Wetting, Spreading and Penetration Phenomena of Slags on MgAl$_2$O$_4$ Spinel Refractories

Taehee YOON,1) Kyuyong LEE,2) Baek LEE3) and Yongsug CHUNG1)*

1) Department of Advanced Materials Engineering, Korea Polytechnic University, Jeongwang 1-dong, Siheung-si, Gyeonggi-do, 429-793 Republic of Korea. 2) Department of Consilience, Korea Polytechnic University, Jeongwang 1-dong, Siheung-si, Gyeonggido, 429-793 Republic of Korea. 3) Thermo Fluid and Process Group, Technical Research Laboratories, POSCO, Donghaean-ro, Nam-gu, Pohang-si, Gyeongsangbuk-do, 37859 South Korea.

(Received on November 4, 2016; accepted on April 13, 2017; J-STAGE Advance published date: July 4, 2017)

The wetting, spreading and penetration phenomena between slags and refractories were investigated by using a dispensed drop technique with a high speed camera (1,000 frame/s) at 1,923 K and 1,873 K and using non-saturated slag and saturated slag on MgAl$_2$O$_4$ spinel. Single crystal spinel was adopted as a substrate to determine the intrinsic values associated with the phenomena including dissolution reaction. Industrial spinel substrates with 35% apparent porosity such as MgO-rich spinel, stoichiometric spinel and Al$_2$O$_3$-rich spinel were used to study the influence of chemical composition and porosity of refractories on those phenomena. In case of the stoichiometric spinel, the values of apparent contact angle and droplet height were found lower in comparison with single crystal spinel. When MgO and Al$_2$O$_3$ content were added to the spinel, the MgO-rich spinel appeared to have larger permeability of slag. On the other hand, the Al$_2$O$_3$-rich spinel showed larger resistance to slags. The change of apparent volume of slag in contact with substrate was analyzed using a spherical cap model.

The experimental values of the spreading rate of non-saturated slag are in good agreement with the value of the De-Gennes’s theoretical model.

KEY WORDS: MgAl$_2$O$_4$; wetting; spreading rate; penetration; refractory; contact angle.

1. Introduction

MgAl$_2$O$_4$ spinel containing refractory castables have been widely used as steel ladle lining, due to their high corrosion resistance to slag attack, low thermal expansion and good thermal conductivity.1−3) Nonetheless, this refractory deteriorates with slag penetration into the refractory because some parts of the refractory are always in contact with liquid slags. Therefore, longer refractory working life can be achieved if slag penetration is suppressed. This penetration phenomenon is related to the wetting between the refractory and slags.4,5) In addition, dissolution reaction between slag and refractory affect wetting and spreading rate.4,6) Several studies have been carried out for wetting behavior between slag and refractory.6,7) Several researchers on corrosion mechanism of MgO-rich spinel and Al$_2$O$_3$-rich spinel by slag attack in steelmaking have been carried out using a dipping test. It was observed that Al$_2$O$_3$-rich spinel showed improved resistance to slag penetration.10,11) However, the changes in the wettability and spreading behavior with time have not been studied.

In this study, single crystal spinel was used as a substrate to measure intrinsic values associated with the wetting and spreading kinetics including dissolution reaction. Addition-
ally, industrial spinel substrates were adopted to determine the influence of chemical composition and porosity of refractories on wetting and spreading. The wetting and spreading behavior between slag and various spinel substrates were investigated using a dispensed drop technique with a high speed camera (1 000 frame/s) at 1 923 K and 1 873 K.

The permeability of slags on the refractories was analyzed using a spherical cap model in which the variation of apparent volume with time was calculated quantitatively.

2. Experimental

The features of industrial spinel substrates such as substrate type, apparent porosity and surface roughness are listed in Table 1. Each spinel is designated by MR-C (MgO-rich), AR-C (Al2O3-rich), SP-C (stoichiometric) and SP-S (stoichiometric), where the letters, C and S, indicate castable and single crystal, respectively.

Apparent porosity was determined by Archimedes’ method using water as an immersion medium.

The stoichiometric spinel with a typical commercial composition (POSCO, Pohang Iron and Steelmaking Co.) used in this study was sieved below 75 μm and was mixed with 8 wt.% water. The mixed specimen was formed at 84 kgf/cm² into a disk with a diameter of 20 mm and thicknesses of 10 mm. The resulting specimen was then dried for 24 h at 333 K and sintered for 3 h at 1 873 K to be used as SP-C substrate.

The other castable specimens, MR-C and AR-C were made by adding magnesia and alumina (Sigma Aldrich, reagent grade) to stoichiometric spinel powder for desired weight ratio and then by following the same method as SP-C. The surface of the MgAl2O4 single crystal (Sigma Aldrich) substrate used in the experiments was (100) plane and the dimension was 10 × 10 × 0.5 mm.

The phase diagram of CASM slag-MgAl2O4 is given in Fig. 1. The chemical composition of slags can be divided into non-saturated composition and saturated composition calculated by Factsage 6.4™.

The composition of slags is made from reagent grade using an induction furnace in a graphite crucible and the specimen was quenched. The composition was confirmed by an X-ray fluorescence analysis (XRF), as listed in Table 2.

When the droplet contacted the substrate, the initial wetting was captured by a high speed camera at 1 000 frame/s. The droplet shape parameters such as contact angle, droplet
radius, and droplet height were measured by analyzing droplet images with the software ImageJ. For comparison of experimental data with slightly varying mass, droplet radius, droplet height, and droplet volume are normalized through dividing by the initial value of each experimental run. The normalized value is indicated as “ratio” in the following graphs. The contact angle data of different experimental runs are directly compared without normalization since the gravity effect is negligible due to low mass of the droplets.

3. Results and Discussion

3.1. Influence of Dissolution Reaction between Slag and Substrate

Figure 3 presents variation of contact angle, apparent droplet radius, and droplet height of the saturated slag and non-saturated slag on SP-S (single-crystal spinel) for 7 s at 1 923 K. The contact angle of saturated slag is drastically decreased to 15° within 0.5 s and then remained close to that angle. The contact angle of non-saturated slag is also quickly decreased within 0.5 s, but then gradually decreased toward the final contact angle, which is lower than that of saturated slag ($\theta_{F}^S = 14°$, $\theta_{F}^NS = 9°$). In Fig. 3(a), only the early stages before reaching the final contact angle are shown. Figure 3(b) shows that the change of the apparent droplet radius of non-saturated and saturated slags in time. The spreading of non-saturated slag is slightly faster than that of saturated slag due to the convection by dissolution reaction of SP-S into non-saturated slag. Figure 3(c) shows the change of the apparent droplet height of non-saturated and saturated slags in time. The apparent height was measured from the substrate to the top of the droplet using the side image of the droplet.

The apparent droplet height of non-saturated slag is lower than that of saturated slag. The reason is that there was crater formation at the interface by dissolution reaction between non-saturated slag and SP-S.

Figure 4 shows cross-section images of the quenched specimen for non-saturated and saturated slags on SP-S substrate.

While the interface between saturated slag and SP-S is flat (Fig. 4(a)), Fig. 4(b) clearly shows that at the interface between non-saturated slag and SP-S the crater is formed by the dissolution of SP-S into the non-saturated slag.

3.2. Effect of Substrate Porosity on Wetting and Spreading Rate

Figure 5 shows the high speed camera images of the non-saturated slag droplet on SP-S (single-crystal spinel) and SP-C (castable spinel) at 1 873 K. In contrast to SP-S, the droplet almost disappears on SP-C within 1 second.

The contact angle of non-saturated slag droplet on SP-S and SP-C are shown as a function of time in Fig. 6(a). Initially, the contact angles for both SP-S and SP-C substrates rapidly decrease to 30° within initial 0.1 seconds. After 0.1 s the contact angle for SP-S is gradually decreased, and after 0.5 s it reaches to the equilibrium angle (about 22°). In contrast, the contact angle for the SP-C is continuously decreased and reaches to 8° at 1 second. The difference in wetting behavior between SP-S and SP-C is due to the penetration of the slag through the pore existing in the SP-C. Figure 6(b) shows the apparent droplet height of slag on SP-S and SP-C. In case of the SP-S substrate, the droplet height rapidly decreases and then, after 0.5 second, it remains at a constant value (about 24% of the initial height). On the other hand, the droplet height on SP-C is continuously decreased toward the value lower than that on SP-S. This is again the result of the slag penetration due to the pore existing in the SP-C substrate.
3.3. Effect of Chemical Composition (MgO, Al₂O₃)

Figure 7 shows the wetting and spreading behavior of the slag when MgO and Al₂O₃ were added to the spinel substrate. In comparison with SP-C, the contact angle of slag on MR-C (MgO-rich castable spinel) is quickly decreased and finally becomes unable to be measured due to the entire penetration of the slag into MR-C as shown in Fig. 7(a). In contrast, the contact angle of slag on AR-C is decreased more slowly than that of slag on SP-C. In case of SP-S, except for the initial stage of quick change, the apparent shape of the slag droplet remains the same. Figure 7(b) shows that for all the castable substrates the spreading rate of the slag is quickly increased and then gradually decreased. Among the castables, the penetration of slag on MR-C proceeds the most rapidly, while the penetration of slag on AR-C proceeds the most slowly. Therefore, the apparent droplet height of slag on MR-C is lower than that of slag on AR-C as shown in Fig. 7(c).
3.4. Apparent Droplet Volume Using a Spherical Cap Model

Using a spherical cap model, apparent droplet volume was calculated to understand the permeability of slags on various substrates. The shape of droplet in contact with the substrate was assumed to be a spherical cap, and its volume was calculated by using Eq. (1).

\[
V = \frac{1}{3} \pi \left[ 2R^3 \left( 1 - \cos \theta \right) - r^2 \left( R - h \right) \right]
\]

Figure 8 shows the geometry of the spherical cap. \( r \) is the apparent droplet radius and \( h \) is the apparent droplet height, which are experimentally obtained. \( R = \sqrt{r^2 + h^2} \) and \( \theta = \sin^{-1} \left( \frac{2hr}{r^2 + h^2} \right) \) are functions of \( r \) and \( h \).

The initial apparent volume of saturated slag droplet on SP-S is 1.5 mm\(^3\) and that of non-saturated slag droplet on SP-S is 2.14 mm\(^3\) at 1923 K. At 1873 K, that of non-saturated slag on SP-S is 9.5 mm\(^3\), and that of non-saturated on SP-C, MR-C and AR-C are 15 mm\(^3\), 10.7 mm\(^3\) and 37.3 mm\(^3\), respectively. Initial apparent volumes are different because the flow of slag is slightly different for each time the droplet is dispensed.

Figure 9 presents the ratio of the changing apparent volume to the initial apparent volume of slag droplet on substrates at 1923 K and 1873 K. \( r \) gradually increases and accordingly \( h \) decreases. In case of the saturated slag on
SP-S, the apparent volume is steady with time because there is no reaction between saturated slag and spinel substrate. In contrast, the apparent volume ratio of non-saturated slag droplet on SP-S decreased down to 0.75 due to the crater formation by dissolution of spinel into non-saturated slag.

In case of all the castable substrates, the apparent volume of non-saturated slag droplet is quickly decreased with time, in comparison to slags on single crystal substrate, due to the penetration of slag into the pore existing in substrate. Slag penetration through the pores existing in the refractories has been studied by previous researches. Open channels connecting the pores are formed during sintering of refractories, which allow the penetration of the slag. Among the castable substrates, MgO-rich spinel shows the most rapid decrease of the apparent volume.

3.5. Driving Force for Spreading of Slag Droplet

The driving force for spreading of droplet is either inertial force or viscous force. In inertial spreading for low viscosity liquid, local equilibrium is rapidly established at the triple line, thus the contact angle between slag and substrate promptly approaches the equilibrium angle. The viscous spreading is controlled by viscous friction. Kim et al. observed that, the spreading behavior of slag is controlled by viscous friction. When $\theta < 90^\circ$, the ratio of inertial force to viscous force is given by

\[
\frac{f_{in}}{f_v} = 0.0024 \frac{\rho \sigma_{LV}}{\eta^2} \theta^5 R \quad \text{............... (2)}
\]

where $f_{in}$ is the inertial force, $f_v$ is the viscous force, $\rho$ is the density (kg/m$^3$), $\sigma_{LV}$ is the liquid/vapor surface tension (J/m$^2$), $\eta$ is the viscosity (Pa·s), $\theta$ is the contact angle, and $R$ is the droplet radius. The values of density, surface tension and viscosity of the experimented slags are indicated in Table 3. The ratio can be used as a measure to determine which effect is dominant in the spreading. As shown in Fig. 10, the viscous force is dominant over the inertial force.

3.6. Non-reactive Viscous Model for Spreading Rate

The spreading rates of two types of slag on SP-S are presented in Fig. 11. The experimental spreading rate obtained by the change of apparent droplet radius is compared with the theoretical spreading rate calculated by De Gennes’s equation. De Gennes’s non-reactive viscous model equation is given by

\[
U = \frac{\sigma_{LV}}{3K\eta} \tan \theta (t) (\cos \theta_f - \cos \theta (t)) \quad \text{............... (3)}
\]

\[
U = \frac{\sigma_{LV}}{6\eta K} \theta (\theta^2 - \theta_f^2) \quad \text{............... (4)}
\]

where $U$ is the spreading rate, $\sigma_{LV}$ is the liquid/vapor surface tension (J/m$^2$), $\eta$ is the viscosity (Pa·s), $\theta$ is the contact angle, $\theta_f$ is the final contact angle at 7 s, and $K (\ln \frac{X_{\max}}{X_{\min}}$ is radius of droplet) is 10. Equations (3) and (4) are valid for $\theta < 90^\circ$ for $\theta < 45^\circ$, respectively.

As shown in Fig. 11, in case of the saturated slag at 1 923 K, since there is no chemical reaction, the experimental spreading rates are in good agreement with the theoretical spreading rates. In contrast to the saturated slag at 1 923 K,
the experimental spreading rate for the non-saturated slag at 1 923 K is slightly not well-fitted because of dissolution reaction. This can be explained that the non-saturated slag properties (surface tension, viscosity) become equivalent to the saturated slag properties.

4. Conclusions

The wetting, spreading and penetration phenomena of slags on various MgAl₂O₄ spinel substrates were investigated at 1 923 K and 1 873 K by using the dispensed drop technique. The following are the results obtained in this study.

1) The contact angles of the saturated slag and the non-saturated slag on SP-S (single-crystal spinel) are not largely different ($\theta_1 = 14^\circ$, $\theta_2 = 9^\circ$). However, the spreading rate of the non-saturated slag is higher than that of the saturated slag because of dissolution reaction of SP-S into non-saturated slag.

2) On both SP-S and SP-C (castable spinel) substrates at 1 873 K, non-saturated slag initially presents the similar behavior, where the contact angle rapidly decreases to 30° within 0.1 seconds. Then, the contact angle of slag on SP-C substrate is more quickly decreased than that on SP-S substrate due to the penetration of the slag into the pore existing in the SP-C. The final contact angles for SP-S and SP-C substrates at 1 s are 22° and 8°, respectively.

3) As MgO content of spinel is increased, the permeability of slag is increased. As Al₂O₃ content of spinel is increased, resistance to the penetration of slag becomes higher. It is analyzed through apparent volume calculated by spherical cap model including the change in contact angle, apparent droplet radius, and droplet height with time.

4) The spreading behavior of the slag in this study is controlled by viscous force. The experimental spreading rates of saturated slag at 1 923 K are well fitted to the theoretical spreading rates. However, experimental spreading rates of the non-saturated slag at 1 923 K are slightly deviated from the theoretical non-reactive model because of dissolution reaction. This can be explained that the non-saturated slag properties (surface tension, viscosity) become equivalent to the saturated slag properties.

Acknowledgement

This work was supported by the Industrial Strategic Technology Development Program (#10044705) funded by the Ministry of Trade, Industry & Energy of Korea.

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