

Wetting Behavior of Molten CaO-Al₂O₃-SiO₂ Slag on Al₂O₃ Substrate

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Abstract

The wetting behavior of molten CaO-Al₂O₃-SiO₂ slags on a Al₂O₃ substrate was investigated using the sessile drop method at 1873K. For the slag compositions along the CaO saturation range, the wetting angle increased with increasing SiO₂ content up to 20 wt.% of SiO₂, but further increase in SiO₂ resulted in decrease in the wetting angle. For a same CaO/SiO₂ ratio, the wetting angle increased with increasing Al₂O₃ content. Using the experimental results maps were constructed for iso-wetting angles and iso-spreading rates. The MgO addition greatly increased the wetting angle and showed a maximum value at MgO content of about 3.5 wt%.

1. Introduction

In steelmaking processes, the reaction rates are influenced by the interfacial characteristics. Particularly when the removal of inclusion is carried out using fluxes, its efficiency is affected mainly by the interfacial properties of molten steel-slag-inclusion system.

A number of investigations^[1-4] have been carried out to determine interfacial tensions and wetting angles for several different molten metal(steel)-inclusion systems. For slag-inclusion systems, however, the number of works reported so far is few^[5-7] mainly due to the difficulty arising from continual change in the wetting angle by reactions between the slag and inclusion. Several mathematical and physical models^[8-10] have been proposed to describe the wetting behavior of a liquid on a solid substrate, but under conditions of no reaction between them. When chemical or dissolution reactions between the two phases undergo at the interface during spreading, the description of the wetting behavior suffers an added complication. Therefore some researchers described only the wetting behavior with time, and other researchers proposed the wetting angle under simplified conditions with a number of assumptions.^[5-7]

In the present study, the wetting behavior of molten CaO-Al₂O₃-SiO₂ slags on a Al₂O₃ substrate was investigated using the sessile drop method at 1873K. Based on the results found through the experimental investigations, a new model is proposed to describe the wetting behavior.

II. Experimental

1) Materials

Substrates were prepared with the sintered Al₂O₃(≥99.8%)(22mm_20mm_3mm). The surface roughness of the substrates was measured by using a non-contacting surface roughness measuring apparatus, and Figure 1 shows a typical result. It was found that the center-line mean roughness(R_a) and maximum height(R_{max}) were 0.553μm and 6.074μm, respectively.

Master slags were prepared by mixing high purity oxides (Al_2O_3 , SiO_2 , CaO and MgO) at an appropriate proportion and melted in a graphite crucible using the high frequency induction furnace. Then the slags were quenched, ground into powder, and decarburized by heating under the atmosphere at 1273K for 12 hours. The composition of the master slags was confirmed by XRF analysis. Slag samples for the measurement of wetting behavior were prepared by mixing the master slags in an appropriate ratio to weigh 0.3 grams in total. Each sample was pressed to form a small pellet. The slag compositions investigated in the present study are given in Figure 2.

2) Experimental Apparatus

The apparatus employed to measure the wetting angle is schematically shown in Figure 3. The alumina substrate was positioned horizontally in the induction furnace (15Kw-20KHz). A slag pellet was held in the graphite slag holder (5) which has a tiny hole at the bottom. The furnace including the substrate and the slag holder with the slag pellet was heated at a rate of $100^\circ\text{C}/\text{min}$ up to 1873K under the inert atmosphere by flowing argon gas. The system was isothermally held for 10 minutes at 1873K for complete melting of the slag sample. Then, the molten slag was slowly squeezed out of the slag holder through the hole at the bottom by pressurizing the tube (3) connected to the slag holder using a bellows. From the moment at which the molten slag drop touched the alumina substrate, the change of the shape, i.e., the wetting behavior, was continually recorded by using a digital video camera, which is capable to record 30 frames/sec. Using an image capturing software (MIRO DC-20 PLUS®), and the image digitizing software (WINDIG®), the change in the height and width of the drop with time was measured.

III. Results and Discussion

1) Spreading behavior

A typical wetting behavior of a slag is represented in Figure 4, in which it is seen that the slag drop spreads out on the alumina substrate as the time lapses. The moment at which the slag drop formed the right angle with the substrate was taken as the zero time. The typical experimental results of spreading behaviors are shown in Figure 5. It is obvious that the spreading occurs in order to approach the equilibrium contact angle between the slag and the substrate. A number of factors may be involved in governing the spreading behavior, i.e., the spreading rate. An additional factor will be imposed when both phases, i.e., the liquid slag and alumina substrate, suffer a chemical interaction. In order to check if a chemical reaction or mutual dissolution had taken place at the interface, some of the specimens (slag + substrate) was rapidly taken out of the heating zone after experiment and immediately quenched by blowing helium gas. Then the compositional change across the slag and substrate interface was investigated using EPMA. The results are given in Figure 6 and Table 1. It is clearly seen that the alumina content in the slag phase increases towards the alumina substrate, whereas CaO and SiO_2 are observed in the alumina substrate. These observations prove that, during spreading, the alumina substrate dissolves into the slag, and CaO and SiO_2 in the slag phase diffuse into the alumina substrate. Therefore, any analysis or modeling of the wetting behavior of a slag with an alumina substrate should take into consideration the effect of the mass transfer at the interface due to dissolution and diffusion.

2) Models for Wetting Behavior

As for the spreading of a liquid drop on a solid substrate, a number of models have been

proposed, and some of them are summarized in the following:

a) Newman^[8], and Cherry-Holmes^[9]

$$\cos \theta = \cos \theta_e (1 - ae^{-ct}) \quad (1)$$

$$\text{where } a = 1 - \frac{\cos \theta_o}{\cos \theta_e},$$

$$c = \frac{\sigma_{LV}}{\mu L},$$

$$\cos \theta = \frac{\sigma_{SV} - \sigma_{LS}}{\sigma_{LV}},$$

θ_o : Wetting angle at $t=0$,

θ_e : Equilibrium wetting angle,

θ : Wetting angle at a given time

μ : Viscosity of liquid drop

σ_{LV} : Surface tension of liquid drop

L : Scaling length

b) Ogarev et al.^[10]

$$t = \frac{\mu(3V_o / \pi)^{1/3}}{8\sigma_{LV}(\cos \theta_e - \cos \theta) \tan^{4/3} \theta} \quad (2)$$

where V_o : Volume of liquid drop

c) Shroeder.^[11]

$$\cos \theta(t) = \cos \theta_o + \cos \theta_e [1 - \exp(-At^b)] \quad (3)$$

In order to ascertain the validity of the above models for the present experimental geometry, a cold model experiment was carried out using liquid glycerol and a glass substrate. Figure 7 shows the experimental results together with the predictions by the various models. It is seen that the Newman's model does not show a good fit except at the initial stage (0 to 7 seconds). Figure 8 shows the experimental results and the application of Ogarev's model. The constants, $\frac{\mu(3V_o / \pi)^{1/3}}{8\sigma_{LV}}$ and $\cos \theta_e$ of Eq(2), are obtained by fitting the Eq.(4). In Figure 8, x-axis is a cosine value of wetting angle at a given time, $\cos \theta$, and y-axis is a $\log(t)$.

$$\log t = \log\left(\frac{\mu(3V_o / \pi)^{1/3}}{8\sigma_{LV}}\right) - \log[(\cos \theta_e - \cos \theta) \tan^{4/3}(\text{Arc cos}(\cos \theta))] \quad (4)$$

Fitting the experimental results gives the $\log[\mu(3V_o / \pi)^{1/3} / (8\sigma_{LV})]$ value of 0.463 and the cosine value of equilibrium wetting angle, $\cos \theta_e$ of 0.829. However, the $\log[\mu(3V_o / \pi)^{1/3} / (8\sigma_{LV})]$ value is not reasonable since the calculated value of that is -1.785.

From the above results, it was found that Newman's and Ogarev's models was not applied in all cases. The reason why they cannot be applied can be thought as the ignorance of the effect of surface roughness. The Shroeder's model which includes the effect of the surface roughness is found to apply well to the present experimental results.

It was also found that the Shroeder's model could not be applied to the system including

reacting media, since the equilibrium $\cos\theta$ value of 1.257 is not reasonable(Figure 9). It can be thought that it is caused by the continuous change of interfacial energy between slag and substrate.

However, the Shroeder's model does not include the effect arisen from the chemical interaction at the interface, which occurs in the present case. Therefore a new model that is capable of accommodating the interfacial energy variation is now proposed. To construct this model, following assumptions are required.

First, the driving force for spreading at any moment will be proportional to the difference between the present wetting angle and the equilibrium one. However, the equilibrium wetting angle changes with time the interface continually suffers the chemical interaction. Therefore the driving force for spreading is influenced not only by the present wetting angle, but also the change of the equilibrium value. Assuming that the interfacial tension between slag and substrate varies exponentially with time, the contact angle at a given time is represented by the following equation with B.C.'s:

Boundary conditions

- 1) $\theta = \theta_e^o$ at $t=0$
- 2) $\theta = \theta_e^\infty$ at $t=\text{infinite}$

$$\cos\theta_e(t) = [\cos\theta_e^\infty - (\cos\theta_e^\infty - \cos\theta_e^o)\exp(-kt)] \quad (5)$$

where θ_e : Equilibrium Wetting angle between slag and substrate at time t,

θ_e^o : Equilibrium wetting angle between slag and alumina substrate

before reaction. (True wetting angle between initial slag and substrate),

θ_e^∞ : Wetting angle at $t=\text{infinite}$

k : constant,

t : Time

The above assumption of the exponential variation of the interfacial tension with time may not be unreasonable, since the compositional change due to mass transfer generally undergoes exponentially with time and the interfacial tension is usually proportional to the materials compositions.

Replacing $\cos\theta_e$ in the Shroeder's model (Eq.3) with Eq. (5),

$$\cos\theta(t) = \cos\theta_o + [\cos\theta_e^\infty - (\cos\theta_e^\infty - \cos\theta_e^o)\exp(-kt)][1 - \exp(-At^b)] \quad (6)$$

where θ : Wetting angle at a given time,

b: Constant related to the surface roughness of substrate,

A : Constant related to the viscosity and surface tension of slag

In the above equation, the exponent b, which represents the surface roughness of the substrate, should be determined. The value of b for the alumina substrate used in the present study ($R_a = 0.553\mu\text{m}$) was determined through a cold model experiment using the glycerol and the glass substrates of various surface roughness. The regression analysis yielded a value of 0.5675. Now, Eq.(6) was applied to the experimental results with different slag compositions, and the various terms involved in Eq.(3) were determined through regression. Figure 10 shows a typical example of the application of this new model to the slag-alumina substrate.

3) Equilibrium wetting angles

Figure 11 shows the equilibrium wetting angles determined from the experimental results and Eq.(6). Iso-equilibrium wetting angle lines are also constructed in the figure. It is seen that, along the CaO saturation line, the equilibrium wetting angle increases with increasing

SiO₂ content up to 20 wt.% of SiO₂ but further increase in SiO₂ resulted in decrease in the wetting angle. For a same CaO/SiO₂ ratio, the equilibrium wetting angle increased with increasing Al₂O₃ content. For a fixed SiO₂ content, the equilibrium wetting angle increases greatly with increasing Al₂O₃ content in the range of Al₂O₃ content more than 30%, but, in the range of Al₂O₃ content less than 30%, the influence of Al₂O₃ content is not large (Figure 12). The variation of the equilibrium wetting angle with respect to the CaO/Al₂O₃ ratio is shown in Figure 13. As the ratio increases the equilibrium wetting angle decreases, but the equilibrium wetting angle for a given CaO/Al₂O₃ ratio shows a minimum value. As the ratio increases the minimum value tend to be deeper, and moves towards the higher SiO₂ content. Most of the minimum values lie in the SiO₂ content range of about 40~60%.

Fenzke^[13] reported that the surface tension of CaO-Al₂O₃-SiO₂ slag at 1873K increased with increasing the Al₂O₃ content while it decreased with increasing the SiO₂ content. As $\cos\theta$ is a function of surface tension of the slag, the equilibrium wetting angle variation with increasing Al₂O₃ content for a fixed SiO₂ content in Figure 12 is accord with the Fenzke's work. In addition, the equilibrium wetting angle variation according to the variation of SiO₂ content is accord with the surface tension variation of other researchers^[14]. And the 44wt.%CaO-56wt.%SiO₂ slag which has the lowest surface tension is nearly same with the composition that has the lowest equilibrium wetting angle.

The wetting angles and iso-wetting angles in 30 seconds after the initial contact are represented in Figure 14. The trend of wetting angle change in 30 seconds is similar to that of the equilibrium wetting angles shown in Figure 11. For the removal of inclusions, it is important to have not only the low interfacial energy between the slag and inclusion but also the high spreading(wetting) rate since the probability of re-entrapment to the molten steel of an inclusion which has arrived at the slag/metal interface will be greatly influenced by how rapidly it is grabbed by the slag phase. Figure 15 shows the spreading rate that is expressed as time to reach the wetting angle of 40°. The variation of the spreading rate with the slag composition shows a similar tendency to that of the wetting angle given in Figure 11 and Figure 12.

4) Effect of MgO addition on the wetting angle

The equilibrium wetting angle was measured with the slag containing 2%, 3.5%, 5%, 6.5% and 8% MgO. The slag compositions are listed in Table.2, and the equilibrium wetting angles are plotted in Figure 16. With MgO addition, the wetting angle changed greatly and shows its maximum value at MgO addition of about 3.5 weight percent.

IV. Conclusions

The wetting behavior of molten was investigated using the sessile drop method at 1873K. The findings are summarized in the following:

- 1) For the slag compositions along the CaO saturation range, the equilibrium wetting angle increased with increasing SiO₂ content up to 20 wt.% of SiO₂, but further increase in SiO₂ resulted in decrease in the equilibrium wetting angle.
- 2) For a same CaO/SiO₂ ratio, the equilibrium wetting angle increased with increasing Al₂O₃ content.
- 3) Using the experimental results a new model for the change of the wetting angle with time has been proposed.
- 4) Using the model, the equilibrium wetting angle was computed and maps for iso-equilibrium wetting angle and for iso-spreading rate were constructed for the system of CaO-Al₂O₃-SiO₂ slags on an Al₂O₃ substrate.
- 5) With MgO addition, the equilibrium wetting angle changed greatly and showed its maximum value at MgO addition of about 3.5 weight percent.

V. Acknowledgement

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VI. References

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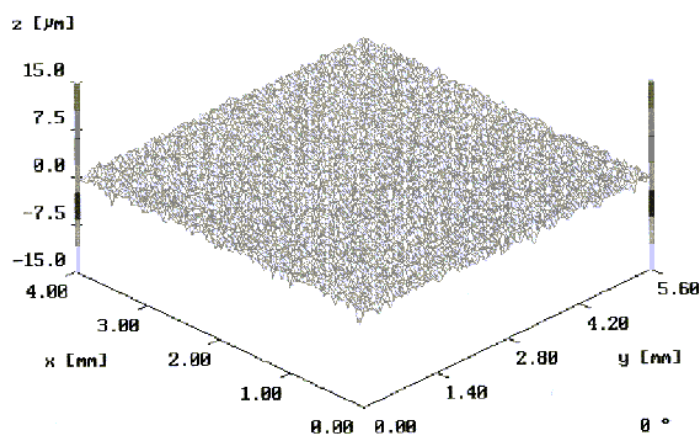


Figure 1 3-Dimensional surface roughness of alumina substrate

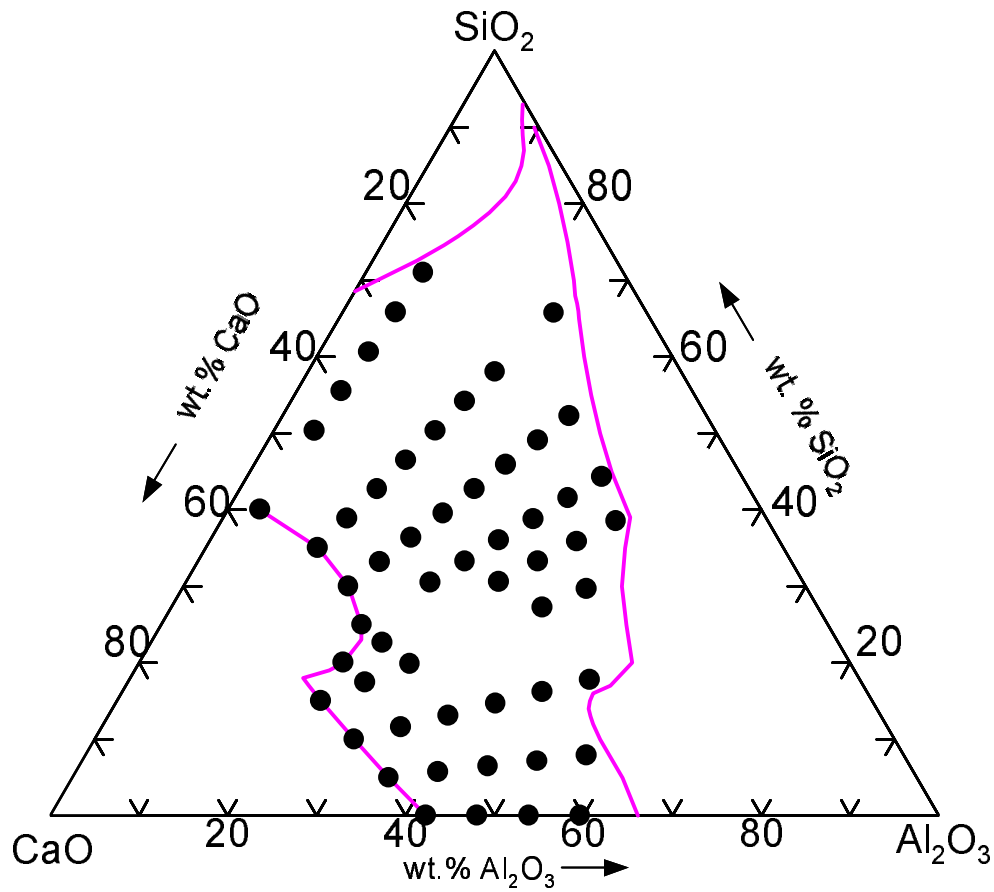


Figure 2 Slag compositions investigated for wetting behavior

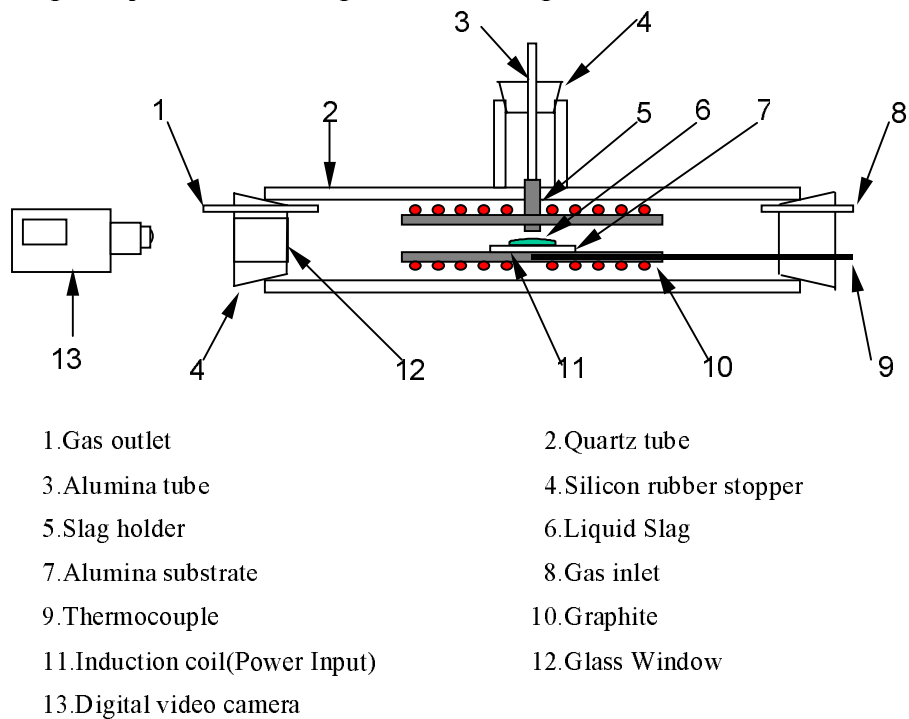


Figure 3 Experimental Apparatus

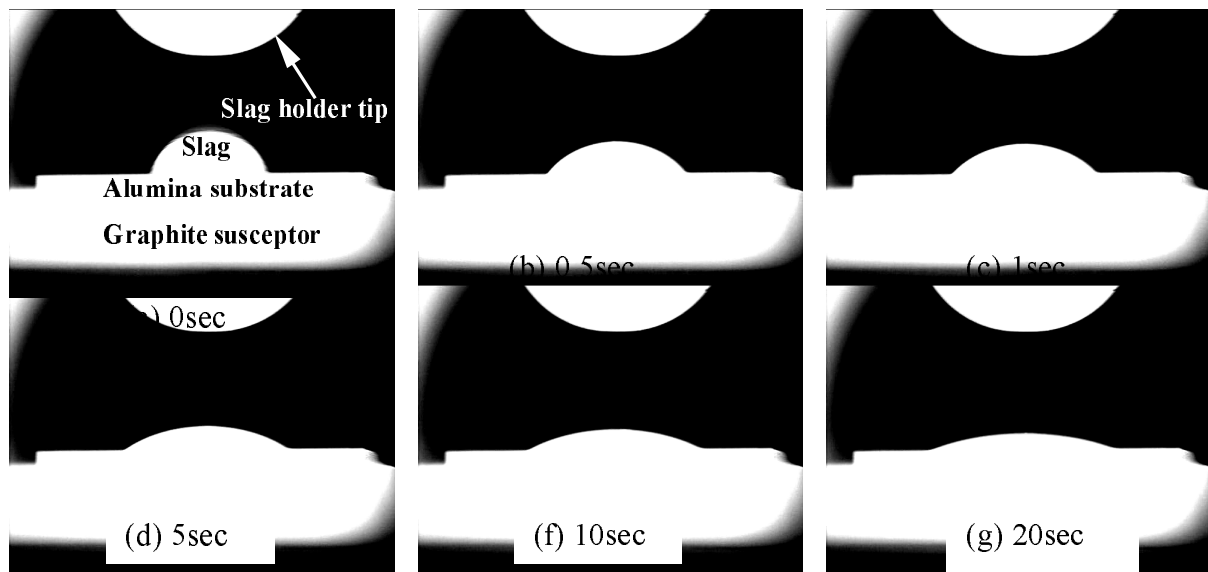


Figure 4 Spreading behavior of 52.3wt.%CaO-12.7wt.%Al₂O₃-35.0wt.%SiO₂ slag on an alumina substrate(1873K)

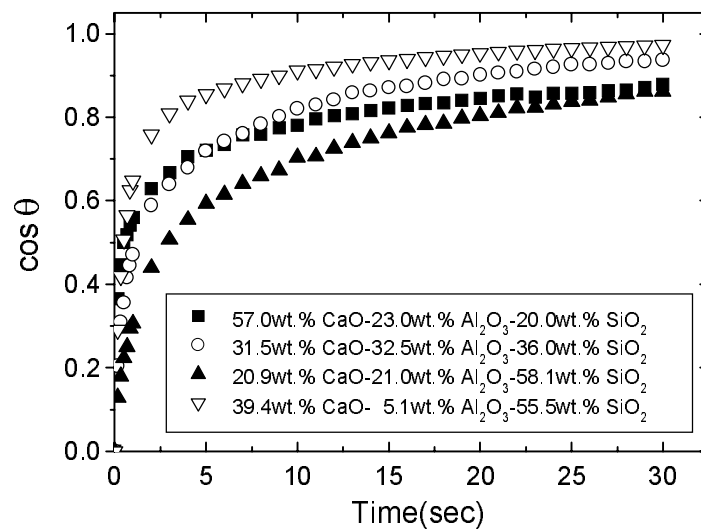


Figure 5. Some typical wetting behaviors of slag on alumina substrate

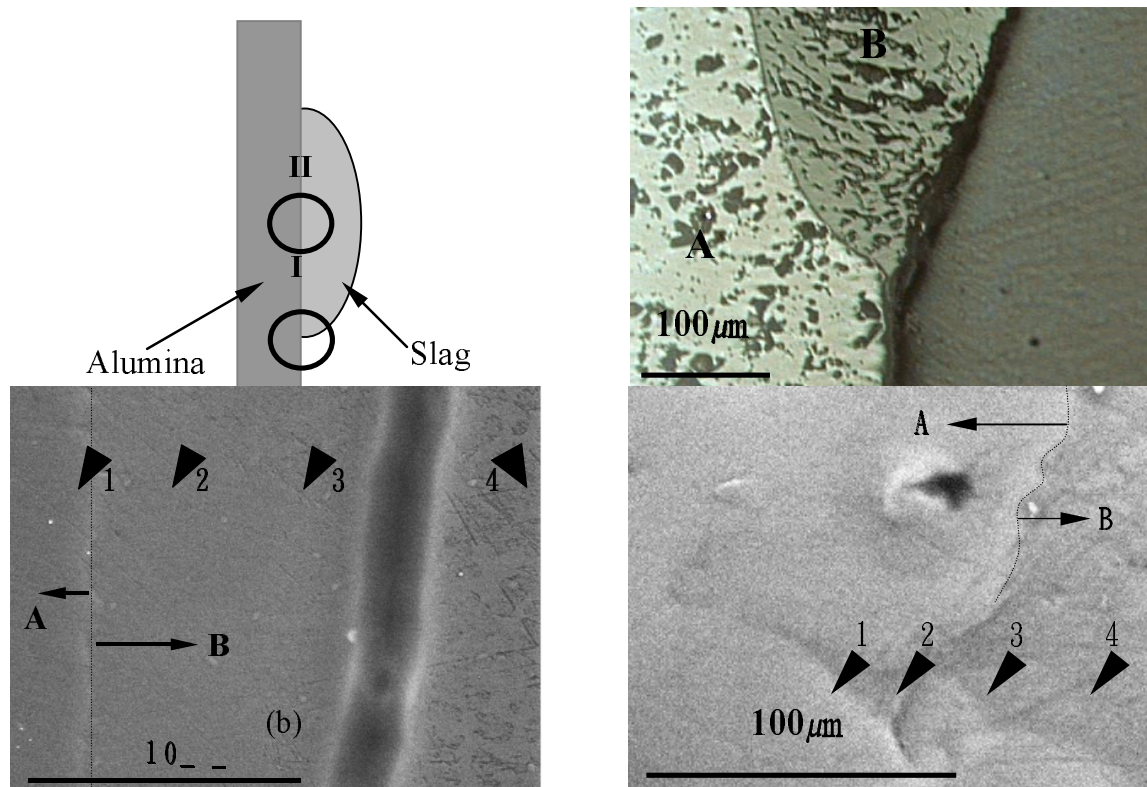


Figure 6 The images of interface between slag and alumina substrate(A:alumina substrate, B:slag)

(a) Macroscopic image of furnace cooled specimen (position I)

(b) Image of interface between 41.6wt.%CaO-51.2wt.%Al₂O₃-7.2wt.%SiO₂ slag and alumina substrate(position II)

(c) Image of interface between 53.5wt.%CaO-40.8wt.%Al₂O₃-5.7wt.%SiO₂ slag and alumina substrate(position II)

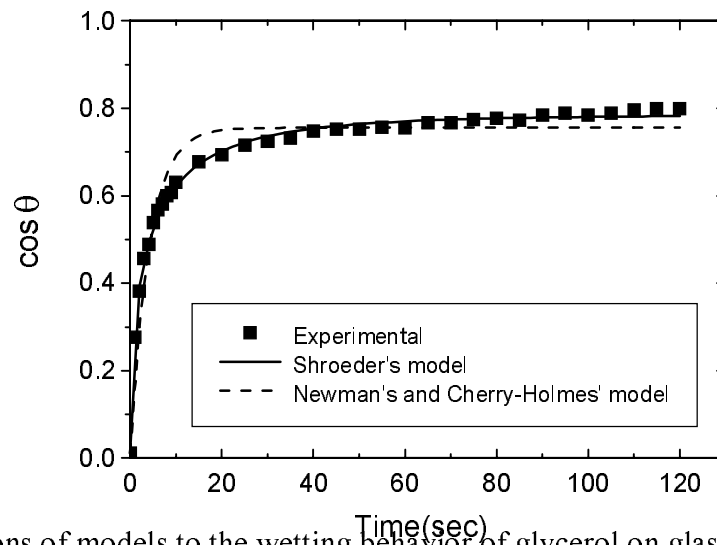


Figure 7. Applications of models to the wetting behavior of glycerol on glass

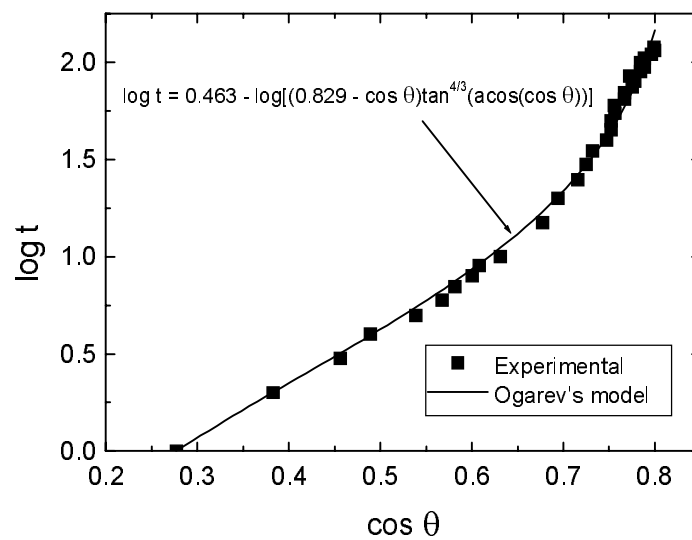


Figure 8 Application of Ogarev's model to the wetting behavior of glycerol on glass

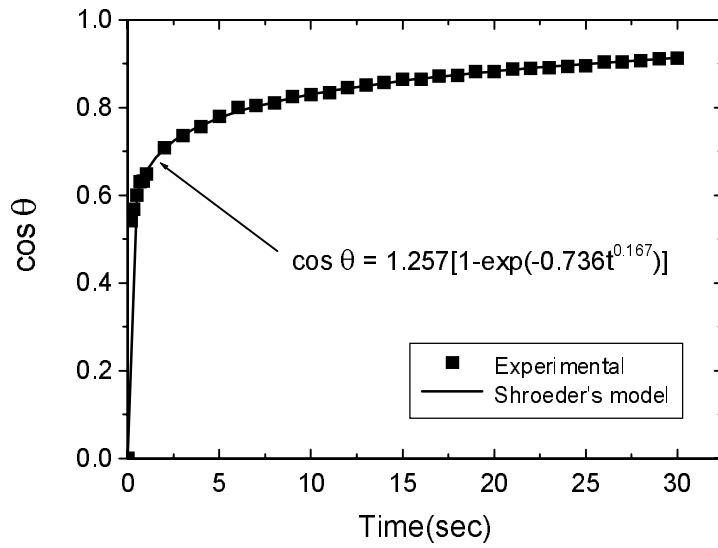


Figure 9 Application of Shroeder's model to the wetting behavior of 51.4wt.%CaO-18.5wt.%Al₂O₃-30.0wt.%SiO₂ slag on alumina substrate

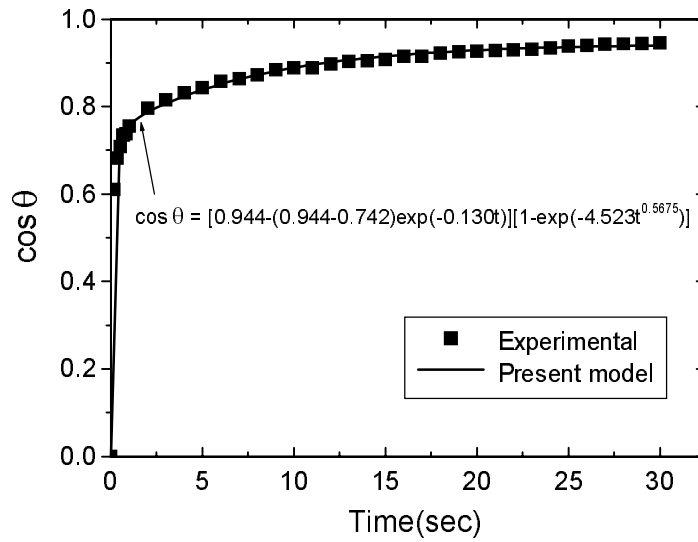


Figure 10 Application of a new model to the wetting behavior of 46.3wt.%CaO-20.5wt.%Al₂O₃-33.2wt.%SiO₂ slag on an alumina substrate

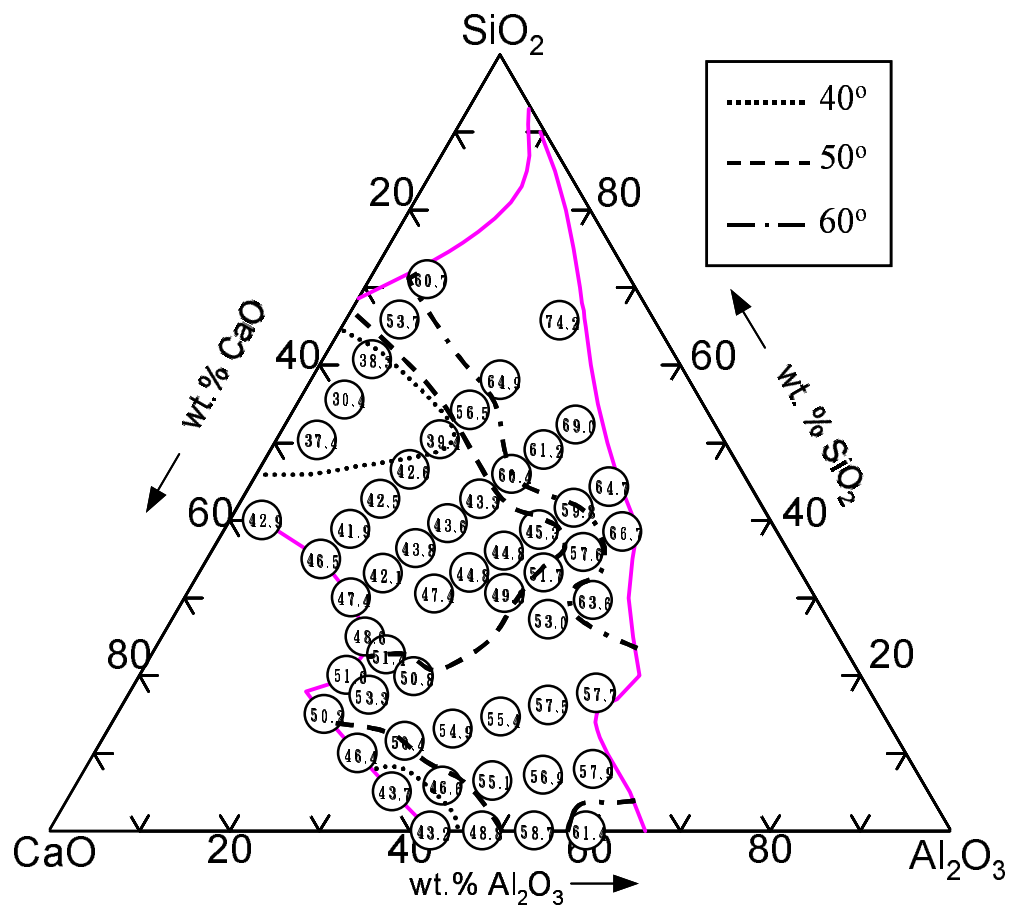


Figure 11 Equilibrium wetting angles and iso-wetting angle lines at 1873K

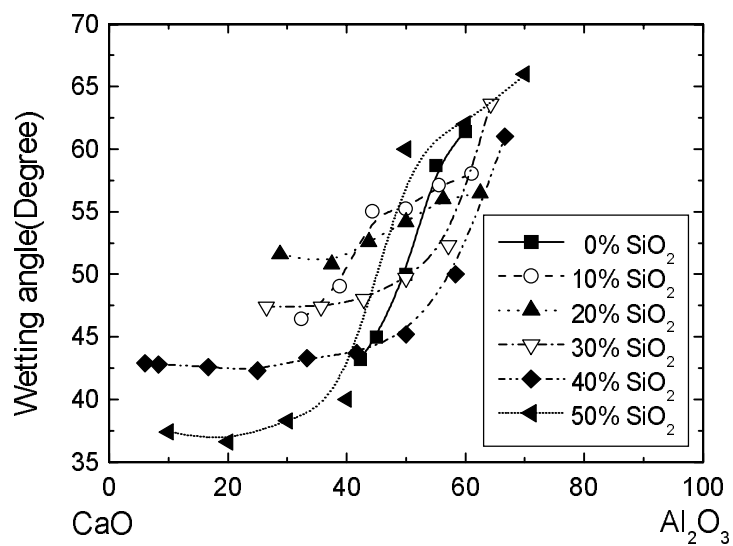


Figure 12 Change of wetting angle for fixed SiO_2 content with increasing Al_2O_3 content

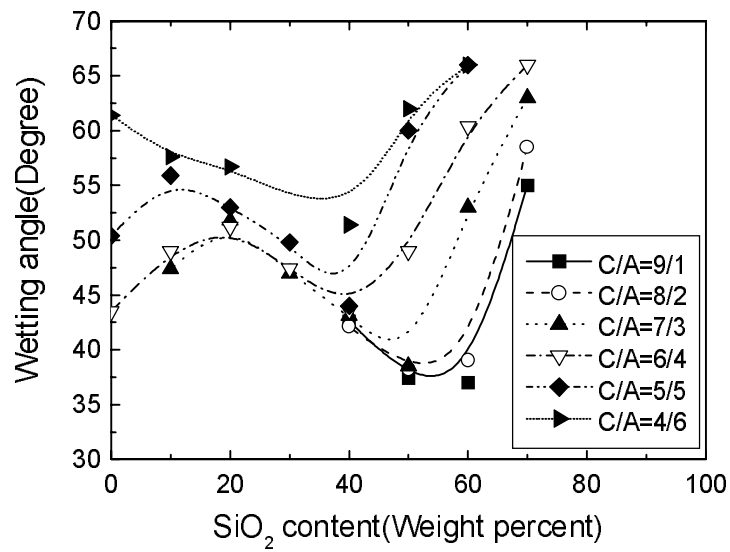


Figure 13 Change of wetting angle for fixed CaO/Al₂O₃ ratio with increasing SiO₂ content
(C:CaO, A: Al₂O₃)

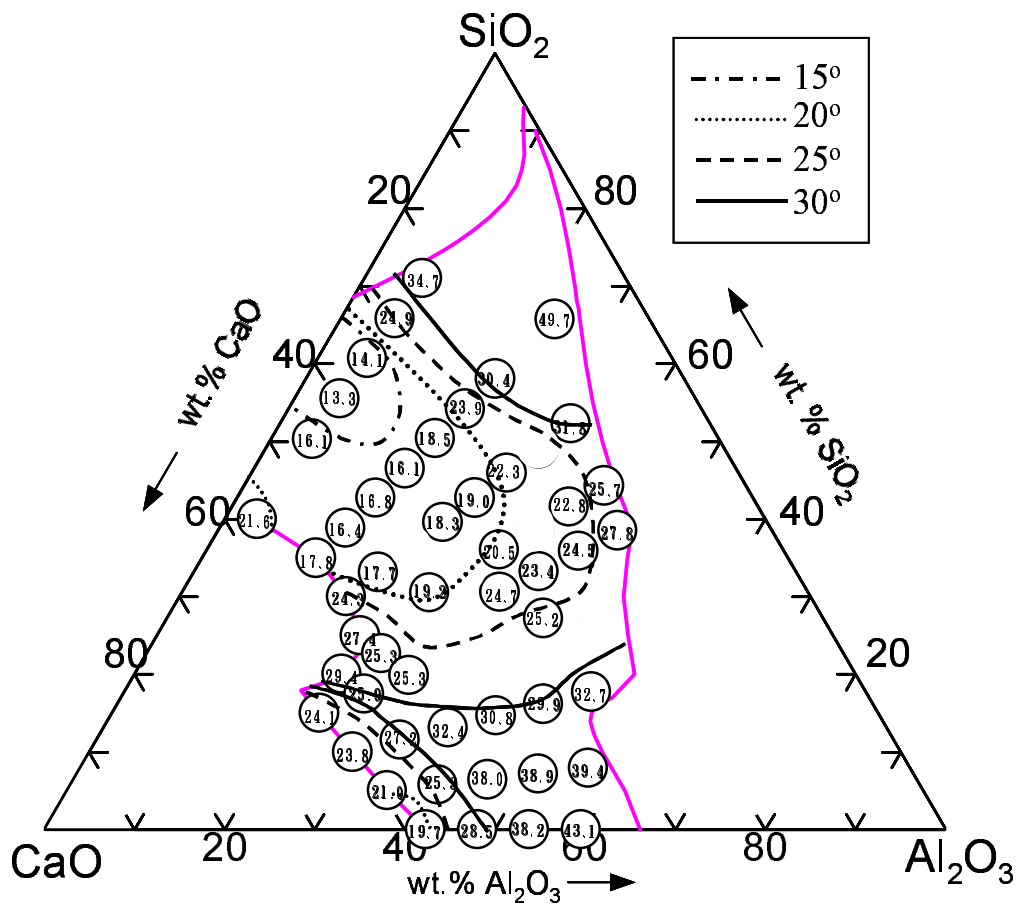


Figure 14 Wetting angles and iso-wetting angle lines in 30 seconds at 1873K

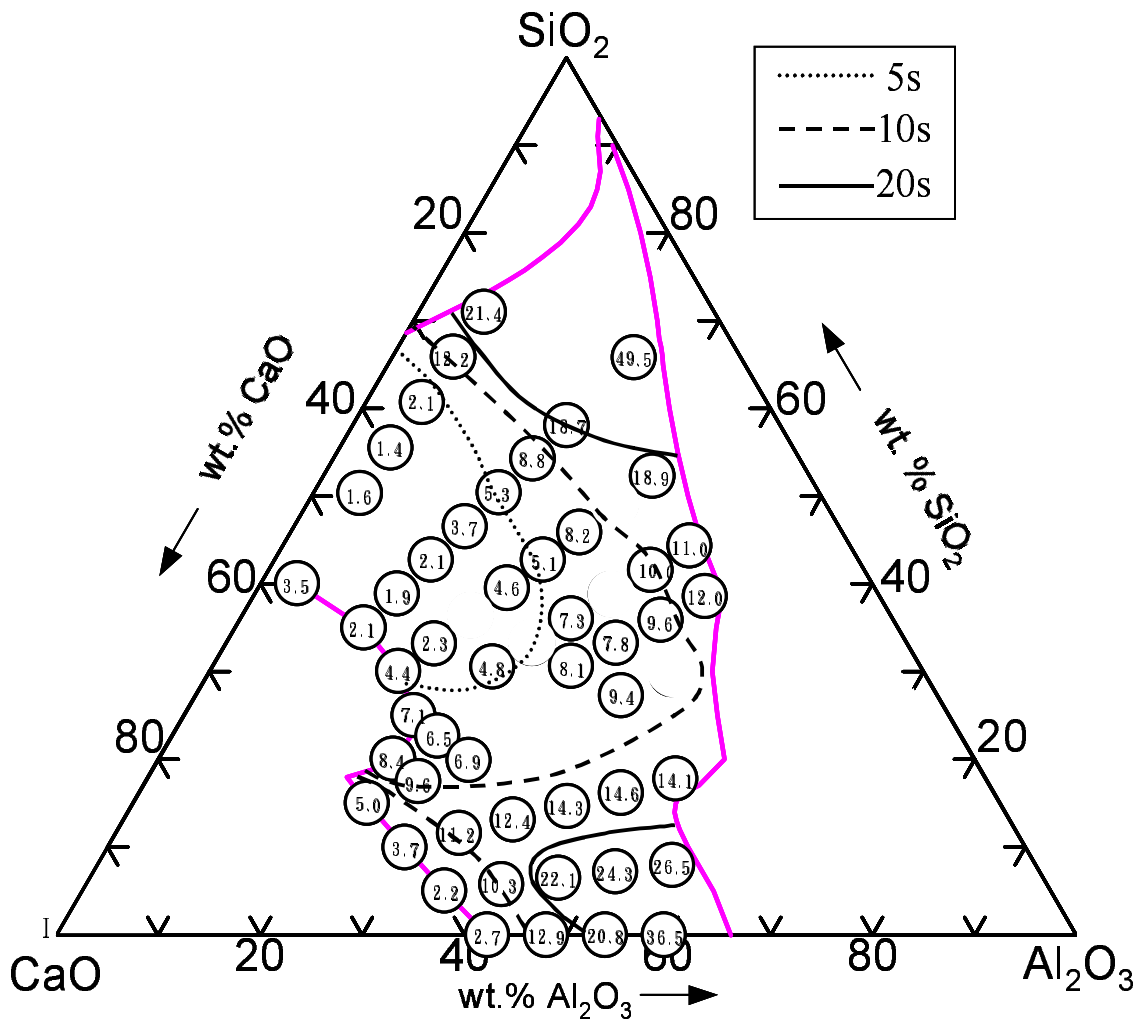


Figure 15 Spreading rates and iso-spreading lines in 30 seconds at 1873K

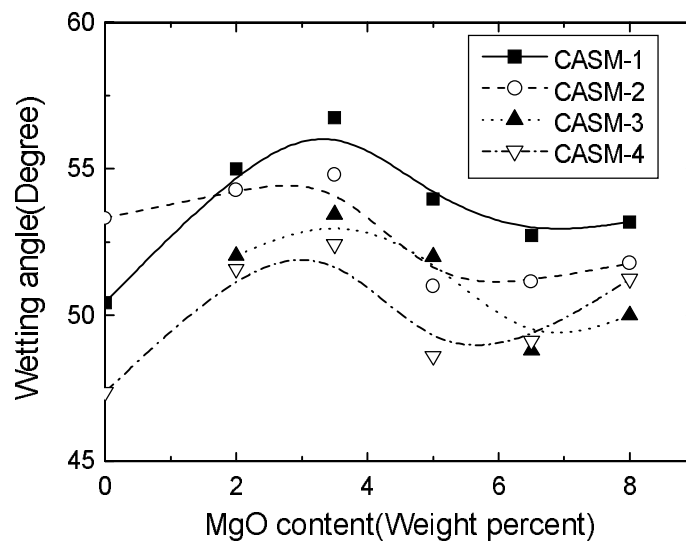


Figure 16 Effect of MgO addition on the wetting angle

(a) Initial slag composition : 41.6wt.%CaO-51.2wt.%Al₂O₃-7.2wt.%SiO₂ (Figure 6-(b))

Position Composition	1	2	3	4
CaO	5.2	23.3	32.9	42.3
Al ₂ O ₃	93.2	74.8	63.7	50.1
SiO ₂	1.6	1.9	3.4	7.6

(b) Initial slag composition : 53.5wt.%CaO-40.8wt.%Al₂O₃-5.7wt.%SiO₂ (Figure 6-(c))

Position Composition	1	2	3	4
CaO	0.8	6.6	36.3	36.5
Al ₂ O ₃	96.8	81.9	60.2	57.3
SiO ₂	2.4	11.5	3.5	6.2

**Table.2 CaO/Al₂O₃, CaO/SiO₂ in each slag
(CASM means CaO-Al₂O₃-SiO₂-MgO slag system)**

	CASM-1	CASM-2	CASM-3	CASM-4
CaO/Al ₂ O ₃	1.6	2.1	1.9	1.5
CaO/SiO ₂	4.7	3.2	1.7	1.4