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Wetting Behavior of Dolomite Substrate by Liquid Fe-19%Cr-10%Ni Alloy at 1753K

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Abstract The use of dolomite refractories has increased during the past several years in the manufacturing of clean steel during the stainless steelmaking process. However, at the same time, the use of dolomite refractories has led to what is known as the skull formation. In the present work, to understand the skull formation, the wetting characteristics of dolomite substrates by liquid Fe-19wt%Cr-10wt%Ni alloys in various oxygen partial pressures were initially investigated at 1753K using the sessile drop technique. For comparison, the wetting characteristics of alumina substrates were investigated with the same technique. It was found that the wetting index, (1+cosθ), of dolomite is approximately 40% higher compared to those of alumina. In addition, the oxygen partial pressure to generate the surface oxide, which may capture the liquid metal on the refractory surface, for dolomite is much lower than that for alumina. From this study, it was concluded that the use of dolomite is much more closely associated with the skull formation compared to the use of alumina due to the stronger wettability and the surface oxide formation at a lower oxygen partial pressure of dolomite.

Kew words dolomite, sessile drop method, skull, stainless steel, wetting.

1. Introduction

Selection of proper refractory material is very important in many steelmaking processes. When a precise adjustment of metal composition is required, skull generation on the refractory surface becomes a problem. For example, the steel composition can be changed by a small amount of skull generated on the refractory surface in the previous steelmaking process. Skull generation is depending on the physic-chemical properties of the refractory. Therefore, it is essential to understand the formation mechanism of skull on the refractory surface.

Typically, the wetting characteristic of liquid alloy on the refractory substrate can be identified by the work of adhesion (W_a): the work to separate liquid metal from a refractory.[1)]

$$W_a = \sigma_{LS} - (\sigma_L + \sigma_S) = \sigma_L(1 + \cos\theta) \qquad (1)$$

where σ_L, σ_S, σ_{LS}, and θ denote the surface energy of liquid, the surface energy of solid, the interface energy between liquid and solid, and the contact angle. According to Eq. (1), it is understood that at a fixed surface energy of liquid metal the work of adhesion would increase by decreasing the contact angle. Therefore, as the contact angle decreases, it becomes more difficult to separate liquid metal from the refractory surface, and easily forms skull. On the other hand, when the liquid metal is exposed to air atmosphere, it is subsequently oxidized, and the contact angle drastically changes.[2-5)] Therefore, it becomes more difficult to separate the liquid metal from the refractory and the surface of the liquid metal will be easily oxidized.

In this study, the wetting characteristics of liquid Fe-19mass%Cr-10mass%Ni alloys on alumina and dolomite substrates were examined by using the sessile drop technique under different oxygen partial pressure.

2. Experimental procedure

A schematic diagram of the experimental apparatus is presented in Fig. 1. A $MoSi_2$ resistance furnace was used in the present study. The maximum temperature to be

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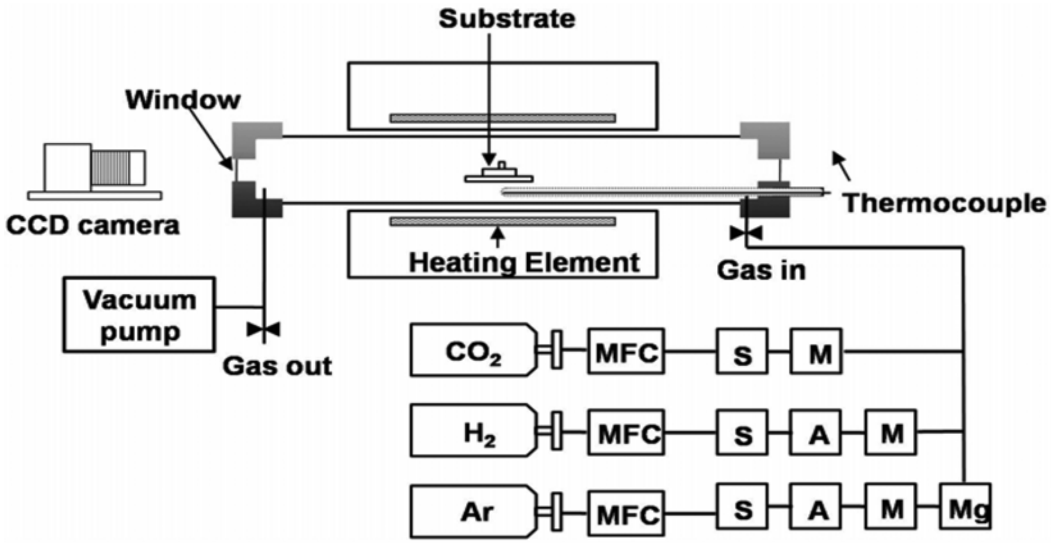

Fig. 1. Experimental apparatus of the wetting measurements. (S: silica gel, M: $Mg(ClO_4)_2$, A: , Mg: magnesium chips at 723 K).

obtained was 1973 K and the operating temperature in the present experiments was 1753 K. The furnace temperature was controlled by a B-type thermocouple. An alumina reaction tube with an inner diameter of 60 mm and a length of 900 mm was placed horizontally in the furnace. Tow quartz windows of 25 mm in diameter were provided on the opposite sides of the reaction tube for observation of the sample inside the furnace. A high resolution CCD camera was equipped to capture the image of the metal droplets on the alumina or dolomite substrates.

In the measurements, a piece of cylinder-type metal sample (approximately 0.3 gram) was placed on an alumina (99.9% purity) or dolomite substrate (54.34%CaO-38.00%MgO-1.02%SiO_2-0.48%Al_2O_3-0.45%Fe_2O_3-0.16%MnO-traces), and then placed in the center of the reaction tube. The H_2-Ar gas mixture was allowed to flow at a flowing rate of 300 ml/min STP. Then, the furnace was heated to the experimental temperature, 1753 K. Then the liquid metal droplet was investigated with the CCD camera. Computer software was used to determine the contact angle from the captured images on the basis of the Laplace equation. Details can be found in elsewhere.[6] A similar procedure was repeated for the contact angle measurements at different oxygen partial pressures.

In order to investigate the effect of oxygen partial pressure, predetermined H_2-CO_2 gas mixture was allowed to flow at a flowing rate of 300 ml/min STP. The oxygen partial pressure was determined as follows.

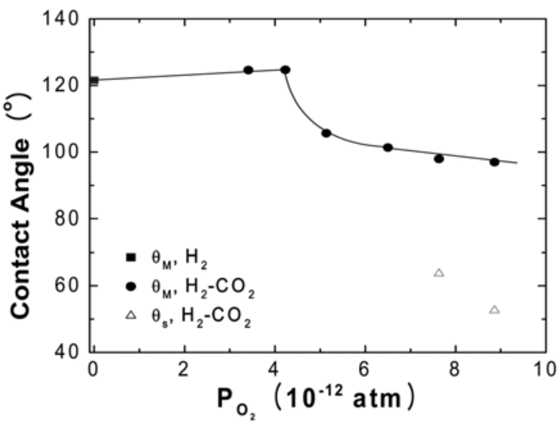

Fig. 2. Effect of oxygen partial pressure on the contact angle of a liquid Fe-19%Cr-10%Ni alloy drop on the alumina substrate. (θ_M: the contact angle between the liquid alloy drop and the alumina substrate, θ_S: the contact angle between the liquid slag and the alumina substrate).

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g) \quad (2a)$$

$$\Delta G^0_{(2)}(\text{Jmol}^{-1}) = -247,500 + 55.9T(\ /K) \quad (2b)^{7)}$$

$$CO(g) + \frac{1}{2}O_2(g) = CO_2(g) \quad (3a)$$

$$\Delta G^0_{(3)}(\text{Jmol}^{-1}) = -281,000 + 85.2T(\ /K) \quad (3b)^{7)}$$

Assuming that 1 mol of H_2 and x mole of CO_2 was flowed to generate y mol of H_2O and y mol of CO at 1753 K, then the equilibrium constants of Eqs. (2) and (3) can be expressed by Eqs. (4) and (5), respectively

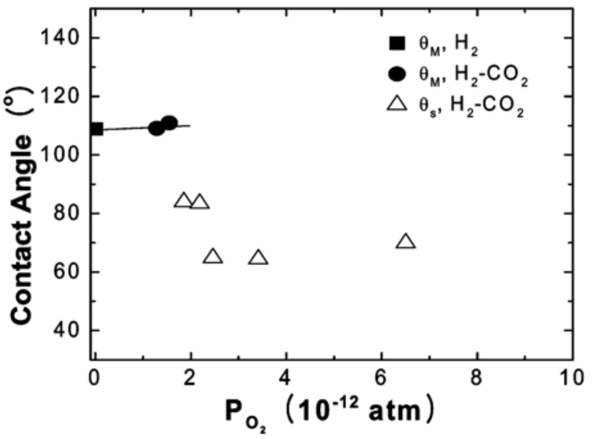

Fig. 3. Effect of oxygen partial pressure on the contact angle of a liquid Fe-19%Cr-10%Ni alloy drop on the dolomite substrate. (θ_M: the contact angle between the liquid alloy drop and the dolomite substrate, θ_S: the contact angle between the liquid slag and the dolomite substrate).

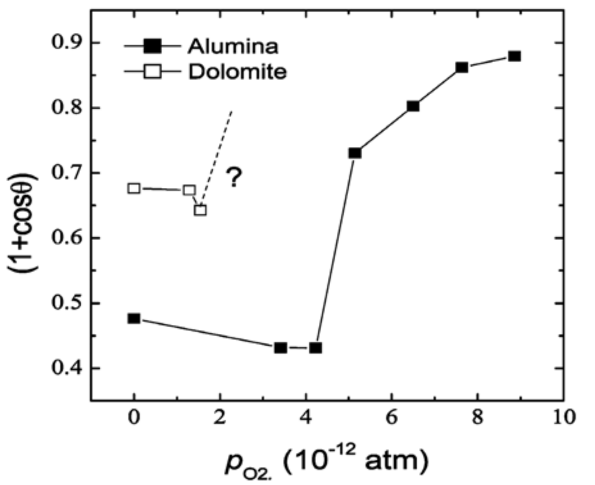

Fig. 4. Effect of oxygen partial pressure on (1+cosθ) of a liquid Fe-19%Cr-10%Ni alloy drop on two different substrates: alumina and dolomite.

$$K_{(2)} = \frac{P_{H_2O}}{P_{H_2}P_{O_2}^{1/2}} = \frac{y}{(1-y)P_{O_2}^{1/2}} \quad (4)$$

$$K_{(3)} = \frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}} = \frac{x-y}{y \cdot P_{O_2}^{1/2}} \quad (5)$$

At a predetermined oxygen partial pressure, x and y values can be obtained from Eqs. (4) and (5). Here, the value of x corresponds to the ratio of CO_2/H_2.

3. Results and discussion

In Fig. 2 is shown the contact angle between liquid Fe-19%Cr-10%Ni alloy and solid alumina under different oxygen partial pressure. When the oxygen partial pressure is less than 4.23 × 10^{-12} atm, the contact angle is almost constant in the range of 122~125°. The present result is very close to our previous results (121~133°).[5] As the oxygen partial pressure increases to 5.14 × 10^{-12} atm, the contact angle suddenly decreases to 106°. As the oxygen partial pressure increases further, the contact angle gradually decreases. It is also noteworthy that the oxide formation on the metal surface was observed when the oxygen partial pressure reaches 7.63 × 10^{-12} atm. The contact angle between oxide and the alumina substrate is as low as ~60°.

In Fig. 3 is shown the contact angle between liquid Fe-19%Cr-10%Ni alloy and solid dolomite under different oxygen partial pressure. When the oxygen partial pressure is less than 1.55 × 10^{-12} atm, the contact angle is almost constant in the range of 109~111°. As the oxygen partial pressure increases over 1.85 × 10^{-12} atm, an oxide layer covers the metal drop and the contact angle measurements could not be carried out. The apparent contact angle between oxide and the dolomite substrate is as low as ~70°.

In Fig. 4, the value of (1+cosθ) is plotted as a function of the oxygen partial pressure for the two different substrates: alumina and dolomite. It is noteworthy that the value of (1+cosθ) of dolomite is approximately 40% higher than those of alumina. As a result, it is considered that it becomes more difficult to separate liquid metal from the dolomite rather than alumina. Moreover, the oxygen partial pressure to form surface oxide layer on the dolomite is much lower than that on the alumina. Accordingly, it is concluded that the surface oxide formation is much easier for dolomite than alumina. Consequently, it is expected that dolomite forms skull easily than alumina, which is in good agreement with the observations in the practical process.

4. Conclusions

The wetting characteristics of liquid Fe-19%Cr-10%Ni alloys on alumina and dolomite substrates in various oxygen partial pressures were investigated at 1753 K using the sessile drop technique. It was found that the wetting index, (1+cosθ), of dolomite is approximately 40% higher than those of alumina. In addition, the oxygen partial pressure to generate surface oxide on dolomite, which may capture the liquid metal on the refractory surface, is lower than that on alumina. It is considered that the results of the present study are useful in understanding the mechanism of skull formation after the secondary steelmaking of stainless steels.

Acknowledgement

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