Communications

The Contact Angle between Liquid Iron and a Single-Crystal Magnesium Oxide Substrate at 1873 K

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The visible contact angle between liquid iron and various ceramic substrates has been the focus of numerous studies over the last 50 years.[1–13] Recent work has indicated that issues such as metal purity, gas-phase oxygen content, surface roughness, and substrate purity must all be controlled in order to accurately determine a visible contact angle.[9–13] In this study, in order to clarify the effect of the oxygen on the interfacial phenomena between magnesium oxide and pure iron, the visible contact angle between liquid iron and a magnesium oxide substrate was measured by the sessile drop technique[1–13] as a function of oxygen partial pressure at 1873 K. The sessile drop technique has been previously described and the details of the experimental apparatus used in this study have been reported.[11,12]

Ultra-high-purity argon gas and CO/CO_2 gas mixtures were used to control the oxygen partial pressure of the chamber gas. Argon was purified by flowing argon over heated copper ribbon, magnesium tips, and titanium sponge to obtain a very low oxygen partial pressure less than 10^{-16} atm in the reaction tube before entry into the sessile droplet chamber. An oxygen sensor was used to measure the oxygen partial pressure in the exhaust argon gas from the reaction tube. The CO/CO_2 was mixed to obtain oxygen partial pressures in the range from 5.2×10^{-14} to 1.0×10^{-9} atm.

To eliminate issues of magnesium oxide substrate purity, single-crystal magnesium oxide substrate materials were purchased from Alfa Aesar. The surface of the magnesium oxide substrate is the (100) plane, and the surface roughness, Ra, of the single crystal was measured as 0.02 μm. The iron samples were also purchased from Alfa Aesar and were of the following chemistry: 99.9985 pct Fe, which included measurable impurity contents of Cu 1 ppm, Mg 2 ppm, and Ti 2 ppm. The weight of the sample was always set to 2.5 g to minimize the effect of line energy on the contact angle, because the purpose of this study is to determine the effect of the partial pressure of the oxygen on the contact angle.

Throughout these experiments, the variation of the visible contact angle between liquid iron and a magnesium oxide substrate was observed under different oxygen partial pressures. For oxygen partial pressures from 10^{-9} to 10^{-14}, atm, a $CO/CO2$ gas mixture was used. Under these conditions, the drop of iron did not adhere to the substrate after the experiment, and the change of the contact angle with the elapsed time at constant oxygen potential is shown in Figure 1. The contact angle varied initially and became constant after 60 minutes. The initial change is mainly due to the time to achieve thermal equilibrium. For very low oxygen partial pressures, the drop adhered to the substrate and was difficult to remove from the substrate. This observation suggests reaction and reactive wetting below oxygen partial pressure of about 10^{-18} atm, and the contact angle for one of these conditions is shown in Figure 2 as a function of time. The variation of contact angles at 1873 K and 60 minutes in different oxygen partial pressure ranging from 2.0×10^{-19} to 1.0×10^{-9} atm is summarized in Figure 3, where the contact angle increased from 78 to 113 deg when the oxygen partial pressure was decreased from 10^{-9} to 10^{-14} atm and decreased to 66 deg when the oxygen partial pressure decreased to 10^{-20} atm.

These data indicate that under conditions where MgO is stable with respect to the gas phase, the contact angle decreases as oxygen potential increases; however, when the oxygen potential decreases to below the stability point of MgO, the contact angle changes dramatically from nonwetting to wetting. Thus, the visible contact angle of liquid iron on an MgO substrate is extremely sensitive to the oxygen partial pressure of the gas phase and can change from wetting to nonwetting by manipulation of oxygen potential.

A cross section (Figure 4) of the substrate in contact with the droplet after the experiment was observed by a scanning electron microscope with energy-dispersive X-ray. A region of interaction between the droplet and the surface can be clearly seen and some penetration of the metal into the substrate is visible. This interfacial penetration accounts for the adhesion between substrate and droplet.

Figure 5 shows the composition change along the line in Figure 4 from droplet top to bottom. A reacted layer was found along the interface between the substrate and the droplet. Its thickness was about 260 μm below the droplet and 100 μm at a distance of 400 μm away from the triple point (droplet-substrate-gas). The content of the iron abruptly changed at the interface between the reactive layer and the droplet, and then gradually decreased to the substrate. The magnesium content gradually increased in the substrate. On the substrate side, the change in composition is more gradual, probably showing that the reaction occurs by diffusion of iron into the MgO substrate. Spot analyses were also performed in the points from "a" to "d" of Figure 4. Points "a" and "d" are pure iron and MgO, respectively. In point "b," the ratio of iron and magnesium, (Mg/Fe), is 2, and in point "c," Mg/Fe is 3. Thus, the postexperimental analysis confirms the postulation that the droplet was reacting with the substrate under the low oxygen content argon gas condition, and the observed wetting droplets are due to reactive wetting and a loss of equilibrium at the iron-magnesia interface.

The contact angle between liquid iron and single-crystal magnesium oxide substrate was measured by the sessile drop technique at constant oxygen partial pressure and temperature. In a CO/CO_2 atmosphere, the contact angle increased from 78 to 113 deg as oxygen partial pressure

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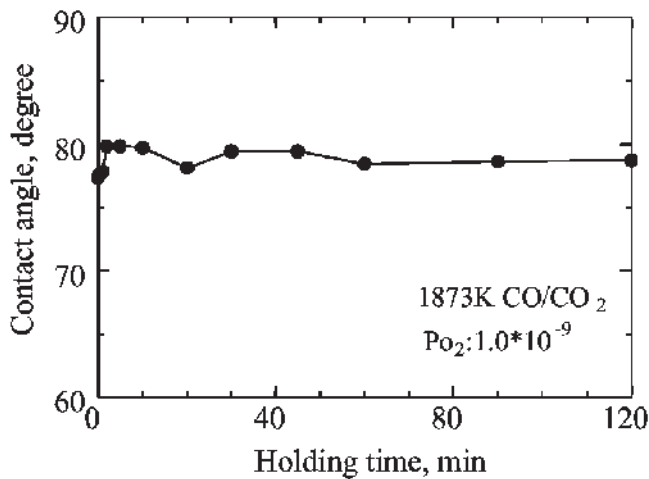
Fig. 1—Contact angle as a function of time for iron in contact with MgO in a CO/CO₂ gas atmosphere at 1873 K.
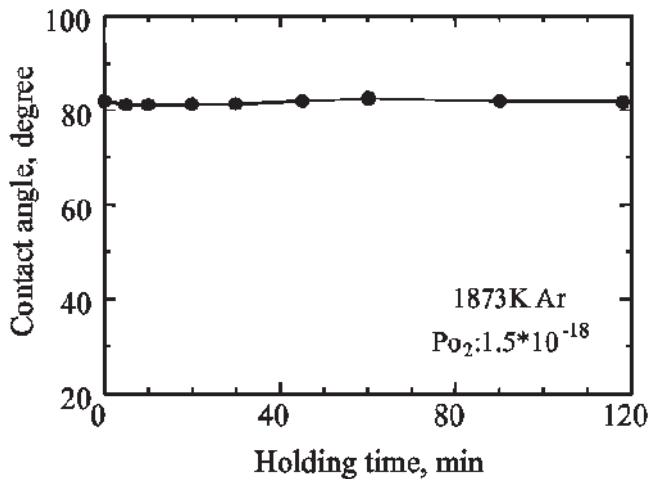

Fig. 2—Contact angle as a function of time for iron in contact with MgO in an argon atmosphere.
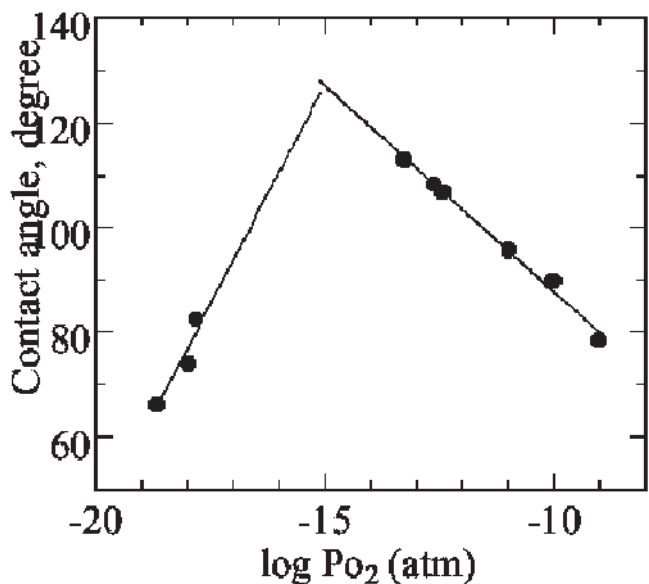

Fig. 3—Contact angle for pure iron on a single-crystal magnesia substrate as a function of oxygen potential in the gas.
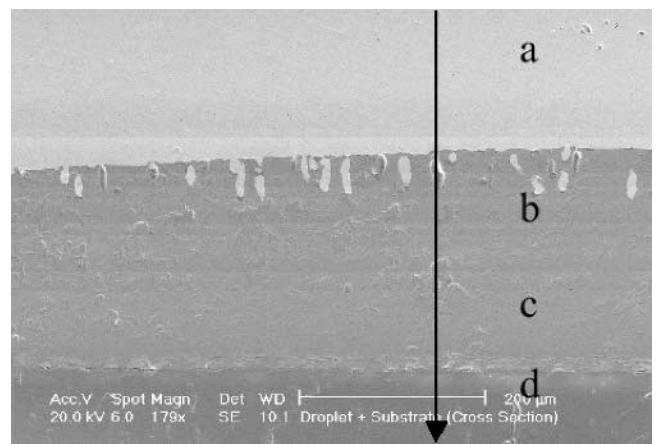

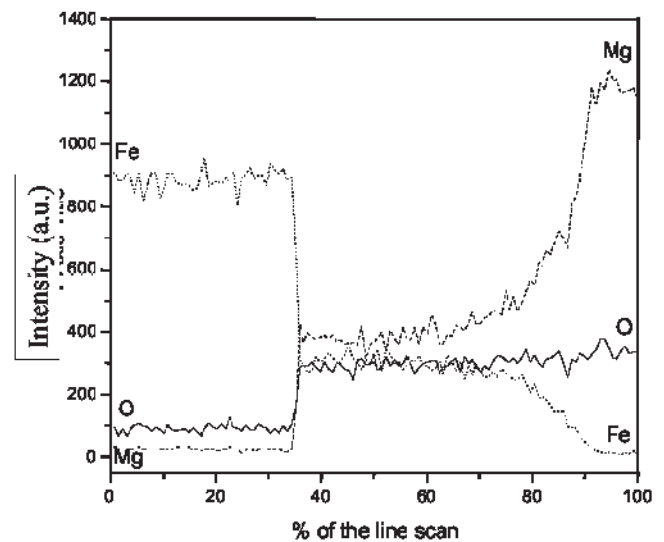Fig. 4—Cross section of droplet interface after droplet solidification.

Fig. 5—Elemental scan through the interface.

decreased from 10^{-9} atm to 10^{-14}. In an argon atmosphere, the contact angle decreased to 83 deg when the oxygen partial pressure was decreased to 10^{-18} atm and further decreased to 66 deg as the oxygen partial pressure was reduced to 10^{-20} atm.

REFERENCES

1. A. Kasama, A. McLean, W. Amiller, Z. Morita, and M.J. Ward: *Can. Met. Q.*, 1983, vol. 22, p 9.
2. I. Jimbo and A.W. Cramb: *Iron Steel Inst. Jpn. Int.*, 1992, vol. 32, pp. 26-35.
3. A.W. Cramb and I. Jimbo: *Steel Res.*, 1989, vol. 60, pp. 157-65.
4. N. Takiuchi, T. Taniguchi, Y. Tanaka, N. Shinozaki, and K. Mukai: *J. Jpn. Inst. Met.*, 1991, vol. 55, pp. 180-85.

5. K. Ogino, K. Nogi and Y. Koshida: *Tetsu-to-Hagané*, 1973, vol. 59, pp. 1380-87.
6. K. Nakashima, K. Takihira, K. Mori, and N. Shinozaki: *J. Jpn. Inst. Met.*, 1991, vol. 55, pp. 1199-1206.
7. K. Nogi and K. Ogino: *Can. Metall. Q.*, 1983, vol. 22, pp. 19-28.
8. N. Takiuchi, T. Taniguchi, N. Shinozaki, and K. Mukai: *J. Jpn. Inst. Met.*, 1991, vol. 55, pp. 44-49.
9. *Wettability at High Temperatures*, N. Eustatopoulos, M.G. Nicholas, and B. Drevet, eds., Pergamon Press, Elmsford, NJ, 1999.
10. K. Nogi: *Tetsu-to-Hagané*, 1998, vol. 84, pp. 1-6.
11. Ueda, H. Shi, and A.W. Cramb: *M. Wolf Symp.*, ISSTech, Apr. 2003, Warrendale, PA, 2003, pp. 665-79.
12. S. Ueda, H. Shi, X. Jiang, H. Shibata, and A.W. Cramb: *Metall. Mater. Trans. B*, 2003, vol. 34B, pp. 0000-00.
13. E. Kapilashrami, A. Jakobsson, A.K. Lahiri, and S. Seetharaman: *Metall. Mater. Trans. B*, 2003, vol. 34B, pp. 193-99.

Phase Equilibria of the Al$_2$O$_3$-CaF$_2$-FeO$_n$ System

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Calcium-oxide- and iron-oxide-based flux have been used to eliminate impurities in hot metal in the steelmaking process. Calcium fluoride is a convenient additive to enhance the fluidity of the flux in steelmaking. It decreases the melting point of the mixture of calcium oxide and increases reactivity of the flux with the molten iron. However, because of its negative environmental effects, reduction in the use of fluoride is also mandated. The disposal of after-use slag may result in the fluoride seeping down into the earth and into the underground water. The objective of the present study is to investigate ways of decreasing the total emission of fluoride and thus minimize its impact on the environment.

Substitution of CaF$_2$ by another oxide to reduce the use of fluorine in the process has been previously proposed by the authors.[1,2] The development of a fluorine recycling system is an alternative to reducing fluoride emissions. One possible process is: (1) concentrating the fluorine in a solid or liquid phase, (2) separating this phase from the other slag phase that is used in the steel making process, and (3) using the recycled CaF$_2$ in the hot metal pretreatment process.

The CaF$_2$-FeO$_n$ system has a miscibility gap between fluorine-rich and oxygen-rich phases at 1673 K.[3] By using phase separation of this system, separation of fluorine from the oxy-fluoride mixture may be possible. The purpose of the present study was to determine the region of the miscibility gap and liquidus of melts saturated with FeO·Al$_2$O$_3$ in the Al$_2$O$_3$-CaF$_2$-FeO$_n$ system at 1673 and 1723 K.

A silicon carbide electric resistance furnace connected to a PID controller with a Pt-6 pct Rh/Pt-30 pct Rh thermocouple was used to equilibrate the slag. The temperature of the specimen was controlled within ±1 K. An iron or molybdenum crucible with an iron liner was used as a container, which held about 2 g of the Al$_2$O$_3$-CaF$_2$-FeO$_n$ mixture.

The mixture was equilibrated in a crucible in a dry Ar or CO/CO$_2$ mixture. Specimens of two liquid phases, or liquid and solid phases, were equilibrated for 30 or 90 minutes, respectively. The equilibration times were determined following preliminary experiments. FeO·Al$_2$O$_3$ was prepared by sintering the stoichiometric mixture of Al$_2$O$_3$, Fe$_2$O$_3$, and Fe at 1723 K for 20 hours in day Ar. The formation of FeO·Al$_2$O$_3$ was determined by X-ray powder diffraction analysis.

After equilibration, the specimen was withdrawn from the furnace, and cooled by Ar gas flushing to maintain the interface between the two liquid phases or others. The quenched specimen was broken into small pieces. The texture of the two phases differed. The CaF$_2$- and FeO-rich phases were light gray and black, respectively. Therefore, the phases could be separated by hand. Then, samples were powdered in an agate mortar for wet chemical analysis. The compositions of separated flux samples were determined by chemical analysis of Al, Ca, and Fe by inductively coupled plasma emission spectrometry of Fe^{2+}, by titration, and of oxygen using a simultaneous nitrogen and oxygen determinator (LECO Corporation, St. Joseph, MI).

A redox titration analysis for a dissolved specimen confirmed that over 98 mass pct of Fe in the melt is present as Fe^{2+} in the slags. The iron oxide in the melt can thus be expressed as FeO.

According to the phase rule, the compositions of two liquids of miscibility gap in the CaF$_2$-FeO$_n$ system should be given based on the Ca-Fe-F-O system with the electronic neutrality. This condition yields the degree of freedom as unity: four components, two liquid phases, temperature and pressure, and electronic neutrality. Therefore, the ratio of O and F in each liquid phase should be given to identify the equilibrium. The compositions of equilibrated liquids, CaF$_2$- and FeO$_n$- rich phases might deviate from the diagonal line of CaF$_2$-FeO in a CaF$_2$-FeO-CaO-FeF$_2$ diagram.

Figure 1 shows experimental results of the phase relation of the CaF$_2$-FeO-CaO-FeF$_2$ diagonal phase diagram at 1723 K.
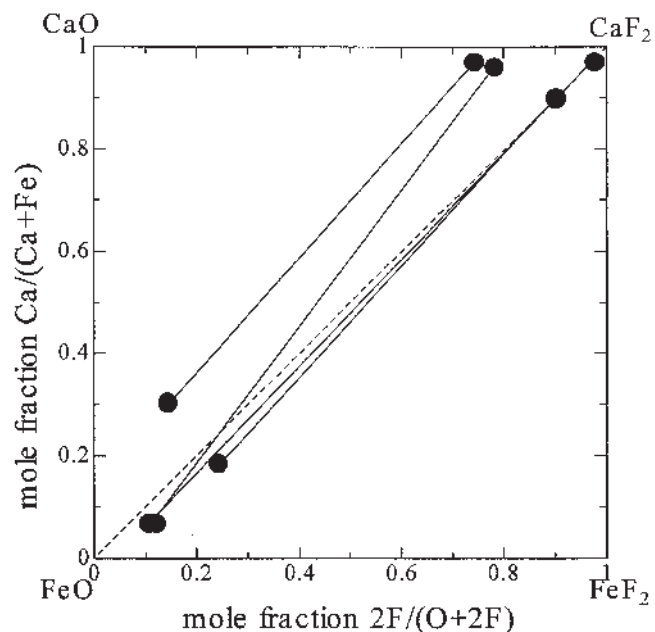

Fig. 1—Phase relations in the CaF$_2$-FeO-CaO-FeF$_2$ reciprocal salt system at 1723 K at metallic iron saturation.

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