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Wetting characteristics of oxygen-containing iron melts on refractory oxides

E. KAPILASHRAMI, S. SEETHARAMAN*
Department of Material Science and Engineering, Royal Institute of Technology,
SE-100 44 Stockholm, Sweden

As part of refractory erosion studies, the wetting behaviour of molten iron containing varying amounts of oxygen on refractory oxides was investigated by the sessile drop method. The oxides investigated in the present work were alumina, silica and mullite. The reactions were followed in static as well as dynamic modes, under isothermal conditions, through contact angle measurements. Other parameters investigated in the present study were temperature and oxygen partial pressure.

For all substrates, the contact angles started decreasing due to the lowering of the surface tension of iron, as oxygen at constant partial pressure, came into contact with the surface of the drop. At a critical level of oxygen in the metal drop, a reaction product started forming at the drop/substrate interface and at this stage the contact angle dropped suddenly. In all cases there was a tendency for the contact angle to increase after this minimum.

In the alumina case, the iron drop moved away from the reaction site, once the product layer had been formed at the interface, probably due to the imbalance in the surface forces. In the case of SiO_2 and mullite, liquid slags were formed.

The substrates were analysed through SEM and EDS. The reaction products identified were in agreement with thermodynamic predictions. In the case of SiO_2, deep erosions were formed along the periphery of the drops, probably due to Marangoni flow.

The possible mechanisms of the reactions and their impact on refractory erosion are discussed in the light of the present experimental results.

1. Introduction

Refractory wear in steelmaking processes creates serious problems, with implications on process economy and environment. Earlier work [1, 2] showed that reactions between "FeO" in slags and refractory linings have a serious impact on the corrosion of the refractories. In the present work, it was felt that reactions between oxygen-containing iron and Al_2O_3, SiO_2, synthetic mullite as well as the aluminosilicate refractory lining could be of utmost importance (XRD analysis of industrial aluminosilicate refractory confirms the presence of mullite). The information obtained is intended to serve as a foundation for industrial refractory practice.

2. Thermodynamic analysis

The present work involved a thermodynamic analysis of the stable phases in the systems investigated. In the case of alumina, the phase diagram for the system FeO-Al_2O_3 [3] shows the existence of one intermediate compound, *viz.* hercynite ($FeAl_2O_4$). A phase stability diagram for the system was constructed [4] using data from literature [5]. In these diagrams; the assumption that the activities of alumina, iron and hercynite are 1 and the interactions from dissolved aluminium and oxygen are negligible were made. The diagram showed that at 1873 K and $P_{O_2} < 2 \times 10^{-5}$ in the atmosphere, solid alumina would be stable in contact with molten iron. At higher oxygen levels, solid hercynite would form.

In the case of the FeO-SiO_2 system, the calculations showed that at steelmaking temperatures, fayelite (Fe_2SiO_4) in liquid form will be stable. Similar to the alumina system, a phase stability diagram for the system FeO-SiO_2 was constructed [6] from literature data [5], with the assumption that silica, iron and fayelite are assumed to be 1 and the interactions from dissolved silicon and oxygen is negligible. In the diagram it was seen that at 1850 K, fayelite forms if the oxygen partial pressure in the gas exceeds 3×10^{-4} Pa.

In the aluminosilicate (mullite) case, the phase stability diagram was constructed for the quaternary system Fe-Al-Si-O and the result is presented in Fig. 1. The

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*Author to whom all correspondence should be addressed.

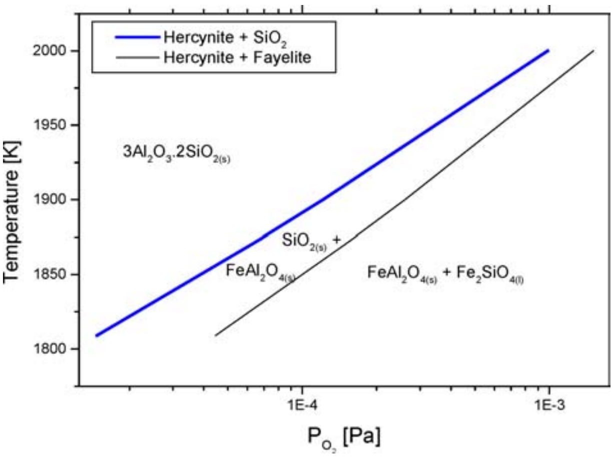


Figure 1 Phase stability diagram for the system Fe-O-Al-Si. Mutual solubility between compounds has not been considered.

reactions involved in the stability diagram calculations are:

$$3\text{Fe(l)} + 3/2\text{O}_2 + 3\text{Al}_2\text{O}_3{\cdot}2\text{SiO}_2\text{(s)} = 3\text{FeAl}_2\text{O}_4\text{(s)} + 2\text{SiO}_2\text{(s)} \quad (1)$$

$$7\text{Fe(l)} + 7/2\text{O}_2 + 3\text{Al}_2\text{O}_3{\cdot}2\text{SiO}_2\text{(s)} = 3\text{FeAl}_2\text{O}_4\text{(s)} + 2\text{Fe}_2\text{SiO}_4\text{(l)} \quad (2)$$

At 1850 K and with approximately $P_{O_2} < 2 \times 10^{-5}$ Pa in the gas, mullite will be stable in contact with Fe. At $P_{O_2} \approx 4 \times 10^{-5}$ Pa at the same temperature, mullite reacts with the iron containing oxygen to form hercynite and silica both in solid state. The diagram also shows that fayalite will form along with hercynite, if the oxygen content in the gas exceeded 1×10^{-4} Pa at 1850 K. The above phase stability analysis does not consider possible solid solution formation between mullite and hercynite or solutions between fayalite and hercynite.

In reality, complications arise in the quaternary system due to the dissolution of hercynite and mullite in the formed liquid fayalite. This leads to the formation of a ternary FeO-Al$_2$O$_3$-SiO$_2$ slag.

3. Experimental work

To investigate the reaction that occurs between molten metal and lining material on a micro scale, the sessile-drop method was used for monitoring the contact angles between molten iron and the oxide substrate in the temperature range 1823–1873 K. The changes in contact angle with time and P_{O_2} were also investigated.

The reaction sequence was followed through an image-recording device. The apparatus used and the experimental procedures have been presented elsewhere [4, 6, 7]. The experiments took place in purified argon gas as well as in mixtures of CO, CO$_2$ and Ar gases. The oxygen partial pressure in the system was measured through an oxygen probe set at the outlet of the furnace; with this the purified argon gas was found to have a $P_{O_2} < 10^{-14}$ Pa. The pressures of oxygen, obtained with the CO-CO$_2$-Ar gas mixtures, were $P_{O_2} = 9.9 \times 10^{-4}$ Pa, $P_{O_2} = 3.0 \times 10^{-3}$ Pa and $P_{O_2} = 1.5 \times 10^{-2}$ Pa as calculated by Thermocalc [8].

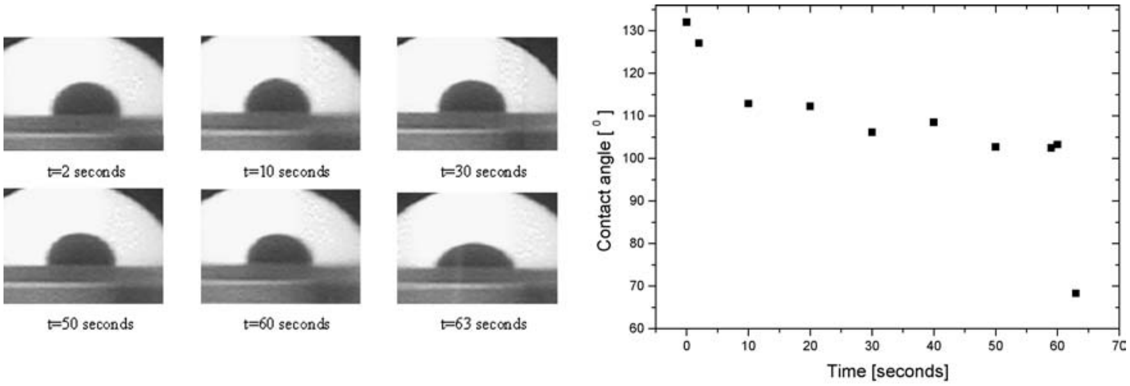
In order to investigate the reaction with industrial aluminosilicate refractory, sessile-drop experiments with industrial refractory substrate and pure iron as well as steel were carried out at at 1873 K in an argon atmosphere. The refractory and the steel grade were obtained from Uddeholm Tooling AB in Hagfors, Sweden.

4. Results

The first sets of experiments carried out were contact angle measurement with iron on alumina in pure argon atmosphere. The result showed very good agreement with data from earlier work [9–13]. Further, the change in contact angle with temperature was investigated for the temperature range 1823–1873 (the system was kept at the temperature for 1 h to allow the system to stabilise) but no significant change was observed.

Dynamic measurements of contact angles were carried out to monitor the change of contact angle as a function of time. The X-ray images and the corresponding calculated contact angle for the experiment at 1823 K and oxygen partial pressure of 3.0×10^{-3} Pa are shown in Fig. 2a and b.

The sharp decrease in the contact angle observed, is when oxygen is introduced into the system. Other



(a) (b)

Figure 2 a and b: X-ray images from the sessile-drop experiment with molten iron on alumina substrate at 1823 K at different time intervals and the corresponding calculated contact angle values, respectively. The oxygen partial pressure of 3.0×10^{-3} Pa was imposed at zero time.

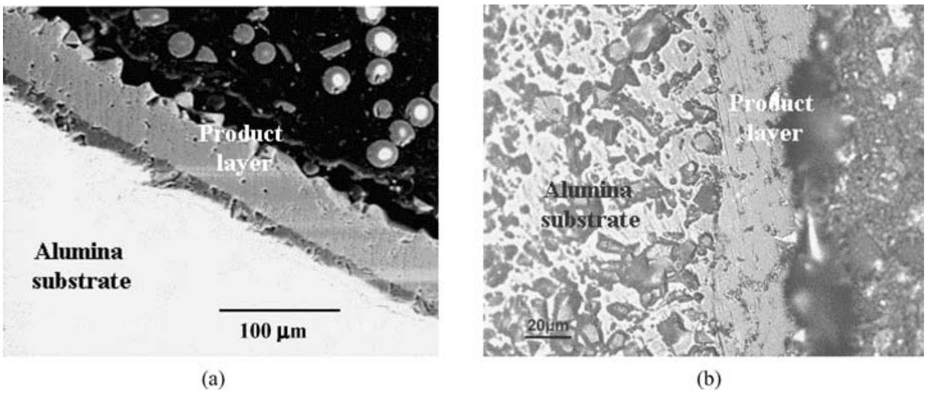


Figure 3 (a) and (b). Photomicrographs of the alumina substrate after the sessile-drop experiments at 1823 K and oxygen partial pressure of $P_{O_2} = 3.0 \times 10^{-3}$ Pa and $P_{O_2} = 9.9 \times 10^{-4}$ Pa, respectively.

research groups [9–17] made similar observations. A peculiar observation in the present work was that when the contact angle reached a minimum value the drop started moving laterally.

Cross sections of the used alumina crucible bottoms and the drops of iron from the experiments at 1823 K were subjected to microscopic as well as SEM analyses. In both cases, a product layer was identified between the alumina substrate and the iron drop. The photomicrographs of the cross sections of the alumina substrate under the experiments with $P_{O_2} = 3.0 \times 10^{-3}$ and $P_{O_2} = 9.9 \times 10^{-4}$are shown in Fig. 3a and b respectively. The wetting behaviour did not differ much between the experiments, except that the change in contact angle for the lower partial pressure was slower than for the higher.

The product layers formed in the two cases, identified as $FeAl_2O_4$ by EDS analysis, were found to be approximately 80 μm in the case of $P_{O_2} = 3.0 \times 10^{-3}$ Pa and approximately 30 μm in the case of $P_{O_2} = 9.9 \times 10^{-4}$ Pa. This suggests that the penetration of the reaction product on the substrate was a function of the oxygen content of the metal, with the layer thickness increasing with increasing oxygen level.

Similar to the alumina case, the change in contact angle of iron on silica with temperature was measured for the same temperature range and time as mentioned above. The contact angle was found not to change significantly with temperature. During the dynamic contact angle measurements ($P_{O_2} = 1.5 \times 10^{-2}$ Pa at 1823 and 1833 K) the contact angle decreased as the CO-CO_2-Ar gas mixture was imposed onto the system. Interestingly, the contact angle exhibited a tendency to increase after reaching a minimum point. This was similar to the observations in the case of the alumina substrate. At the end of the experiments, examination of the substrate and the drop revealed a thick layer of a slag phase at the base of the drop, surrounding it. Examination of the spot originally occupied by the drop revealed the formation of a small circular groove corresponding to the periphery of the drop in its initial position.

The SEM micrograph of the iron drop and the substrate, after the experiment at 1833 K is presented in Fig. 4. The low contact angle between the drop and the slag phase is quite evident in the figure.

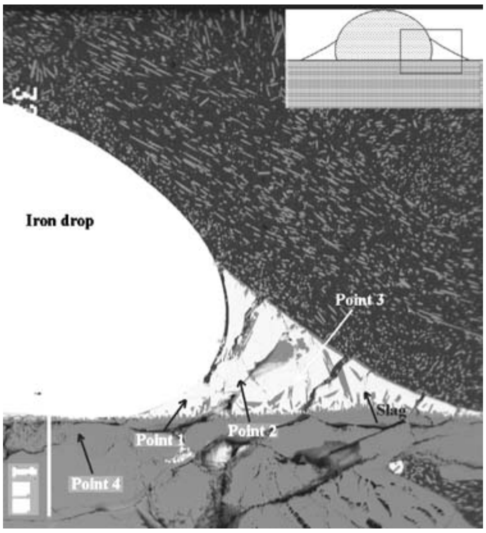


Figure 4 Photomicrograph of a section of the reacted drop and the silica substrate after the sessile-drop experiments at 1833 and oxygen partial pressure,$P_{O_2} = 1.5 \times 10^{-2}$ Pa.

In the case of pure iron on mullite, the contact angle measurements were carried out at 1823 and 1833 K for $P_{O_2} = 1.5 \times 10^{-2} P_{O_2} = 3.0 \times 10^{-3}$ and $P_{O_2} = 9.9 \times 10^{-4}$ Pa. For these experiments, an optical sessile-drop unit was used [7].

Similar to the observations made in the experimental work with alumina and silica, the contact angle between the drop and the substrate decreases as the surface-active oxygen reached the metal.

After the experiments, a slag layer was observed at the slag/substrate interface and this layer was examined in SEM. EDS analysis were carried out to determine the elements present. A micrograph from the SEM analysis for the experimental run at 1823 K and $P_{O_2} = 1.5 \times 10^{-2}$ Pa is shown in Fig. 5.

The 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 has also sunk into it. A slag layer entrapped in the metal drop was observed and in this slag, small particles were distinguished.

EDS mapping of the slag showed that it consisted of varying amounts of aluminium, silicon, iron and oxygen. The large particles in the slag were found to be

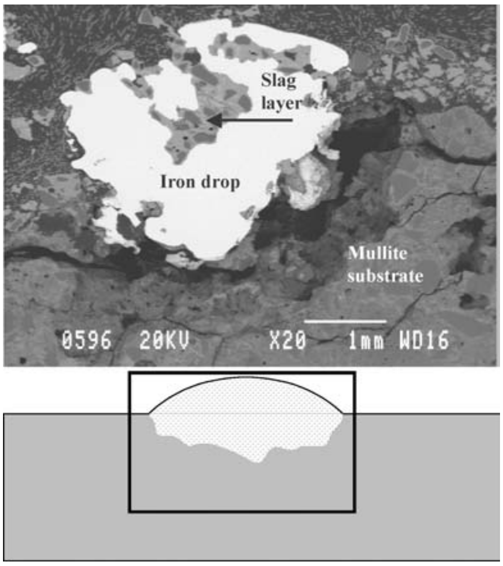


Figure 5 Photomicrograph of a section of the reacted drop and the mullite substrate after the sessile-drop experiments at 1823 and oxygen partial pressure, $P_{O_2} = 1.5 \times 10^{-2}$ Pa. The schematic figure shows the location of the field of vision *vis-à-vis the iron drop.*

alumina and in the periphery of these particles, there was a layer of hercynite.

In the case of the investigation of industrial refractory material with pure iron the contact angle was calculated to be 111° at 1 min and 109° at 2 min.

For the experiments conducted with refractory and steel (steel grade ORVAR 2M, Fe-0.37C-1.05Si-5.15Cr), the results were similar to the results for pure iron. The angle was found to be approximately 106° and did not change much with time, even after 1200 seconds.

5. Discussion

The contact angle behaviour of liquid iron drop on alumina substrate obtained by the sessile-drop experiments gave some indication of the formation mechanism of hercynite. The change in contact angle with time at 1823 K and $P_{O_2} = 3.0 \times 10^{-3}$ Pa has been presented in Fig. 2b. It is seen that when the gas mixture is imposed onto the system, there is an initial decrease in contact angle, which is likely to be due to the adsorption of oxygen on the surface of the metal drop. As the surface concentration of oxygen becomes high, diffusion of oxygen from surface to bulk becomes significant. Due to this, the surface concentration of oxygen cannot increase fast. Consequently, this leads to slow decrease of contact angle, and a pseudo-steady state. Finally, when the droplet becomes saturated with oxygen corresponding to the P_{O_2} imposed, it attains the equilibrium contact angle. The rapid decrease of contact angle after this point is probably due to change of dynamic contact angle to its equilibrium value. At this point there should be enough oxygen in the metal to form hercynite. In this case, the reaction gets stagnant and the contact surface would be covered completely by the product layer. The conditions change from wetting to non-wetting causing an imbalance in the forces acting on the drop and a lateral movement of the drop.

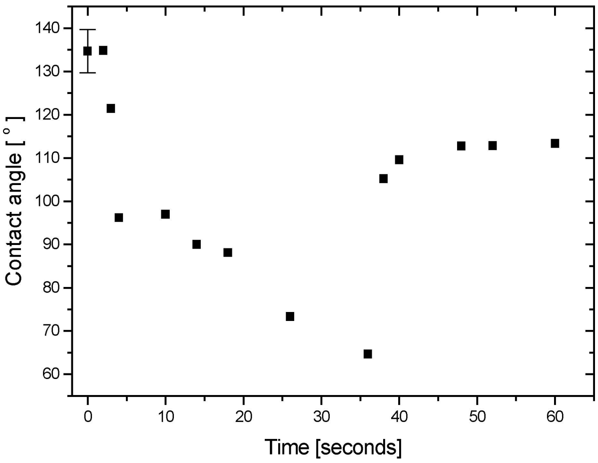


Figure 6 The change in contact angle with time for silica at $T = 1833$ for $P_{O_2} = 1.5 \times 10^{-2}$ Pa.

This phenomenon was clearly seen in the experimental work.

The experimental work on silica substrate showed the same tendency in contact angle change as in the case of alumina. Here, a reaction product starts to form when the drop reaches the equilibrium oxygen content with respect to the gas phase. At this point there would be enough oxygen in the system for fayalite slag to form. There is a likelihood of a thin fayalite layer formation between the substrate and the drop, which would arrest the reaction. At this stage, the contact angle measured would most probably be between the iron drop with oxygen potential equal to that of the gas phase and the thin slag film on the silica substrate. Beyond this point, the contact angle showed a tendency to increase. The change in contact angle with time at 1833 K and $P_{O_2} = 3.0 \times 10^{-3}$ is seen in Fig. 6.

In some of the experiments, there was a preferential corrosion observed along the periphery of the drop. A plausible explanation for this is that the erosion is caused by Marangoni flow in the melt induced by differential surface tension due to concentration gradients. The difference between the experiments at 1823 and 1877 K was that the extent of the decrease in the contact angle for the lower temperature was not as pronounced as for 1833 K.

Analysis of the images from the sessile-drop experiments with iron on mullite substrate showed that the contact angle in purified argon atmosphere was 128°, which is slightly lower that the contact angles obtained for alumina and silica. The change in contact angle with time for mullite and $P_{O_2} = 1.5 \times 10^{-2}$ Pa at 1823 and 1873 K is presented in Fig. 7.

It is seen that, similar to alumina and silica, there is a decrease in the contact angle when oxygen is introduced into the system and for the higher temperature, it continues to decrease. For the lower temperature the contact angle seems to be stabilized for a while, but even in this experimental series, the contact angle decreased after some time.

The slag formed during the reaction between mullite and molten iron would be different from the silica system. The thermodynamic analysis shows that when mullite and iron containing some amounts of oxygen

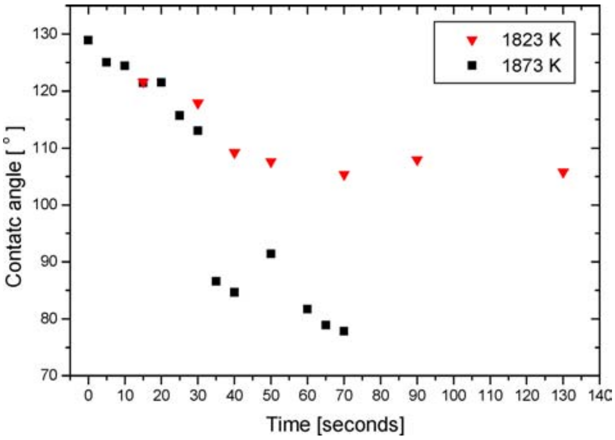


Figure 7 The change in contact angle with time for mullite $P_{O_2} = 1.5 \times 10^{-2}$ at 1823 and 1873 K.

start reacting, fayalite and hercynite will be formed. The mullite, fayalite and hercynite will then start to dissolve into each other and form a ternary slag. At the experimental temperature, the ternary slag would consist of FeO-Al_2O_3-SiO_2 and it would be in equilibrium with mullite and corundum. This is in agreement with the results of the SEM-EDS analyses. However, due to the kinetics of the reactions, there could still be particles of iron cordierite and hercynite as the reactions may not reach equilibrium. The composition of the slag would also change during cooling and low temperature phases could precipitate. This makes the interpretation of the results from the EDS analysis of the slag very complicated and difficult.

The experimental work on mullite also showed that other factors, besides the composition of the substrate, would have an impact on the reaction mechanism. Factors like inhomogeneity, surface roughness and amounts of pores may also be of importance. The analysis of the porous 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.

In the work on pure iron on industrial refractory, the results showed that the contact angle did not change much with time. This is expected, as the oxygen content in the atmosphere is low, which is similar to the conditions prevailing at the metal-refractory interface during casting. The contact angle was found to be approximately 110°, which is lower than the values for alumina, silica and mullite in purified argon. This is most probably due to the oxygen concentration. Similar observations were made for the experiments with industry refractory and steel. The contact angle was somewhat constant around 106° during the time interval of 3–1200 s.

6. Conclusions

In the present work, the reaction between iron containing oxygen and different oxides was investigated. In the case of alumina, the results showed the formation of a non-wetting product layer, which according to thermodynamic analysis should be hercynite. This was confirmed by EDS analysis of the layer. The thickness of the product layer was found to be a function of the reaction time and the oxygen content of the metal.

In the case of silica and mullite refractories, the reactions resulted in the formation of a slag. With silica substrate, the slag was found to be fayalite ($2FeO \cdot SiO_2$). In the case of mullite, the slag phase formed contained alumina. The slag formation led to non-wetting conditions and the movement of the iron drop.

Experiments with industrial refractories and steel as well as plant trials show that the contribution of runner refractories to the inclusion population of the final product is insignificant.

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