Investigation of the Wetting Characteristics of Liquid Iron on Mullite by Sessile Drop Technique

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In the present work, reactions occurring between molten iron containing varying amounts of oxygen and mullite substrate were investigated through optical Sessile drop experiments. The reactions were followed in static as well as dynamic modes through contact angle measurements. Further, the reactions were followed as functions of time, temperature and oxygen partial pressure. The latter was changed by means of imposing a gas mixture of Ar–CO–CO2 into the furnace. The results showed that the contact angle between the substrate and the iron in purified argon gas was lower than the contact angles reported in literature for alumina and silica. Formation of a ternary slag during the reaction was observed and was subjected to SEM and EDS analysis. The thermodynamic criteria for slag formation and possible mechanisms of the reaction are discussed in the light of the experiments.

The results are of relevance in understanding the mechanism of corrosion of aluminosilicate refractories by molten iron.

KEY WORDS: wetting; contact angle; alumina; silica; mullite; iron drop; refractories.
2. Thermodynamic Background

In previous works, thermodynamic studies were carried out mapping the stabilities of the various phases in the systems Fe–O–Al and Fe–O–Si using thermodynamic data in literature. In the present work, an attempt was made to construct the phase stability diagram for the quaternary system Fe–O–Al–Si from thermodynamic data available in literature. The reactions involved in the stability diagram calculations are:

\[
3\text{Fe}(l) + \frac{3}{2} \text{O}_2 + 3\text{Al}_2\text{O}_3 - 2\text{SiO}_2(s) = 3\text{FeAl}_2\text{O}_4(s) + 2\text{SiO}_2(s)
\]

\[
7\text{Fe}(l) + \frac{7}{2} \text{O}_2 + 3\text{Al}_2\text{O}_3 - 2\text{SiO}_2(s) = 3\text{FeAl}_2\text{O}_4(s) + 2\text{Fe}_2\text{SiO}_4(l)
\]

The Gibbs energy of formation of solid hercynite, \( \text{FeAl}_2\text{O}_4 \), is given by the equation:

\[
\Delta G_f^{\circ} = -328348 + 82.044 \times T \quad \text{(J·mol}^{-1}\text{)} \quad \text{[1809 K and above]}
\]

This could be compared with the equation for Gibbs energy change for reaction (3) given by Chan et al.:

\[
\Delta G_f^{\circ} = -306248 + 76.316 \times T \quad \text{(J·mol}^{-1}\text{)} \quad \text{[1809–1973 K]}
\]

As can be seen, there is a difference between the two values reported in the literature. In the present work, for the sake of consistency in the calculations, only the values from Barin have been used.

In the case of reactions involving silica, thermodynamic calculations showed that two silicates are likely to be formed in the system, viz. orthosilicate and metasilicate. However, at steelmaking temperatures, only the orthosilicate (fayalite) in liquid form will be the stable phase. The reaction and the Gibbs energy for fayalite is:

\[
2\cdot \text{Fe} + \text{O}_2 + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4
\]

\[
\Delta G_f^{\circ} = -518959 + 71168.2 \times T \quad \text{(J·mol}^{-1}\text{)} \quad \text{[1490–1700 K]}
\]

which was extrapolated in the present calculations.

The stability diagram in Fig. 1 shows that at very low oxygen partial pressures in the gas, for example \( 2 \times 10^{-7} \) Pa at about 1850 K, mullite will be stable in contact with Fe. With higher oxygen contents in the gas, up to \( 4 \times 10^{-5} \) Pa oxygen at the same temperature, mullite reacts with the oxygen-containing iron drop to form hercynite and SiO\(_2\) both in solid state. The diagram also shows that fayalite, \( \text{Fe}_2\text{SiO}_4 \), will be formed along with hercynite, if the oxygen content in the gas exceeded \( 1 \times 10^{-6} \) Pa at 1850 K. This is likely to happen during certain steelmaking steps where the oxygen potential in the melt is locally high. The phase stability analysis does not consider any possible solid solution formation between mullite and \( \text{FeAl}_2\text{O}_4 \) solutions between fayalite and hercynite.

In reality, in the case of the above system, complications arise due to the dissolution of hercynite and mullite in the liquid fayalite formed. This will lead to the formation of a ternary \( \text{FeO}_3-\text{Al}_2\text{O}_3-\text{SiO}_2 \) slag (assuming that \( \text{Fe}^{3+} \) in the slag is negligible), the composition of which will change with the progress of the dissolution reaction in accordance with the phase diagram presented in Fig. 2. Further, as the slag is cooled, the phases stable at lower temperatures, like \( \text{FeSiO}_3 \) can precipitate. It should be noted that the formation and composition of this slag would not only be dependent on the thermodynamics factors but also on the kinetics of the reaction.

3. Experimental

In the present work, the reaction between mullite substrate and iron drop containing oxygen were investigated by means of the sessile drop technique. The experiments were carried out in purified argon as well as in atmospheres with varying oxygen partial pressures obtained by imposing a suitable mixtures of \( \text{CO} \), \( \text{CO}_2 \) and \( \text{Ar} \) onto the system. The changes in contact angles were followed with temperature as well as with time.

3.1. Materials

Pure iron was used in the present work and the batch analysis from the supplier is presented in Table 1. The elements in extremely small amounts have been deleted by the authors. The dense sintered mullite (with 95% theoretical density) consisted of 74% \( \text{Al}_2\text{O}_3 \) and 26% \( \text{SiO}_2 \). The gases, \( \text{CO} \), \( \text{CO}_2 \) and argon were used in the present work. The gas cleaning system used to clean the argon gas to \( P_{\text{O}_2} < 10^{-13} \) Pa has been described elsewhere.

3.2. Apparatus and Procedure

The apparatus used for the optical sessile drop measurements is schematically shown in Fig. 3. It consisted of a horizontal tube furnace could be heated up to a maximum temperature of 2073 K. The alumina reaction tube was closed on one side by a stainless steel lid with a sliding device, making it possible to move the experimental assembly inside the reaction tube. The other end of the reaction tube was closed by a quartz window allowing the camera to fol-
low the experiments visually. A thermocouple was also inserted into the furnace through the quartz window. The camera used during the experiments consisted of a charge-coupled camera (CCD), which was connected to a videocassette recorder (VCR). A date/time recorder connected between the two made it possible to record the images as a function of time. Thus, it was possible to analyse a dynamic wetting process.

In the experiments, approximately 0.3 g of pure iron was placed onto a mullite plate, which has previously been carefully polished and cleaned in an ultrasonic bath. The mullite plate was placed onto an alumina holder, which was attached to the sliding device in the furnace and was initially kept in the cold zone. The reaction tube was properly sealed to prevent air infusion into the system. The sample was heated up in purified argon gas and the appropriate Ar–CO–CO₂ gas mixture was then introduced into the system after the attainment of the experimental temperature. The furnace was then allowed to stabilize for at least 60 min before the substrate/metal assembly was carefully pushed into the hot zone of the furnace. At the end of the measurements, the Ar–CO–CO₂ gas mixture was replaced by purified argon gas and the sample was then quenched. The substrate was taken out and the cross section was examined by Scanning Electron Microscope (SEM). Some selected experiments were repeated in order to confirm the reproducibility of the results.

The contact angle between the mullite substrate and iron drop was evaluated by the video film frames obtained adopting a procedure identical to that used by Jimbo and Cramb.14) The data analysis was carried out using a software developed at the Department of Material Science and
4. Results

The contact angle measurements of pure iron on mullite were carried out for three different partial pressures of oxygen at two temperatures. The targeted oxygen partial pressures, viz. $1.5 \times 10^{-2}$ Pa (experimental series A), $3.0 \times 10^{-3}$ Pa (experimental series B) and $9.9 \times 10^{-4}$ Pa (experimental series C) were obtained by imposing a suitable mixture of Ar–CO–CO$_2$ mixture onto the system. The liquid iron droplets were brought to equilibrium with these gas mixtures.

Figure 4 shows the optical images of an iron drop at different time intervals. These images are from experimental series B carried out at 1823 K. The oxygen partial pressure was imposed onto the system at 0 s and it can be seen that the initial contact angle between mullite and liquid iron, in purified argon atmosphere, is an obtuse angle. With the onset of the gas mixture, it is clearly seen that the obtuse angle changes to an acute angle with time and at around 100 s the angle reaches its lowest point. After this, there is a slight increase in the contact angle seen in the image corresponding to 126 s. This behaviour was also observed in the other experiments.

The partial pressure of oxygen and the contact angle observed for the different temperatures are presented in Table 2. In a number of cases of the dynamic measurements, it was not possible to obtain the zero time values as it was difficult to get the images at the very start. In these cases, the values from about 10 s are reported in the table. Repeated calculations of the optical images gave the estimation of the uncertainties in the reported contact angle values to be $6^\circ$.

When the experiments were finished and the samples were removed from the furnace, a slag layer was observed at the slag/substrate interface. The interface was examined in SEM and EDS analysis was carried out to determine the elements present. A micrograph from the SEM analysis for experimental series B at 1823 K is shown in Fig. 5.
schematic figure shows the location of the field of vision vis-à-vis the iron drop. It is seen that the iron drop has reacted with the substrate and had sunk into it. A slag layer was observed and in this slag, small particles could be seen. The micrograph of the enlargement of the slag layer is seen in Fig. 6. The EDS analysis showed that the slag formed consisted of different ratios of aluminium, silicon, iron and oxygen. The particles found were alumina and in the periphery of these particles, there was a layer of hercynite formed.

5. Discussion

Analysis of the images from the sessile drop experiments showed that the contact angle of molten iron on mullite, in purified argon atmosphere was 128°. This value is in agreement with the observations of Nogi and Ogino.7) The values are slightly lower than for those reported earlier by Kapilashrami et al.2,6) for alumina and silica. Espié et al.8) observed a similar behaviour. The lowering of the contact angle for iron on mullite was attributed by these authors to the substrate structure. In their work, the contact angle for sapphire was found to deviate slightly compared to the contact angle values for polycrystalline alumina. Mullite used in the present work was also polycrystalline with only 95% theoretical density. These factors could affect the contact angle. van Muu et al.9) observed a higher contact angle for alumina compared with mullite but lower contact angle for silica. To the best knowledge of the authors, no literature value is available for the wetting of iron on fayalite or the ternary Fe–O–Al–Si slag.

The dissolution of the silica part in the mullite substrate under pure argon, would lead to higher oxygen potentials in the iron drop, the reaction being:

$$\text{SiO}_2(\text{mullite}) \rightarrow \text{Si}(\text{Fe}) + 2 \cdot \text{O}_2(\text{Fe})$$

It can be expected that the oxygen levels in the iron melt due to the dissolution of the silica part, would be higher than those compared with that for pure alumina; but it is likely to be less than for pure silica. This would be in line with the observations of van Muu et al.9) On the other hand, in earlier works by Kapilashrami et al.,2,6) the results indicated that the contact angle values for alumina and silica substrates were somewhat similar, irrespective of the substrate. The reason could be traced to the very low oxygen levels in the argon gas maintained in the experiments by extreme precautions taken in purifying the gas. The iron drop in contact with this gas atmosphere may be expected to lose oxygen to the gas phase, resulting in higher contact angle values. The surface activity of silicon and aluminium has been reported to be less significant15); hence the impact of these elements on contact angle was neglected in the present discussion.

5.1. Temperature

The change in contact angle with time in the case of Experimental series A, at 1823 and 1873 K for the targeted oxygen level of $1.5 \times 10^{-2}$ Pa, is presented in Fig. 7. It is seen, for 1873 K, that the contact angle decreases gradually from the initial value of 128° at zero time to approximately 113° at 30 s. After this first stage, there is a sudden drop in the contact angle to 87°, which is followed by the second stage, where the contact angle shows a tendency to decrease slowly. Similar behaviour is also seen for the results at 1823 K. In this case, the drop after the first stage came at around 30 s and the contact angle changed from 118° to 109°. In this case the contact angle was stabilized at around
5.2. Oxygen Partial Pressure

The change in contact angle was measured with time and three different oxygen partial pressures at 1823 K. Experimental series A corresponds to “high oxygen” partial pressure and Experimental series B and C to “low oxygen” partial pressures.

Figure 8 shows the change in contact angle with time for Experimental series A and B. As mentioned before, in the case of the higher oxygen partial pressure, there are two main stages, the first when there is a gradual drop of contact angle during the first 30 s. This is followed by a slightly sharper decrease in the contact angle, which is more noticeable. The angle is finally stabilised at 105°. The trend for the lower oxygen partial pressure of oxygen is somewhat similar to the earlier case; but the changes in contact angles were found to be more drastic.

The trend in change in contact angle observed in the present work, viz. the immediate decrease in contact angle with the introduction of the gas mixture with high oxygen potentials, the somewhat steady state when oxygen diffuses from the surface of the drop to the bulk and then the final drop in the contact angle were similar to those seen in earlier work by the authors on silica substrate. At a critical point, there will be enough oxygen in the metal drop to initiate the reaction with the substrate.

The thermodynamic analysis shows that, when mullite and iron containing oxygen start reacting, fayalite and hercynite are likely to be formed. According to the ternary phase diagram of the system FeO-Al₂O₃-SiO₂ presented in Fig. 2, the hercynite, (along with mullite) will start to dissolve into the liquid fayalite and form a ternary liquid slag. The composition path of the slag will lie towards mullite in equilibrium with the solid phases mullite and corundum. The eventual presence of FeO in the slag has not been considered in the above discussion. The above reasoning is in agreement with the results of the SEM-EDS analyses. It should however be mentioned that, due to the kinetics of the reactions, there could still be particles of iron cordierite and hercynite due to the prevalence of non-equilibrium conditions. The composition of the slag would also change during cooling and low temperature phases could precipitate. This makes the EDS analysis of the slag very complicated.

As pointed out earlier, the SEM micrograph of the reacted drop in Fig. 5 shows the presence of solid particles in the slag phase. The corresponding EDS mapping, presented in Fig. 6 shows that the slag mainly consists of alumina, silica and iron oxide. The particles are found to be alumina particles and at the periphery of these particles, there is a layer containing aluminium, oxygen and iron. This layer was found to be hercynite. The EDS mapping also shows that the composition of the slag varies. The EDS mapping of other samples at various temperatures and oxygen partial pressures are in conformity with the expected path of the slag in accordance with the ternary phase diagram.

5.3. Substrate Morphology

It is likely that other factors, like inhomogeneity, surface roughness and amounts of pores, besides the composition of the substrate, may have an impact on the reaction mechanism. The substrates used in this work were not fully dense and smooth, but contained some amounts of pores and some surface roughness, despite the attempt to polish the surface. The analysis of the mullite substrate revealed that, along with the surface reaction with the substrate, reactions were taking place downwards into the substrate, which could escalate the slag formation and corrosion of refractories. However, Ogino et al. found that the impact of the surface roughness on contact angle was not pronounced. In the present work, it is assumed that the roughness of the substrates will play no significant role for the change in contact angle at the different temperatures and partial pressures of oxygen.

5.4. Wetting characteristics and Mechanism of corrosion

The results of the present study point to some of the mechanisms involved in the wetting phenomena of liquid iron on mullite refractory and the consequent effect on the corrosion phenomenon of aluminosilicate refractories. Thermodynamic analysis indicates clearly that at extremely low oxygen potentials, mullite is stable in contact with molten iron. This is indicated by non-wetting conditions and a high contact angle. This is also supported by the results of Nogi and Ogino. With the imposition of certain oxygen potential, the melt starts reacting with the substrate, the reaction products being different depending upon the oxygen levels in the melt. At oxygen partial pressures of the order of 4 × 10⁻¹³ Pa at 1850 K, the reaction products would be hercynite and SiO₂ according to the thermodynamic calculations. At higher oxygen levels (about 10⁻¹⁰ Pa at 1850 K), the products would be hercynite solid and fayalite liquid. In this case, the mutual solubilities of the products would lead to a complex slag.

While the instant decrease in the contact angle is likely to be due to the surface adsorption of oxygen, the oxygen
potential at the interface cannot be high enough so that any of the above reactions can occur. As oxygen diffuses into the bulk and reaches the interface, the chemical potential of oxygen at the melt-substrate boundary is likely to rise to the level needed for the chemical reaction. Preliminary diffusion calculations carried out by the present authors seem to support this. The situation is somewhat complicated by eventual convection currents in the drop that could hasten the transport of oxygen across the drop. Further, the reaction would be instantaneous at the periphery of the drop, while, the time taken could be longer near the centre of the contact area. Thus, there is also the possibility of the migration of the reaction front from the sides to the centre along the melt-substrate interface.

However, the attainment of mature oxygen levels for the reaction is marked by the decrease in the contact angles after 30 s. At this point, the contact angles correspond to the reaction products as substrates. The corrosion of mullite refractory by oxygen containing iron would be favoured by the low contact angles. With hercynite and SiO2 as the reaction products, there is risk for iron would be favoured by the low contact angles. With hercynite and SiO2 as the reaction products, there is risk for iron to end up in the melt. At higher oxygen potentials, the formation of liquid ternary slag is likely to accelerate the corrosion phenomenon. This, consequently, would contribute to the inclusion population in the melt apart from the chemical erosion of the mullite refractory.

6. Summary and Conclusions

The present work was focused on studying the wetting characteristics of oxygen-containing liquid iron on mullite by means of a dynamic sessile drop method. Well-defined oxygen partial pressures were imposed through gas mixtures containing CO, CO2 and Ar. The parameters studied were temperature (1 823 and 1 873 K), oxygen partial pressure (9.9 · 10⁻⁴, 3.0 · 10⁻³ and 1.5 · 10⁻²Pa). The results showed that the contact angle between pure iron and mullite in pure argon atmosphere was in agreement with earlier results by Nogi and Ogino. With the imposition of a higher oxygen partial pressure in the gas phase, the contact angle was found to decrease due to adsorption of surface-active oxygen on the surface of the drop. The contact angle decreased with time most probably due to the diffusion of oxygen to the bulk of the drop. The reaction with the mullite substrate was marked by the minimum in the contact angle, attained in 30–70 s. The contact angle corresponding to the minimum point was higher in the case of lower temperature. The lowering of the contact angle was more significant at higher partial pressures.

During the wetting process, the reactions at the interface were found to result in the formation of a molten slag. The slag phase formed contained alumina, silica and iron oxide. A thermodynamic analysis carried out in the present work shows that mullite is stable in contact with liquid iron at extremely low oxygen levels (corresponding to P02 = 2 · 10⁻³ Pa at 1850 K). At slightly higher potentials (about P02 = 4 · 10⁻³ Pa at the same temperature), mullite reacts with the metal phase to form hercynite and SiO2. If the oxygen content at this temperature exceeds 0.1 stranded hercynite and liquid fayalite are formed. Results of the SEM examination of the substrates after the experiments were in conformity with these calculations.

The present results indicate that the composition of the refractory plays a great role in corrosion of the furnace linings resulting in slag formation, which, in turn, can result in the formation of non-metallic inclusion in the steel matrix. While earlier work showed that alumina forms a thin, dense, non-wetting hercynite layer at the interface with a protective influence on the refractories, addition of SiO2 will result in the dissolution of this layer due to the formation of ternary liquid slag.

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