten slag; viscosity; Al$_2$O$_3$.

1. Introduction

There is a demand for decreasing the process temperature to reduce energy consumptions in the current iron and steelmaking processes. However, the viscosity of molten slag increases considerably at lower temperatures in the conventional process and it causes various troubles in the operation. Therefore, it is required to search adequate slag systems with good fluidity at lower temperatures. In order to design the slag satisfying the requirement, the viscosity of molten slag with low melting point should be investigated to develop an improved blast furnace operation at low temperature such as 1 673 K for saving energy consumption.[1]

Iwase *et al.*[2] investigated the phase diagrams for SiO$_2$–CaO–MgO–Al$_2$O$_3$ system, and proposed candidate slags with low melting temperature as follows. **Figure 1** shows the composition range with low melting temperature ($T_{liquidus} \leq$ 1 673 K) in SiO$_2$–CaO–MgO–Al$_2$O$_3$ system for 0, 5, 10, 15, 20, 25, 30 and 35 mass% of Al$_2$O$_3$. BFS in Fig. 1(d) is the composition of a conventional blast furnace slag. As shown in these figures, when we try to find the liquid phase with $T_{liquidus} \leq$ 1 673 K at 0–30 mass% of Al$_2$O$_3$, we have to increase SiO$_2$ content from the BFS composition, which causes the increase of the viscosity (*e.g.* at the composition of Slag 3 in Fig. 1(c)). On the other hand, a liquid region with $T_{liquidus} \leq$ 1 673 K exists at high CaO/SiO$_2$ at 35 mass% of Al$_2$O$_3$ in Fig. 1(h). Although the viscosity is expected to be low at high CaO/SiO$_2$ region (*e.g.* at the composition of Slag 1 and Slag 2 in Fig. 1(h)), the viscosity has not been reported so far.

To find an adequate slag system with low viscosity at low temperature based on Fig. 1, it is necessary to examine viscosity of slag in the wide composition range in multi-com-
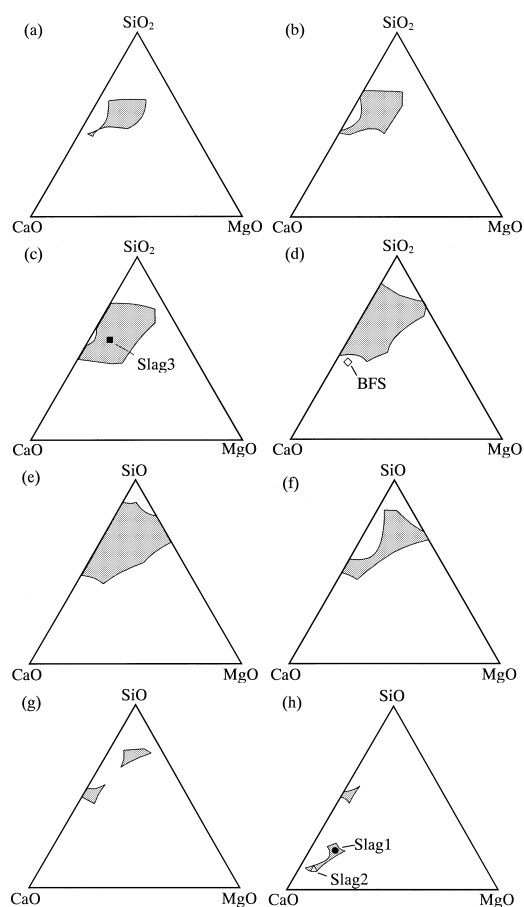

Fig. 1. Composition range with low melting temperature ($T_{liquidus} \leq$ 1 673 K) in SiO$_2$–CaO–MgO–Al$_2$O$_3$ system. Al$_2$O$_3$=(a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25, (g) 30 and (h) 35 mass%.

ponent systems. Therefore, it is useful to evaluate the viscosity of slags not only by measurements but also by using theoretical models. In particular, when Al_2O_3 content changes widely as the above examples in Fig. 1, the composition dependence of the viscosity of slags is expected to depend on the amphoteric behavior of Al_2O_3. However, few models have been applied so far to the viscosity of slags at wide Al_2O_3 concentration range. Consequently, we have derived a viscosity model in order to reproduce the amphoteric behavior of Al_2O_3,[3–5] which has been applied so far to the evaluation of viscosity in ternary systems such as SiO_2–CaO–Al_2O_3 system.[3–5]

The purpose of the present work is to measure the viscosity of molten slag at the compositions of Slag 1, Slag 2 and Slag 3 in Fig. 1 to accumulate the viscosity data for the development of low temperature operation in iron and steelmaking processes. Then, the above model derived by the authors[3–5] was applied to the above SiO_2–CaO–MgO–Al_2O_3 quaternary system.

2. Experimental

The samples were prepared from Al_2O_3, CaO, MgO and SiO_2 powders, where CaO powder was obtained by heating $CaCO_3$ powder for 5 h at 1 273 K. A mixture of those powders, which corresponds to a given composition of slag (**Table 1**), was fed into an Fe crucible. The sample was heated up to and held at 1 673 K with flowing Ar (more than 1 L/min (s.t.p.)) for 1 h to melt the slag.

The rotating cylinder method was employed to measure the viscosity of molten slag. The apparatus is shown in **Fig. 2**. The viscometer is connected with an Fe spindle through a W rod. The spindle consists of a bob and a shaft, of which dimensions were shown in Fig. 2. The crucible has 45-mm i.d. and 100-mm height. The thickness of wall and base of the crucible was 5 mm. The Fe crucible containing the sample was placed in given position of the furnace where temperature distribution was uniform. The sample was heated at a rate of 150 K/h under Ar flow (more than 1 L/min (s.t.p.)) to a given temperature. After the sample was held at the temperature for 1 h, the spindle was immersed into the molten slag. The torque values, which are stabilized for more than 10 min, were measured at 4 rotating velocities of spindle, and the average value was used to determine the viscosity of molten slag. The viscometer was calibrated with three glycerol aqueous solutions and standard silicon oil. The viscosity range of those liquids is between 0.05 and 10 Pa·s. The viscosity measurements were conducted at a given temperatures between 1 573 and 1 723 K. In the case of Slag 1 (Run 4), Slag 2 (Run 5) and BFS in Table 1, the viscosity was measured at a-minute intervals with decreasing the temperature continuously at a rate of 0.5 K/min after the measurement at 1 673 K. The experimental uncertainties for viscosity measurements were about $\pm 20\%$ as a maximum.

Some of the slags were sampled for chemical analysis

Table 1. Chemical compositions of samples and experimental results of viscosity of molten SiO_2–CaO–MgO–Al_2O_3 system.

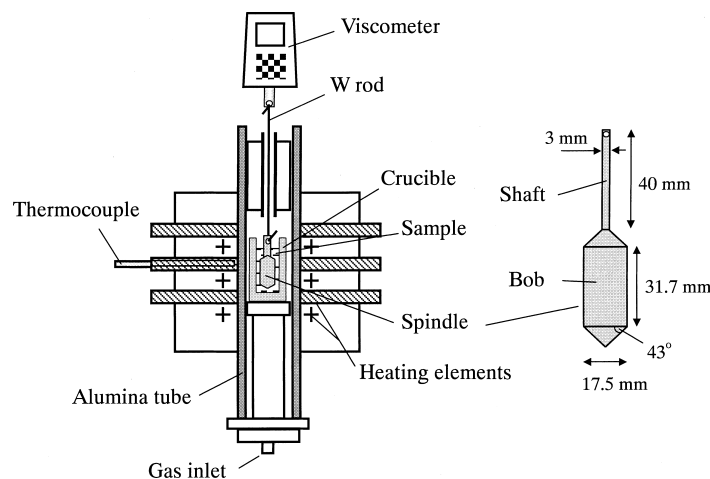|	Chemical composition (mass%)				Run	Viscosity (Pa·s)			
	SiO_2	CaO	MgO	Al_2O_3		1573 K	1623 K	1673 K	1723 K
Slag1	14.4	43.1	7.5	35.0	1			0.69	0.44
					2			1.00	0.46
					3			0.90	
					4			0.67	
Slag2	7.4	52.7	4.9	35.0	1			0.43	0.29
					2			0.50	0.31
					3			0.61	
					4			0.37	
					5			0.51	
Slag3	48.6	33.1	8.3	10.0	1	2.89	1.74	1.09	0.72
					2	2.81	1.72	1.08	0.72
BFS	36.4	43.6	5.0	15.0	1			0.77	0.51

Fig. 2. Apparatus for viscosity measurements.

after the viscosity measurements. The content of FeO in slag was less than 1 mass%. Sugiyama *et al.*[6] examined the effect of FeO on the viscosity measurement of molten slag, and derived an equation to expresses the change in the viscosity with FeO content. It is estimated that the viscosity of the slag containing 1 mass% FeO is 20% lower than that of the slag without FeO.

3. Results and Discussion

3.1. Experimental Results of Viscosity of Molten Slag

Experimental results of viscosity of molten slag are listed in Table 1. **Figure 3** shows the change in the viscosity of Slag 1 to 3, and BFS with temperature. The plots are the average values of viscosity at each temperature, and the broken lines indicate the experimental values measured with continuously decreasing temperature. The viscosity of BFS increases with decreasing temperature below 1 673 K. Since the liquidus temperature of the sample BFS is about 1 673 K, the solid and liquid phases are coexisted below 1 673 K, where the viscosity may increase considerably with large scatter. It is generally known that the viscosity of molten slag of the conventional blast furnace should be less than 0.6 Pa·s in order to maintain good fluidity.[6] The viscosity is, however, 0.77 Pa·s at 1 673 K, which means that the conventional blast furnace slag doesn't have good fluidity at low temperatures like 1 673 K or less. The viscosity of the sample Slag 3, which exists as a uniform liquid phase at the experimental temperature range ($T \geqq 1\,573$ K), gradually increases with decreasing temperature. This slag is also not suitable for the operation at low temperatures because the viscosity of the sample Slag 3 between 1 573 and 1 723 K are higher than 0.6 Pa·s. The viscosity of samples Slag 1 and Slag 2 with high CaO contents and 35 mass% Al_2O_3 are the same as that of slag BFS at 1 723 K, and slightly increases with decreasing temperature. The viscosity of the sample Slag 1 at 1 673 K is higher than 0.6 Pa·s, while that of the sample Slag 2 is lower than 0.6 Pa·s at 1 673 K. Even if the effect of FeO on the viscosity, which was explained above, is taken into consideration, the average viscosity of Slag 2 at 1 673 K is not higher than 0.6 Pa·s. On the molten slag with high CaO and 35 mass% Al_2O_3 as Slag 2, Hasegawa *et al.*[7] reported that the sulfide capacity of this slag is higher than that of the conventional blast furnace slag. Consequently, the sample Slag 2 is considered to be one of the candidates to satisfy the operating condition for the low-temperature blast furnace process.

3.2. Viscosity Model of Molten Slag

Recently, the authors developed a viscosity model for molten silicate slag system.[3–5] In this model, the following Arrhenius type equation is applied to express the temperature dependence of the viscosity η:

$$\eta = A \cdot \exp\left(\frac{E_V}{RT}\right) \quad\text{............................(1)}$$

where A is Arrhenius constant, R is the gas constant, T is the temperature, and E_V is the activation energy.

Silicate slag has a network structure, made from bonding of SiO_4^{4-} units, and those SiO_4^{4-} ions are combined with each other through bridging oxygen O^0, the vertex oxygen
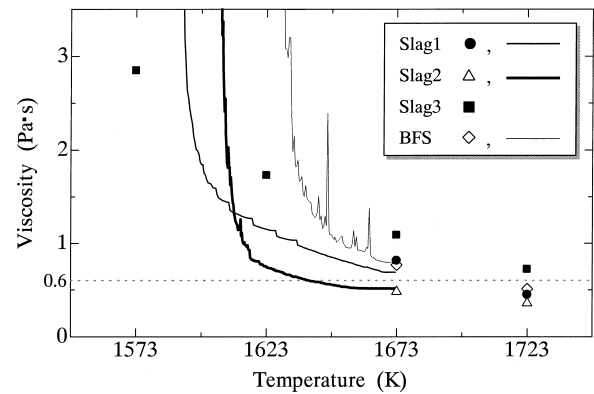
Fig. 3. Experimental results of temperature dependence of the viscosity of Slag 1, Slag 2, Slag 3 and BFS.

in tetrahedron structure of SiO_4^{4-} units. When some basic oxides such as CaO, Na_2O are added in the silicate slag, the network structures are cut off partially by the oxygen ion decomposed from the basic oxides to produce some numbers of free oxygen ion O^{2-} and non-bridging oxygen O^-. Since these "cutting-off" points near the free oxygen ion O^{2-} and the non-bridging oxygen O^- in the network structure control a viscous flow. In other words, it is considered that the viscosity of molten silicate slag is determined from the frequency of the occurrence of "cutting-off" of the network structure in the silicate slag. Then, the activation energy was assumed to become smaller as the number of the free oxygen ion O^{2-}, $N_{O^{2-}}$ and that of the non-bridging oxygen O^-, N_{O^-} increase, which is defined in Eq. (2):

$$E_V \equiv \frac{E}{1 + \{\alpha \cdot (N_{O^{2-}} + N_{O^-})\}^{1/2}} \quad\text{..................(2)}$$

A in Eq. (1) and E of Eq. (2) are determined from the temperature dependence of the viscosity of pure molten SiO_2 as follows: $A = 4.80 \times 10^{-8}$, $E = 5.21 \times 10^5$ (J).

$N_{O^{2-}}$ and N_{O^-} are evaluated from Gaye's model[8] with thermodynamic database. The values of α for various basic oxides in Eq. (2) are determined from the application of the above equation to various SiO_2–M_iO ($M_iO = CaO$, FeO, Al_2O_3, MgO) binary systems as follows:

$$\alpha_{CaO} = 2.0, \ \alpha_{FeO} = 3.8, \ \alpha_{Al_2O_3} = 0.95, \ \alpha_{MgO} = 1.8 \quad\text{......(3)}$$

In multi-component systems, the activation energy E_V is defined in Eq. (4).

$$E_V \equiv \frac{E}{1 + (\alpha_m)^{1/2}} \quad\text{............................(4)}$$

where α_m is evaluated by the following equation.

$$\alpha_m = \sum_{i=1}^{m-1} \alpha_{M_iO} \cdot (N_{Si-O-M_i} + N_{M_i-O-M_i})$$
$$+ \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} \frac{(\alpha_{M_i} + \alpha_{M_j})}{2} \cdot N_{M_i-O-M_j} \quad\text{..........(5)}$$

where m is the number of component oxides M_iO except SiO_2, N_{Si-O-M_i} and $N_{M_i-O-M_i}$ represent the mole fraction of non-bridging oxygen O^- and the free oxygen ion O^{2-}, respectively, which are calculated from Gaye's model.

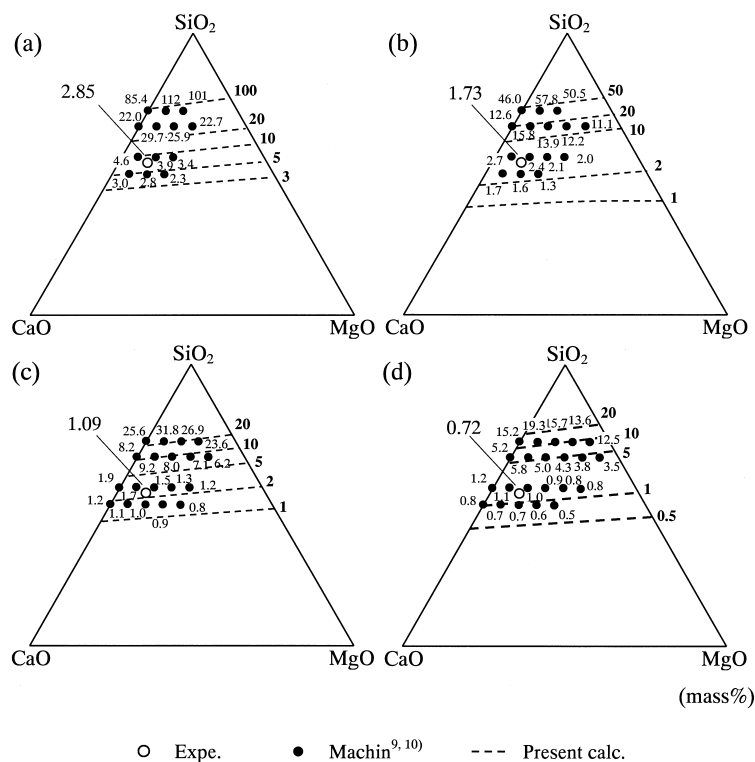**Figures 4** to **6** show the comparison of the experimental

Fig. 4. Viscosity (Pa·s) of molten SiO_2–CaO–MgO–10mass%Al_2O_3 at (a) 1 573 K, (b) 1 623 K, (c) 1 673 K and (d) 1 723 K.

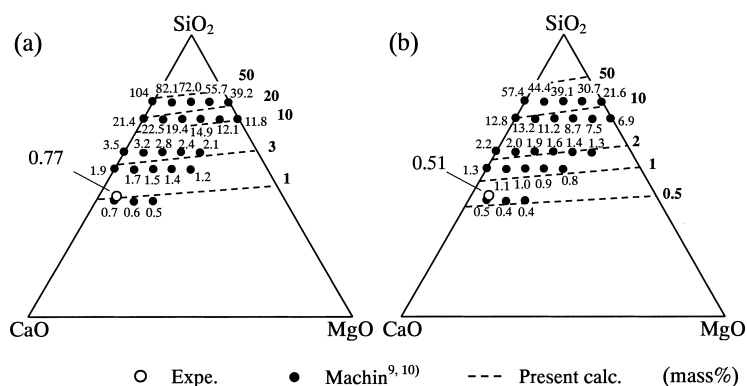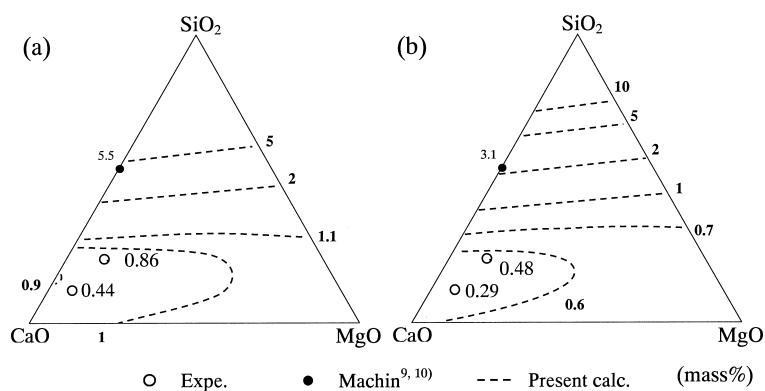**Fig. 5.** Viscosity (Pa·s) of molten SiO_2–CaO–MgO–15mass%Al_2O_3 at (a) 1 673 K and (b) 1 723 K.

Fig. 6. Viscosity (Pa·s) of molten SiO_2–CaO–MgO–35mass%Al_2O_3 at (a) 1 673 K and (b) 1 723 K.

results and literature values[9,10] with the calculated results of the viscosity for SiO_2–CaO–MgO–Al_2O_3 quaternary systems. The calculated iso-viscosity curves are drawn in the whole composition region by assuming that the slag exists as liquid phase. Machin *et al.*[9,10] measured the viscosity of molten slag in wide composition range for SiO_2–CaO–MgO–10 and 15mass%Al_2O_3 system, as shown in Figs. 4 and 5. The present experimental results are in good agree-
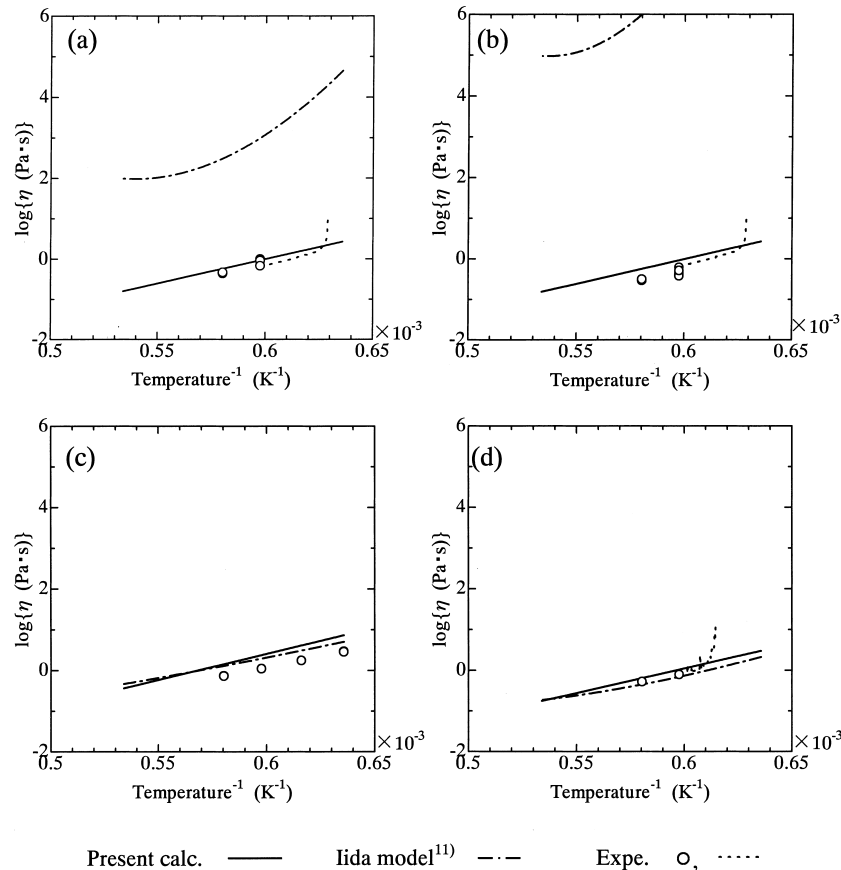
Fig. 7. Temperature dependence of the viscosity for the molten slag at composition (a) Slag 1, (b) Slag 2, (c) Slag 3 and (d) BFS.

ments with those literature values, and the calculated results reproduce reasonably the composition dependence of the viscosity of molten slag with SiO_2–CaO–MgO–10 and 15mass%Al_2O_3 system. Since the information on the viscosity in SiO_2–CaO–MgO–35mass%Al_2O_3 system have not yet been reported so far, the literature values[10] for SiO_2–CaO–Al_2O_3 ternary system are shown with the experimental results in Fig. 6. **Figure 7** shows the comparisons of the temperature dependence of the measured viscosity for Slag 1 to 3 and BFS with the calculated results obtained from the present model as well as the modified Iida model,[11] which is reported to perform well for blast furnace slags.[12] The modified Iida model reproduces well the temperature dependence of the viscosity of the samples Slag 3 and BFS. At the compositions of 35 mass% Al_2O_3 for Slag 1 and 2, however, the calculated results of the modified Iida model deviate considerably from the measured values, whereas those of the present model at the compositions reproduce the experimental results. Thus, the present model can be applied to evaluate the viscosity of molten SiO_2–CaO–MgO–Al_2O_3 in wide Al_2O_3 concentration range.

4. Conclusions

The viscosity of molten SiO_2–CaO–MgO–Al_2O_3 slags was measured using the rotating cylinder method and was compared with the calculated results of the model derived

by the authors. The experimental results showed that the 35mass%Al_2O_3–43.1mass%CaO–7.5mass%MgO–14.4 mass%SiO_2 slag, which melts below 1 673 K, had the viscosity below 0.6 Pa·s at 1 673 K. The viscosity of molten SiO_2–CaO–MgO–Al_2O_3 system can be evaluated from the present model in wide Al_2O_3 concentration range.

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