Wettability between Fe-Al alloy and sintered MgO

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ABSTRACT: In the current study, the wettability between Fe-Al alloy and sintered MgO substrate was investigated. The stable contact angle between the sintered MgO substrate and the liquid iron was approximately 134° at 1550°C , hardly influenced by Al concentrations of 18 ppm and 370 ppm in the liquid iron. By changing hydrogen partial pressure from 0 vol% to 1 vol%, the oxygen partial pressure decreased. Meanwhile, the contact angle between the MgO substrate and the liquid iron with 370 ppm Al increased with the decrease of oxygen partial pressure. The oxygen partial pressure and contact angle were scarcely affected by increasing hydrogen partial pressure from 1 vol% to 5 vol%. In all cases with 370 ppm Al in the liquid iron, oxide layers were detected on the surface of iron samples. The oxidation of iron could be effectively prevented by increasing the hydrogen partial pressure. The MgO substrate was reduced to Mg vapor in the reducing atmosphere at a high temperature. Then the Mg vapor was dissolved into the iron even before iron melting. Under thermodynamic equilibrium condition, an oxide layer containing two components, i.e. $\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase and $\text{CaO}\cdot\text{SiO}_2\cdot\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase, was generated on the surface of the iron sample. Due to the different wettability between the iron and the two phases, $\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase was repelled, while the $\text{CaO}\cdot\text{SiO}_2\cdot\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase adhered to the inside area.

KEY WORDS: contact angle; wettability; liquid iron; MgO substrate; Fe-Al alloy

1. Introduction

The choice of lining refractory material is always of great importance for the manufacturing of clean

steel. The interfacial phenomenon between the lining refractory and the liquid steel related to the erosion of the lining refractory^[1, 2], the contamination of the liquid steel^[3], the removal of inclusions^[3], the nozzle clogging^[4], etc. It is of great importance to study the wettability between the liquid steel and the lining refractory to characterize the interfacial phenomenon and improve the cleanliness of steel products.

In secondary refining process, deoxidizers are added in the molten steel to lower the dissolved oxygen. Aluminum is one of the most popular deoxidizers due to its strong deoxidization ability. Recently, MgO containing lining refractory, such as MgO-C brick, dolomitic brick, etc. is extensively used at steel mills. Wettability between the liquid iron and the MgO substrate had been widely studied in previous works^[3, 5-7]. Many researchers^[8-10] had studied the reaction between the Al-killed steel and the MgO-based lining refractory. However, few studies focused on the influence of Al in the liquid iron on the wettability between the liquid iron and MgO.

At steelmaking temperature, the liquid steel is easy to react with refractory. The previous wetting studies mainly focused on the reaction between the liquid iron and the substrate at the interface. It was regretful that the examination of the metal drop surface was usually neglected. Shin^[11] et al. observed the climbing of the oxide layer on the surface of Fe–19%Cr–10%Ni alloys from the bottom. Nevertheless, the formation mechanism of the oxide layer was not clearly elucidated. In the current study, the wettability between Fe-Al alloy and sintered MgO substrate was investigated. In particular, the formation of oxide layer on the surface of iron sample was clearly indicated based on the current experiment condition.

2. Experimental details

2.1 Sample preparation

The purity of MgO used for the contact angle measurement is 98.0%. MgO powder was pressed into a thin substrate with 3 mm in height and 35 mm in diameter under a load of 200 MPa. Then the substrate was sintered at 1600 °C for 2 hours to increase its strength and hardness. Whereafter, the surface of the sintered substrate was polished by abrasive papers and a diamond paste. The surface roughness of the substrate was 0.55 μm, measured by a profilometer (Dektak 150). The iron was machined into a cylinder

with 5.5 mm in height and 3.0 mm in diameter, and cleaned in ethanol using an ultrasonic cleaner. The composition of the initial iron samples are listed in Table 1. It should be noted that Al concentrations in the samples A and B are 18 ppm and 370 ppm respectively.

Table 1 Compositions of iron samples A and B (ppm)

Iron samples	Al	C	Si	Mn	S	Ca	Mg	O
A	18	5	<5	1	6	—	4	70
B	370	8	4	2.5	10	32	5	70.8

2.2 Experimental setup and procedure

In the current study, the sessile drop method was employed to study the wettability between the liquid iron and the sintered MgO substrate. The contact angle measurement was conducted in a horizontal tube furnace. The experimental setup is shown in Fig. 1. Before heating, the substrate was put on an alumina plate, while the iron was placed in the center of the MgO substrate. The assembly was then placed in the constant temperature zone of the furnace and heated to the desired temperature at a heating rate of 5 °C/min. The alumina tube was sealed by flange plates, and the terminal was fixed with quartz glass. Argon gas mixed with 5 vol% of H₂ was introduced into the tube at a flow rate of 30 L/h. The light of a halogen lamp passed through the tube, and then the melting and wetting process were recorded by a CCD camera at a frame rate of 5 frames per minute. The movie including the image of the sample and substrate, temperature, time, etc. was recorded in a software for the measurement of contact angle.

3. Results

3.1 Effect of aluminum concentration

Fig. 2 shows the contact angles between the sintered MgO substrate and the liquid iron with different Al concentrations. The contact angle remained stable and showed the similar values during the whole heating and holding process. It was defined that the average value of the final 60 min is the stable contact angle between the liquid iron and the MgO substrate. The measured contact angles of the iron samples A and B were 133.5° and 134.6°, respectively.

Fig. 3 shows the morphology of the surface of iron drops after experiment. The surface of the iron

with 18 ppm Al was not smooth, which might be caused by the solidification of iron. The EDS result indicated that the composition of the surface of the iron sample with 18 ppm Al was relatively uniform Fe. However, the iron sample with 370 ppm Al was covered with an oxide layer. The morphology and composition of different areas are given in Fig. 4 and Table 2. The oxide layer mainly consisted of plenty of small $\text{MgO}\cdot\text{Al}_2\text{O}_3$ particles and individual iron drops. The angular shape particles should be $\text{MgO}\cdot\text{Al}_2\text{O}_3$ spinel phase^[12, 13]. Fig. 5 was the elemental mapping of the iron surface. There were SiO_2 and CaO detected in the gap of $\text{MgO}\cdot\text{Al}_2\text{O}_3$ particles.

Table 2 Compositions of different areas analyzed using EDS (wt%)

No.	Fe	O	Al	Mg	Ca	Si
1	10.4	56.4	19.9	9.9	2.4	1.0
2	98.3	1.4	0	0.1	0	0.1
3	1.6	59.7	23.3	11.7	2.8	0.9
4	1.1	63.3	23.3	11.9	0.2	0.2
5	98.9	0.3	0.3	0.2	0.2	0.1

After the analysis of the iron surface, the substrate and the iron were cut perpendicularly from the center. The cross section of the substrate and the iron were analyzed using SEM-EDS. In Fig. 6, it should be noted that there is no reaction layer in the interface between the substrate and the iron. Several $\text{CaO}\cdot\text{SiO}_2$ rich impurities were detected in the substrate. In Fig. 7, the oxide layer consisted of a $\text{MgO}\cdot\text{Al}_2\text{O}_3$ outer phase and the $\text{CaO}\cdot\text{SiO}_2\text{-MgO}\cdot\text{Al}_2\text{O}_3$ inner phase, agreeing with the small $\text{MgO}\cdot\text{Al}_2\text{O}_3$ particles and the $\text{SiO}_2\text{-CaO}$ -rich gap in Fig. 5. The schematic of the distribution of the oxide layer is illustrated in Fig. 8.

3.2 Effect of oxygen partial pressure

It was reported that the oxidation of metal can be effectively prevented by adding 5 vol% H_2 in Ar gas^[14, 15]. In the current study, the volume percent of H_2 in Ar gas was adjusted from 0% to 5% to change oxygen partial pressures. Fig. 9 shows that the oxygen partial pressure distinctly declined with the increase of H_2 volume percentage. With the volume percentage of H_2 exceeding 1%, the oxygen partial pressure changes little.

Fig. 10 shows the contact angle between the substrate and iron ($Al_t = 370$ ppm) in different atmospheres. The contact angle slightly decreased with time. Fig. 11 shows the initial and stable contact angle in different atmospheres. When the volume percentage of H_2 in the gas was higher than 1%, the contact angle can hardly be changed. With H_2 in the gas lower than 1%, the contact angle apparently reduced with the decrease of volume percentage of H_2 .

Fig. 12 shows the morphology of the surface of iron samples ($Al_t = 370$ ppm) after experiments. All the iron samples were covered with an oxide layer. With $V(H_2) \geq 1\%$, the morphology and composition of the oxide layers were similar to that shown in Fig. 4 and Table 2. It can be seen that the iron drop was obviously oxidized in the atmosphere with $V(H_2) \leq 1\%$. The main composition of the oxide layer at the condition of $V(H_2)=0\%$ was FeO , $FeO \cdot Al_2O_3$, and $CaO \cdot SiO_2$, while the oxide layer consisted of FeO and $MgO \cdot Al_2O_3$ at the condition of $V(H_2)=0.6\%$.

3.3 Effect of temperature and holding time

In order to figure out the formation mechanism of the oxide layer on the surface of the iron ($Al_t = 370$ ppm), the holding temperature and the holding time was adjusted as listed in Table 3. In the first three experiments, the holding temperature was lower than the melting point of iron, the iron sample kept the cylinder shape after the experiment. The measured contact angles between the liquid iron drop and the substrate were generally similar in the last two experiments. The morphology of the final samples is shown in Fig. 13. When the temperature was lower than $1200^\circ C$, there are no oxides generated on the surface of the iron sample. After 30 min and 120 min holding at $1550^\circ C$, the iron samples were covered with an oxide layer with roughly the same chemistry composition. At $1525^\circ C$, a number of small individual $MgO \cdot Al_2O_3$ particles formed on the whole surface of the solid iron sample. Fig. 14 and Fig. 15 show the elemental mapping result at the middle and the bottom of the iron surface. The MgO content in $MgO \cdot Al_2O_3$ particles gradually increased with closing to the bottom of the iron sample. In the position $400 \mu m$ from the bottom, the formed particles were MgO -rich oxides.

Table 3 Experiment conditions

No.	Temperature (°C)	Holding time (min)	Atmosphere
1	25	0	Ar+5 vol% H ₂
2	1200	0	Ar+5 vol% H ₂
3	1525	0	Ar+5 vol% H ₂
4	1550	30	Ar+5 vol% H ₂
5	1550	120	Ar+5 vol% H ₂

4. Discussion

4.1 Formation of the MgO·Al₂O₃ particles

Due to the high concentration of Al in the Fe-Al alloy, it was expected that the dissolved Al might react with MgO^[16, 17] as Eq.(1). However, there was no reaction layer detected in the interface between the substrate and the iron drop in Fig. 6, indicating that the formation of the oxide layer on the surface of iron was not dominated by reaction 1. Besides, the formation of MgO·Al₂O₃ particles on the surface of the cylinder iron sample at 1525 °C could hardly be explained by reaction 1.

Due to the reducing atmosphere, the MgO substrate might be reduced to Mg vapor as reactions in Eqs. (2) and (3). According to the measured oxygen partial pressure, the equilibrium partial pressure of Mg vapor in the gas can be calculated by Eqs. (2) and (3), as expressed in Fig. 16. The partial pressure of Mg vapor distinctly dropped to a low level with the decrease of temperature, indicating that reaction 2 can hardly occur at the low temperature. At the temperature higher than 1500 °C, the equilibrium partial pressure of Mg vapor goes up, especially under the condition that Ar gas with higher than 1 vol% H₂. The Mg vapor may dissolve into the alloy even before the melting of alloy. The initial Mg concentration in the alloy was 5 ppm. The formation of inclusions on the surface of the iron with the Mg concentration from 5 ppm to 40 ppm was predicted using FactSage 7.0. With the Mg concentration lowering than 15 ppm, the formed solid oxides are mainly CaO-Al₂O₃ and MgO·Al₂O₃. With the Mg concentration reaching 20 ppm, the oxides transformed to MgO·Al₂O₃, as shown in Fig. 17, in consistent with the observed results. At 1525 °C, the Mg vapor leads to the formation of the individual MgO·Al₂O₃ particles on the surface of the unmelted solid iron as reaction 4^[16]. Moreover, the detected CaO-SiO₂-MgO-Al₂O₃

phase agrees with the calculated slag phase and SiO₂, which might be from the impurities in the substrate. In Fig. 15, the formation of MgO particles formed at the bottom of the iron sample may be caused by the stronger dissolution of Mg in the iron, which is in line with the predicted phases in the Fe-Al alloy containing 40 ppm Mg in Fig. 18.

4.2 Separation of two oxide phases

In Fig. 8, there were two oxide phases, the outer phase was mainly MgO·Al₂O₃ particles, the inner phase was liquid CaO-SiO₂-MgO-Al₂O₃ slag. The contact angle between the MgO·Al₂O₃ and the pure iron was usually larger than 90° ($\theta_1 > 90^\circ$)^[7, 18, 19], while the contact angle between the liquid oxide phase and the pure iron was usually smaller than 90° ($\theta_2 < 90^\circ$)^[3].

In Fig. 19, it is assumed that there is a rigid flat substrate made of MgO·Al₂O₃ and CaO-SiO₂-MgO-Al₂O₃, respectively. The liquid iron drop forms in the center of the substrate contacting the two oxide phases. The initial contact angles at both left and right sides were assumed to be the same. Obviously, the initial state is not in equilibrium. It is defined that the force direction is positive when pointing to the right. The residual force acts on left side and right side can be calculated by Eqs. (5) and (6). Under the current assumptions, the left stable contact angle is θ_1 , while the right stable contact angle, θ_2' , might be a little different from its true contact angle, θ_2 ^[3]. However, θ_2' should be still smaller than 90°.

$$F_1 = \gamma_l \cos \theta + \gamma_{s1-l} - \gamma_{s1} \quad (5)$$

$$F_2 = \gamma_{s2} - \gamma_l \cos \theta - \gamma_{s2-l} \quad (6)$$

In the case that the liquid drop and the left substrate is in equilibrium, i.e. $\theta = \theta_1 > 90^\circ$, it can be inferred $F_1 = 0$. Meanwhile, $\theta > 90^\circ > \theta_2'$, then $F_2 > 0$. Consequently, the right side of the iron drop moves in the right

direction, leading to the decrease of left contact angle, and then $F_1 > 0$. As a result, the left side of the iron drop also moves in the right direction. In conclusion, the iron drop prefers to wet the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ phase and repel the $\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase. In the case that the liquid drop and the right substrate is in equilibrium, i.e. $\theta = \theta_2' < 90^\circ$, the iron drop also moves in the right direction. Therefore, the formed $\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase and $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ phase on the surface of the iron drop shown in Fig. 8 shows the stable two phases distribution.

5. Conclusion

- (1) The measured contact angles between the sintered MgO substrate and the liquid iron were approximately 134° , hardly influenced by Al concentrations of 18 ppm and 370 ppm in the liquid iron.
- (2) The MgO substrate was reduced by H_2 at the high temperature, leading to the formation of Mg vapor even before the melting of the iron. The Mg vapor dissolved into the iron with 370 ppm Al, resulting in the formation of an oxide layer on the surface of the iron sample. The oxide layer containing two components, i.e. $\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase and $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ phase. Due to the different wettability between the iron and the two phases, $\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase was repelled, while the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ phase adhered to the inside area.
- (3) With $V(\text{H}_2) \geq 1\%$, the contact angle changed little due to the similar oxygen partial pressure. There was an oxide layer formed on the iron drop without the oxidation of iron drop. With $V(\text{H}_2) \leq 1\%$, the contact angle reduced with the decrease of the volume percent of H_2 . The iron sample was obviously oxidized and FeO -rich oxides may form on the surface of the iron drop.

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References

- [1] Z. Yuan, Y. Wu, H. Zhao, et al. Wettability between molten slag and MgO–C refractories for the slag splashing process[J]. ISIJ International, 2013, 53(4): 598-602.
- [2] S. H. Heo, K. Lee, Y. Chung. Reactive wetting phenomena of MgO-C refractories in contact with CaO-SiO₂ slag[J]. Transactions of Nonferrous Metals Society of China, 2012, 22(S3): 870-875.
- [3] A. W. Cramb, I. Jimbo. Interfacial considerations in continuous casting[J]. Iron & Steelmaker, 1989, 16(6): 43-55.
- [4] C. Bernhard, G. Xia, A. Karasangabo, et al. Investigating the influence of Ti and P on the clogging of ULC steels in the continuous casting process[J]. World Iron & Steel, 2012, (5): 19-28.
- [5] C. Xuan, H. Shibata, S. Sukenaga, et al. Wettability of Al₂O₃, MgO and Ti₂O₃ by liquid iron and steel[J]. ISIJ International, 2015, 55(9): 1882-1890.
- [6] K. Ogino, A. Adachi, K. Nogi. The wettability of solid oxides by liquid iron[J]. Tetsu-to-Hagane, 1973, 59(9): 1237-1244.
- [7] H. Shibata, Y. Watanabe, K. Nakajima, et al. Degree of undercooling and contact angle of pure iron at 1933K on single-crystal Al₂O₃, MgO, and MgAl₂O₄ under argon atmosphere with controlled oxygen partial pressure[J]. ISIJ International, 2009, 49(7): 985-991.
- [8] W. Yang, L. Zhang, H. Duan, et al. Formation of non-metallic inclusions in the molten steel in MgO crucibles[C]. EPD Congress 2014 Proceedings, TMS 2014 Annual Meeting & Exhibition. San Diego,

CA, USA, February 16-20, 2014: TMS, 2014: 269-276.

- [9] V. Brabie. A study on the mechanism of reaction between refractory materials and aluminium deoxidised molten steel[J]. Steel research, 1997, 68(2): 54-60.
- [10] J. Lehmann, M. Boher, M. Kaerle. An experimental study of the interactions between liquid steel and a MgO-based tundish refractory[J]. CIM bulletin, 1997, 90(1013): 69-74.
- [11] M. Shin, J. Lee, P. Joo-Hyun. Wetting Characteristics of Liquid Fe–19%Cr–10%Ni Alloys on Dense Alumina Substrates[J]. ISIJ International, 2008, 48(12): 1665-1669.
- [12] S. Yang, Q. Wang, L. Zhang, et al. Formation and modification of MgO • Al₂O₃-based inclusions in alloy steels[J]. Metallurgical and Materials Transactions B, 2012, 43(4): 731-750.
- [13] J. H. Park, H. Todoroki. Control of MgO·Al₂O₃ spinel inclusions in stainless steels[J]. ISIJ international, 2010, 50(10): 1333-1346.
- [14] S. Ueda, A. W. Cramb, H. Shi, et al. The contact angle between liquid iron and a single crystal, alumina substrate at 1873 K: Effects of oxygen and droplet size[J]. Metallurgical & Materials Transactions B, 2003, 34(5): 503-508.
- [15] G. Parry, O. Ostrovski. Wetting of solid iron, nickel and platinum by liquid MnO-SiO₂ and CaO-Al₂O₃-SiO₂[J]. ISIJ International, 2009, 49(6): 788-795.
- [16] L. Zhang, Y. Ren, H. Duan, et al. Stability diagram of Mg-Al-O system inclusions in molten steel[J]. Metallurgical & Materials Transactions B, 2015, 46(4): 1809-1825.
- [17] S. Won-Gap, W. H. Han, K. Jeong-Sik, et al. Deoxidation equilibria among Mg, Al and O in liquid iron in the presence of MgO·Al₂O₃ spinel[J]. ISIJ International, 2003, 43(2): 201-208.
- [18] N. Shinozaki, N. Echida, K. Mukai, et al. Wettability of Al₂O₃-MgO, ZrO₂-CaO, Al₂O₃-CaO

substrates with molten iron[J]. Tetsu-to-Hagane, 1994, 80(10): 748-753.

- [19] N. Fukami, R. Wakamatsu, N. Shinozaki, et al. Wettability between porous MgAl_2O_4 substrates and molten iron[J]. Journal of the Japan Institute of Metals, 2009, 50(11): 2552-2556.

1- argon purification device; 2-dry pipe; 3- gas flowmeter; 4-Gas mixing chamber; 5-Mg furnace; 6-vacuum pump;
7-halogen light; 8-resistance furnace; 9-alumina tube; 10-CCD camera; 11-computer; 12-metal sample; 13-substrate

Fig. 1 Schematic of the experiment setup

Fig. 2 Contact angles between sintered MgO substrates and Fe-Al alloys

Fig. 3 Surface morphology of the iron after experiment

Fig. 4 SEM image of the iron surface ($Al_t = 370$ ppm)

Fig. 5 Mapping of the iron surface ($Al_t = 370$ ppm)

Fig. 6 Mapping of the interface between substrate and iron ($Al_t = 370$ ppm)

Fig. 7 Mapping of the surface of the iron ($Al_t = 370$ ppm)

Fig. 8 Schematic of the surface of the iron ($Al_t = 370$ ppm)

Fig. 9 Oxygen partial pressure in the gas

Fig. 10 Contact angle in Ar gas with different volume percent of H₂

Fig. 11 The stable contact angle in Ar gas with different volume percentage of H₂

Fig. 12 Surface morphology of the iron after experiment in different conditions

Fig. 13 Surface morphology of the iron after experiment in different conditions

Fig. 14 Mapping of the iron surface in the middle (1525 °C, 0 min)

Fig. 15 Mapping of the iron surface at the bottom (1525 °C, 0 min)

Fig. 16 Equilibrium partial pressure of Mg vapor

(a) Main composition in iron

(b) Main composition in slag

Fig. 17 Thermodynamic equilibrium phases at different temperatures (20 ppm Mg)

(a) Main composition in iron

(b) Main composition in slag

Fig. 18 Thermodynamic equilibrium phases at different temperatures (40 ppm Mg)

Fig. 19 Schematic of the iron drop lies on the substrate