Original Article

Corrosion behavior of Al$_2$O$_3$ substrate by SiO$_2$–MgO–FeO–CaO–Al$_2$O$_3$ slag

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1. **Introduction**

Nickel plays an important role in modern manufactures. It is one of the essential elements for stainless steel production, which accounts for 65 wt% of the nickel consumption [1,2]. In recent years, the world annual demand for nickel has increased tremendously due to soaring stainless steel production [3,4]. Nickel sulfide and laterite ores are two main resources for extracting nickel. With continuous consumption of high-grade sulfide resource, the use of nickel laterite has drawn increasing attention [5,6]. China is short of nickel resource, and has depended on importation for a long period. Utilizing low-grade nickel laterite is regarded as a main solution of the increasing demand for ferronickel alloy production. However, the extraction of nickel from laterite ore is relatively difficult because of the low Ni content and nickel mainly exists as isomorphic substitution in serpentine.

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 Rotary kiln–electrolysis furnace (RKEF) process is one of the main pyrometallurgical technologies to deal with nickel laterite ore [7–9]. An alternative route of direct reduction–physical separation has also been widely studied [10,11]. The ferronickel alloy obtained from physical separation is considered as superior material for manufacturing stainless steels. For example, Nippon Yakin Kogyo Co., Ltd. has employed the above route by reduction in a rotary kiln and then followed by magnetic/gravity separation [12]. However, this process still requires a relatively high temperature and long reduction time for partially melting of the matrix. The formation of ring inside the kiln is still an intractable problem during the reduction process. Besides, lots of additives, such as sodium sulfate, calcium sulfate, etc., were added to enhance the reduction of laterite ore as well as the aggregation of ferronickel particles [13].

Recently, non-electric process with simple technological flow and low energy consumption becomes great potential in the production of ferronickel from laterite ore. In the last decades, non-blast furnace ironmaking processes applying rotary hearth furnace (RHF) technology have made huge progress. Representative processes included ITmk3, DryIron, Inmetco, FASTMET, and Redsmelt [14]. In particular, ITmk3 process is regarded as the most promising technology in which the RHF was used to produce iron nugget directly from iron ore [14–16]. The RHF process was also alternative to directly produce ferronickel nugget from nickel laterite ore. In the RHF process, nickel laterite ore pellets containing reduc tant were placed on the bed of alumina–based refractory lining, and heated from room temperature to 1400 °C for about 30 min. During the reduction process, nickel and iron oxides were reduced to metallic state while the gangue minerals entered into the slag. As the slag melted, it would wet on the lining and even corrode the refractory.

Alumina–based refractory is widely used as lining material due to its good corrosion and dissolution resistance. The corrosion behavior of high–alumina refractories has been intensively investigated [17]. Various slags, such as synthetic CaO–Al2O3, CaO–Al2O3–SiO2 systems and industrial slags, etc., have been employed to study the corrosion behavior [17–19]. The corrosion process generally included the dissolution of alumina and the precipitation of phases with high melting point. In contrast, the properties of alumina–based refractories on the corrosion resistance has also attracted increased attention. The study by Fu et al. indicated that the apparent porosity and pore size have pivotal impact on slag resistance [20]. The slag penetration and corrosion would also relieve after incorporating reinforced phases (such as magnesia–alumina spinel, nano-silica, and so on) into the refractories or castables [21–24]. With respect to the corrosion mechanism, the corrosion of refractories was mainly resulted from a reactive transport mechanism in many cases. The corrosive species (slag or gas) firstly impregnate the open porous space preferentially within the matrix and react with the material. The reactions usually proceed via a dissolution–precipitation mechanism [25,26].

Actually, no matter reducing in the RHF process or rotary kiln, the corrosion and sticking phenomena between molten slag and furnace refractory lining are the crucial problems. The life of refractories and the stability during discharging would be affected severely if the refractories were eroded by the slag. However, few studies have been carried out to investigate the corrosion behavior of refractory lining by the slag from smelting nickel laterite ore. In order to simulate the RHF process, in this study, the wetting and corrosion behaviors of SiO2–MgO–FeO–CaO–Al2O3 quinary slag on Al2O3 substrate were investigated by the sessile drop method. The pre–melted slag was placed on Al2O3 substrate and heated from room temperature to the desired temperature. The microstructure of interface between the slag and Al2O3 substrate was analyzed. Then the corrosion mechanism of slag samples with different basicity were also discussed.

2. Experimental

2.1. Preparation

Pure grade reagents (Kenong Chemical Co., Inc.) were used and pre–melted to prepare the slag samples for the wetting experiments. In order to improve the grade of Ni in ferronickel nugget, the reduction of iron oxides was restricted and part of iron remained as wustite (FeO) in the slag during reduction roasting. The chemical composition of the slag samples, which simulate the components of laterite ore after smelting in RHF process, is shown in Table 1. The content of FeO was fixed as 10 wt%, and the basicity (MgO + CaO)/SiO2 given by weight ratio was set at 0.43 and 0.63, respectively. According to the quinary phase diagram of CaO–MgO–SiO2–Al2O3–FeO [27], it can be observed that the basicity located at the low-melting field is in the range of 0.430.83. Higher basicity means greater amount of CaO should be added in the melting process. Thus the slags with basicity of 0.43 and 0.63 were compared in this study.

Before the wetting experiment, pure reagents were weighed according to the above proportion and mixed manually, 10 g of the mixture was pressed into a cylindrical briquette (ø20 mm) using a uniaxial hydraulic presser with 10 MPa pressure. The briquettes were then loaded in platinum crucible and pre–melted in an electric resistance furnace by roasting at 1500 °C for 2 h. The slag samples were totally melted into liquid state under Ar atmosphere. After melting, the slags were naturally cooled to room temperature in the furnace under Ar atmosphere. Cubic slag samples with 3 mm × 3 mm × 3 mm in dimension and approximately 60 mg in weight were then incised from the cooled slag and used for wetting experiment.

The Al2O3 substrate used in this experiment was 20 mm × 20 mm × 5 mm in dimension, and 99 wt% in purity. The porosity of substrate is 2.7% [28]. A smooth surface is important to achieve an accurate measurement of wettabi lity behavior [29]. To obtain a smooth surface, the Al2O3 substrate was smoothed with abrasive paper (400, 600, 800 and 1200 CW successively) and polished with diamond paste. The average surface roughness of the polished substrate was approximately 300–500 nm measured by a microscope (Boyue Instruments Co. Ltd., Dektak 150). The slag samples and Al2O3 substrate were cleaned with acetone (≥99.5 wt%) using an ultrasonic wave cleaner and prepared for wetting experiment.
Table 1 – Chemical composition of the slag samples (mass% and mole%).

<table>
<thead>
<tr>
<th>Slag</th>
<th>Basicity</th>
<th>Proportion, %</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.43</td>
<td>mass</td>
<td>57.47</td>
<td>2.53</td>
<td>22.19</td>
<td>7.81</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mole</td>
<td>54.02</td>
<td>2.55</td>
<td>31.28</td>
<td>4.32</td>
<td>7.83</td>
</tr>
<tr>
<td>B</td>
<td>0.63</td>
<td>mass</td>
<td>50.96</td>
<td>12.43</td>
<td>19.67</td>
<td>6.94</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mole</td>
<td>48.82</td>
<td>12.76</td>
<td>28.26</td>
<td>3.91</td>
<td>6.25</td>
</tr>
</tbody>
</table>

![Fig. 1 – Schematic diagram of the apparatus for wetting experiment.](image)

2.2. Methods

In order to simulate the RHF process, in this study, the wetting behavior of quinary slag on Al₂O₃ substrate was investigated by the sessile drop method. The slag sample was firstly placed on the Al₂O₃ substrate at room temperature. High temperature–vacuum furnace was used in the wetting experiment. The schematic diagram of apparatus is shown in Fig. 1.

The furnace chamber was evacuated to $7 \times 10^{-4}$ Pa by molecular pump to expel the air. High pure argon gas (99.999%) was charged and the furnace chamber was controlled at approximately 1.05 atm during the experiment. All the experiments were carried out under high purity argon to prevent the oxidation of FeO. In the RHF process, the duration of pellets in high temperature reduction zone is about 10 min, and hence in this study, the furnace was then heated to 1200 °C at 60 °C/min and to 1400 °C at 20 °C/min. The changes in drop profiles were recorded continuously by high-resolution (2000 × 1312 pixels) digital camera to reflect the change in contact angle. Laser was used to irradiate the sample for obtaining clear and distinct images of the slag. SurfSenes43 software with an accuracy of ±1° was used to facilitate the calculation of appearance contact angle [28,30]. Each experiment was repeated at least once, and the results were regarded as credible if the relative error was less than 5%. The average of two reproducible runs was regarded as the final results.

The slag samples together with the substrate after wetting were cooled down naturally and then prepared for subsequent analyses. The slag samples were separated manually and analyzed by X-ray diffraction using a diffractometer (XRD, RIGAKU D/Max 2500PC, Japan) under the conditions as follows: Cu Kα, tube current and voltage: 250 mA, 40 kV, scanning range: 10°–90° (2θ), step size: 0.02° (2θ) and scanning speed: 8°/min. The microstructure of the cross-section between the slag and substrate was examined by scanning electron microscopy (SEM, EVO18, Carl Zeiss, Germany). The solubility of Al₂O₃ in the specified slag samples was calculated by the software of FactSage 6.2 under the conditions of 1400 °C and 1 atm. The quinary phase diagram was also calculated by FactSage 6.2 under 1 atm.

3. Results and discussion

3.1. Change in contact angle

The profile of SiO₂–MgO–FeO–CaO–Al₂O₃ slag droplets on Al₂O₃ substrate at different temperatures is shown in Fig. 2. The apparent contact angle ($θ$) was measured from these images. For each droplet in view, the contact angle on both edges was measured and the average value was defined as the instant apparent contact angle.

Fig. 3 shows the change of apparent contact angle as a function of temperature. When the slag samples started to melt, the contact angle decreased distinctly with increasing temperature. Both of the slags quickly spread along the Al₂O₃ substrate and gradually approached to equilibrium where the contact angles were almost unchanged at temperatures above 1360 °C. The equilibration apparent contact angles were determined as approximately 25° and 30° for the slags with basicity of 0.43 and 0.63, respectively. The results in Figs. 2 and 3 indicate that the slag samples wet well on Al₂O₃ substrate at 1400 °C. Good wettability would possibly bring sticking problems between pellet and alumina refractory in RHF process. The slag formed during reduction roasting process would wet and even erode the alumina refractory materials, which will bring adverse impact on the RHF process.

3.2. Mineralogical composition of slags

The XRD patterns in Fig. 4 show the phase composition of slags A and B, which were separated from the substrate after cooling to room temperature. The obvious amorphous diffraction was mainly attributed to the fast cooling rate (60 °C/min) after wetting experiment. The results reveal that various silicates including Mg₂SiO₄, Mg₃SiO₇, Fe₂SiO₄, and Fe₃SiO₅ were formed in both slags A and B. More calcium–containing phases (ie. CaAl₂Si₂O₈) were observed in slag B due to its higher amount of CaO. Besides, a small amount of forsterite (Mg₂SiO₄, Mg₃SiO₇) was transformed into monticellite (Mg₃CaSiO₄). The phase composition will be further discussed according to the phase diagram in Sec. 3.4.3.
3.3. Microstructure and elemental distribution analyses

The microstructure of the slag-substrate interface after wetting experiment was investigated by SEM-EDS analysis. Figs. 5 and 6 show the morphology of different regions for slags A and B, respectively. The slag-substrate sample after corrosion was incised vertically and the microscopic morphology is shown in Fig. 5(a). A schematic diagram of the sample after wetting is shown in Fig. 5(b).

It can be seen from Fig. 5 that the microstructure can be divided into three layers, layer I is the slag, layer II is interfacial layer and layer III represents the original Al$_2$O$_3$ substrate. The thickness of the interfacial layer is about 10 $\mu$m. The results of line scanning in Fig. 5(b) reveal the distribution of the main elements. It indicates that the contents of Mg gradually decrease from layer I to III, while the Al content exhibits an opposite change. It is evident that the phases of Mg would diffuse from the slag towards the interfacial layer, while Al$_2$O$_3$ was dissolved and Al ion diffused from the substrate to the interfacial layer. Regarding the slag with basicity of 0.63, the distribution of main elements was observed to be similar with that of slag A, as shown in Fig. 6.

The chemical composition of EDS results (mole%) is plotted in Table 2. The EDS analysis indicates that the chemical composition of spot 1 (layer I) in either Figs. 5 or 6 is closed to the original components of slag samples. According to the XRD results in Sec. 3.2, the slags may consist of calcium silicates, forsterite (Mg$_2$SiO$_4$) as well as fayalite (Fe$_2$SiO$_4$) after crystallization. The comparison of Ca atom percentage of spot 1 in Figs. 5 and 6 is also in accordance with original components. The EDS results of spots 2 and 3 which were located at the interface layer II revealed Al and Mg were the main components. The contents of Si was far less than that of spot 1 while Al was obviously higher. It can be predicted that magnesium aluminate spinel may be formed in the interface layer. By comparing the Al atom proportion in layer II, it is found that the Al content of slag basicity 0.63 is a little higher than that of basicity 0.43. It can be deduced that higher basicity would result in heavier corrosion on the substrate.

3.4. Discussion on the corrosion mechanism

3.4.1. The change of surface tension of the slag

Surface tension, an important parameter of surface property, is directly related to the wetting phenomenon. Zisman et al. [31] reported that the degree of wetting improves with decreasing surface tension. T. Young [32] has studied the theories of surface tension and capillarity. On the basis of those theories, he asserted that a tension equilibrium exists at the inter-
Table 2 – Chemical composition of the EDS results (mole%).

<table>
<thead>
<tr>
<th>Slag</th>
<th>Spot</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>55.00</td>
<td>2.58</td>
<td>31.88</td>
<td>2.56</td>
<td>7.98</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.44</td>
<td>4.48</td>
<td>34.62</td>
<td>45.82</td>
<td>6.63</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.78</td>
<td>4.80</td>
<td>33.31</td>
<td>46.69</td>
<td>5.92</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>47.81</td>
<td>18.86</td>
<td>22.21</td>
<td>2.20</td>
<td>8.93</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.51</td>
<td>7.20</td>
<td>29.60</td>
<td>48.77</td>
<td>5.92</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.13</td>
<td>6.98</td>
<td>29.67</td>
<td>48.75</td>
<td>5.47</td>
</tr>
</tbody>
</table>

face of solid/liquid/gas during wetting equilibrium, namely $\sigma_{s/g} = \sigma_{s/l} + \sigma_{l/g} \cdot \cos \theta$ (Fig. 5(a')). In the present wetting experiment, the interfacial tension of solid/gas phase ($\sigma_{s/g}$) was kept constant, $\sigma_{s/l}$ can be neglected as it was much less than $\sigma_{l/g}$, and $\sigma_{l/g}$ was very close to the surface tension of the liquid ($\sigma_l$) measured in vacuum [32]. Thus, $\sigma_l$ could be considered as the major factor that affected the value of $\theta$ (apparent contact angle).

A model developed by Mills et al. was widely used to estimate the surface tension of the molten slag system [33]. Surface tension in the model is a function of temperature and chemical composition of the slag. The surface tension as
Fig. 7 – Surface tension of slags A and B as a function of temperature.

a function of temperature is calculated based on the above model and presented in Fig. 7. The value below 1360 °C was not calculated because solid particles were still existed in the briquette. As shown in Fig. 7, the surface tension of both slags A and B decreased slightly with increasing temperature. According to the results in Fig. 3 and Fig. 7, it can be observed that the surface tension of slag A is smaller than that of slag B regardless of temperature, which was in consistent with the results that the equilibration contact angle of slag A was smaller than that of slag B.

3.4.2. The dissolution of Al2O3 into the slag
As can be seen from Figs. 5 and 6, the amount of Mg, Al and Si was quite different between layers I and II. It is probably attributed to two reasons. The first one is the diffusion of Mg and Si towards the Al2O3 substrate, and the other one is the dissolution of Al2O3 into the slag. The solubility of Al2O3 in the specified slag samples calculated (1400 °C, 1 atm) by FactSage 6.2. It is found that the content of Al2O3 was as high as 23.8 wt% and 21.8 wt% when Al2O3 was saturated in slags A and B, respectively. Compared to the original Al2O3 contents of slag samples, it indicated that the content of Al2O3 in slags A and B was far from saturating, which means Al2O3 in the substrate will dissolve into the molten slag. In the study of Choi et al [34], the authors discussed the dissolution rate of Al2O3 into molten CaO–SiO2–Al2O3 slag. It was found that the dissolution rate was dependent on the temperature, CaO content as well as the viscosity and diffusivity of slag [20,35].

Meanwhile, the diffusion of Mg, Si as well as the dissolution of Al2O3 may be inhibited due to the formation of layer II. The Al2O3 substrate would not be further corroded by the slags as high melting point phases was formed in layer II. Yu et al. [28] have studied the wetting behavior of Al2O3 substrate by calcium ferrite (CF) series melts, and they found that the interface structure and products of the CF–2M (calcium ferrite melt with 2 wt% MgO) differed from those of the other slag systems (CF–2S (2 wt% SiO2), CF–2A (2 wt% Al2O3)). No obvious corrosion phenomenon was observed by CF–2M slag, which may be also attributed to the formation of high melting phases in the interfacial layer.

3.4.3. The crystallization process after wetting
In the RHF process, the reduced pellets will be discharged at about 1000 °C after reduction. That is to say, as the wetting was finished, the semi–molten slag will crystallize, which can be analyzed according to the quinary phase diagram in Fig. 8. The diagram was calculated by fixing the contents of CaO and FeO. The sum of other three phases (SiO2, MgO, Al2O3) were 100%. Point O represents the original composition according to that in Table 1 (slag A).

Assuming that the dissolution of Al2O3 only affected the composition of interfacial layer, it can be deduced that the main body of slag crystallized along the direction of O→A→B. Thus, MgSiO3, SiO2 and Mg2Al2Si2O8 were expected to be formed in the final product. However, other phases, such as fayalite and calcium alumino–silicate, were observed in the XRD patterns. This may be attributed to the reason that the cooling process was in non–equilibrium condition and the slag was not uniform after crystallization. With respect to the interfacial layer after Al2O3 was dissolved, the composition of the molten slag will transfer in the direction of O→C (towards the position of Al2O3) depending on the dissolution rate of Al2O3. If the composition was transferred into the preliminary crystallization region of Mg2SiO4 or Mg2Al2Si2O8, the phases of MgSiO3, Mg2SiO4 and Mg2Al2Si2O8 will be formed in the interfacial layer after cooling. From the atom percentage of EDS results in Figs. 5 and 6, it was observed that Al and Mg were the main components at spots 2 and 3 while the content of Si was far less than the original percentage. As a result, it can be predicted that the diffusion of Mg as well as the dissolution of Al2O3 were promoted after the slag wetted on the substrate.

From the above discussion, the corrosion mechanism of Al2O3 substrate by the specified slags can be explained in Fig. 9. Upon heating, the solid slag melted gradually into liquid state accompanied by a decrease in the contact angle. Initially, the slag was not completely melted, and the surface tension of the slag was relatively high because of the existence of solid phase. Surface tension was the main resistance of wetting and the dissolution of Al2O3 was restrained at this stage. With increase in the temperature, the surface tension of slag decreased obviously, thus the contact angle decreased correspondingly and then remained stable. Wetting was the first step that caused the corrosion of Al2O3 substrate. As the slags melted into liquid state, the dissolution of Al2O3 from the substrate was accelerated. However, the heating rate was relatively fast which lead to a short dissolution time. Meanwhile, Mg and Ca ions in the slag would diffuse towards the substrate to react with Al2O3. The dissolution of Al2O3 was another important reason that caused the corrosion of substrate. Line scanning results in Figs. 5 and 6 also proved the distribution of Mg and Al from layer I to layer III. With the dissolution of Al2O3 as well as the proceeding of reaction among MgO, SiO2 and Al2O3, high melting point phases were deduced to be precipitated in the interfacial layer. The generated products gradually covered the substrate surface under the droplet which would inhibit further dissolution of Al2O3. Therefore, no obvious corrosion was observed on the Al2O3 substrate after the wetting experiment. The difference between the exper-
imental slags was not distinct which may be accounted for similar solubility of Al₂O₃ in the slags. However, the experimental slags will be tightly bonded with the substrate after cooling. Good wettability and the dissolution of Al₂O₃ into slag would result in severe sticking problems between burden and alumina refractory which was adverse to the discharge stage of RHF process.

4. Conclusions

(1) The corrosion process was summarized as three stages: melting & wetting, dissolution & diffusion and crystallization. Good wettability and the dissolution of Al₂O₃ into slag are two main factors that caused the corrosion of substrate.

(2) The specified slags with basicity of 0.43 and 0.63 had a relatively low apparent contact angle of approximately 25° and 30°, respectively. The wetting and corrosion phenomenon between these two slags was not distinct which may be accounted for similar solubility of Al₂O₃ in the slags.

(3) These two slag samples could wet well on the Al₂O₃ substrate under the experimental conditions. The spreading of slag on Al₂O₃ substrate was mainly ascribed to the decrease of surface tension at the initial stage.

(4) As the wetting process went on, Al₂O₃ dissolved into the slag and Mg,Al-bearing compound was expected to be formed in interface between slag and substrate. Superior wettability would possibly bring sticking problems between pellet and alumina refractory and even erode the alumina-based refractories, which will bring negative impact on the RHF process.

Conflict of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.
Zhixiong You, on behalf of the others.

**Declarations of interest**

None.

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