Excess Vaporization of Na from Na$_2$O-SiO$_2$ Molten Slag by Transfer Thermal Plasma of Ar

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The transfer thermal plasma of argon (Ar) was deposited onto the surface of a Na$_2$O-SiO$_2$ molten slag at about 1200 to 1350°C, using a hybrid plasma furnace composed of transfer- and non-transfer plasma. Only the non-transfer plasma of Ar was deposited onto the slag, there was little vaporization of Na according to the thermodynamics. When the transfer plasma current was greater than 3 A, the amount of Na vaporized from the surface was seven times larger than the amount calculated by Faraday’s Law.

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1. Introduction

When transfer plasma was applied onto incinerator ash, lead and zinc were selectively evaporated. The slag is an unavoidable by-product that remains after iron smelting production. An understanding of the vaporization mechanism would make the ore refining process more efficient. The mechanisms are not yet clear except for physical aspects such as the electromagnetic fields.

During transfer plasma processing, it is well accepted that the charge quantities through the plasma are important for determining the amount of the plasma-molten salt reaction.1) Transfer thermal plasma was applied onto the surface of 25 mol% Na$_2$O-SiO$_2$ molten slag. A hybrid plasma furnace composed of the transfer and the non-transfer plasma was used in this study.2) A part of Ar gas in the thermal plasma decomposes into Ar$^+$ ions and electrons. The number of electrons increases with an increase in collisions of Ar molecules and the breeding of electrons makes a plasma flame. In this study, a model was proposed that the transfer plasma acts as a cathode electrode and the molten slag acts as an electrolyte. Faraday’s Law was employed to estimate the reaction amount. It was found that the amount of SiO gas evaporated from the slag was more than that of Na, and was about 100 times more than that calculated by Faraday’s Law. It must be emphasized that excess vaporization of SiO was measured in less than 1.0 A of current, of the transfer thermal plasma. Thermodynamically, Na gas vaporized more than SiO gas.

In the present work, the transfer thermal Ar plasma of more than 3 A was applied onto the surface of a Na$_2$O-SiO$_2$ molten slag. The aim of the present experiment is to investigate the amount of the high current plasma-slag reaction. The differences in the reaction mechanism are discussed based on the amounts in comparison with cases less than 1.0 A of current plasma.

2. Experiment

2.1 Preparation of slag sample

A plasma jet of 20 kW was used, as shown in Fig. 1. The hybrid thermal plasma was composed of a non-transfer plasma of Ar gas (99.999%), and transfer plasma. The non-transfer plasma was blown from a plasma gun, and the transfer plasma was between a tungsten electrode in the gun and a water-cooled copper stand. An auxiliary resistance furnace was set-up in the furnace chamber for heating samples.

One end of an alumina tube with a 28 mm inside diameter, and a 30 mm length was sealed with a polished 5 mm iron rod to make a crucible. A 18.1–25.8 mol% Na$_2$O-SiO$_2$ slag was prepared from a mixture of NaCO$_3$ and SiO$_2$ reagent powders. The slag was pre-melted in a platinum crucible in an Ar gas atmosphere for 2 h, and then cooled back to room temperature. The depth of the molten slag was about 5 mm in the center, and about 8 mm near the wall. The temperature of the molten slag was measured using an R-type thermocouple near the crucible wall.

2.2 Generation of transfer plasma and analysis of sample

A crucible was made from an aluminum tube (ϕ25 mm × 300 mm, SSA-S, Nikkato) and a 99.5%-iron bar. The shape of the iron rod was changed by plasma radiation for use as the bottom. The crucible with the slag was set on a water-cooled copper stand. The chamber was evacuated three times and rinsed with Ar gas. When the slag melted at 1200 °C, the copper stand was controlled to be 200 mm. Ar gas flowed from the plasma gun with a flow rate of 5 l/min under 0.1 MPa. The non-transfer plasma was ignited with a direct current of 150 A, and then a stable plasma jet flame was generated with a constant current of about 10 A. After 30 s, in addition to the non-transfer plasma, the transfer thermal plasma was generated with a constant current of 3 to 5 A using an electric power generator. The flame of the transfer thermal plasma was spread over the slag surface. The current and voltage of the transfer and the non-
transfer plasma were computer recorded. The surface of the molten slag was monitored by a video camera through a window in the chamber.

The concentration distributions of Na, Si and Fe in the slag samples after the experiments were analyzed by an EPMA (Electron Probe Micro Analyzer, Shimazu Co.). The compositions of the slag samples before and after the experiments were determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry), and the samples that adhered under the lid of the chamber after the experiments were also analyzed. The compounds near the anode electrode were identified by XRD (X-ray Diffractometer, rint-TTR-3C/PC, Rigaku Denki).

3. Results

As shown in Fig. 2, for 3 A of the electric current of the transfer plasma, the voltage was not stable at around 60 V. For the voltage 30 V, the current initially increased to 0.8 A, and then gradually decreased to about 10 mA. The current over 1.0 A was stable, while the voltage was not stable. The stable part was defined as the current in each run.
Table 1 shows the compositions of the slag samples of Runs 1 to 6 before and after the experiments, for 3 to 4 A of the transfer plasma current, at different times. The initial composition of the slag varied from 18.1 to 25.8 mol% Na$_2$O-SiO$_2$. These slag samples melted because the temperature of the slag surface increased to about 1350°C by applying the transfer plasma, while the composition of the Na$_2$O-SiO$_2$ slag was in equilibrium. Solid SiO$_2$ is 18 mol% of Na$_2$O at 1200°C, and 15 mol% at 1350°C. After applying the transfer plasma, the composition of Na$_2$O in the slag decreased to 6.9, to 13.4 mol% Na$_2$O.

These slag samples were in a region of coexistence with the molten slag and some solid compounds. As shown in Fig. 3, for the current of 4 A, the dendrite crystals of SiO$_2$ and FeSiO$_3$ precipitated onto the anode electrode of the iron plate.

4. Discussion

4.1 Excess evaporation of Na (g)

Samples adhered under the lid of the chamber after experiments, and were mainly made of Na$_2$CO$_3$·H$_2$O. Plasma irradiation decreased the Na$_2$O compounds in the slag. This indicates that the plasma vaporized Na from the slag.

Because the Fe substrate can be regarded as an anode electrode in the system, the slag phase near the Fe substrate
will be discussed. Currents of 3 to 4 A on the slag produced solid compounds such as dendrite crystals of SiO$_2$ and FeSiO$_3$ near the anode electrode of the iron plate, as shown in Fig. 3. For currents less than 1 A, the Fe ion concentration in the slag gradually decreased from the anode electrode, according to the rules of diffusion, as shown in Fig. 4. It is important that the bubbles could be observed in this current. These results showed that the reaction of the Fe-slag interface changed in response to the plasma current.

This discussion will focus on the cathode reaction. The amount of Fe in the slag diffused from the anode electrode and followed Faraday’s Law in this system, and the law was employed to calculate the reaction amount at the plasma-slag interface. Figure 5 shows the deviation of composition change of Na$_2$O mol% in molten slag by applying the transfer plasma, from that calculated according to Faraday’s law. The quantity of electricity that passed through the molten slag was measured by the integration of the electric current with the reaction time. The integration was measured by a trapezoid approximation method. This result shows that the thermal transfer plasma irradiation causes more slag to evaporate than the calculated amount. When a low current plasma (less than 1.0 A) was applied onto the slag surface, there was a large vaporization of SiO (g). For the transfer plasma current of more than 3 A, the amount of Na that vaporized from the surface was seven times larger than that calculated by Faraday’s Law. The reaction mechanism of the plasma-slag interface is different for each current.

4.2 Experimental uncertainty of Fig. 5
This discussion will focus on experimental uncertainty. The thermal transfer plasma irradiation causes the slag to evaporate. This phenomenon was thought to be caused by three dominant mechanisms, electrochemical reaction, thermal vaporization and ions sputtering onto the surface. The amount of electrochemical reaction is described by Faraday’s law in Fig. 5. It must be considered that all other errors may have been caused by other mechanisms.

Thermal vaporization can be estimated by the Hertz-Knudsen equation. The vapor pressures of Na and SiO, in equilibrium with 25 mol% Na$_2$O-SiO$_2$ molten slag, were calculated from the standard Gibbs energy of formation of Na$_2$O and SiO$_2$, the activity of Na$_2$O and SiO$_2$ in the slag, and the partial pressure of oxygen in the atmosphere. The activity of Na$_2$O and SiO$_2$ were 2.5 x 10$^{-3}$ and 0.15 at 1473 K, respectively. The variation of the activity coefficient of the oxide in the silicate slag based upon temperature was small. If is assumed that a coefficient of evaporation equals 1, the Hertz-Knudsen equation shows the maximum amount of thermal evaporation at these vapor pressures. The calculated amount of Na (g) was about 5.1 x 10$^{-6}$ (mg·s$^{-1}$·m$^{-2}$), and SiO (g) was negligibly-small in Fig. 5. This uncertainty might be caused by ion sputtering. The amount by plasma sputtering can be estimated by calculating the number density of each ion at the surface. It is well accepted that the number densities of the ions in the thermal plasma follows Saha’s equation. This equation was solved using distribution functions and other values, such as statistical weight, which readily available in literature. The calculations indicated that the plasma on the slag surface was Na plasma. The number density of an Na ion particle at the surface was about 10$^{14}$ (cm$^{-3}$) at 4000 (K), and was also negligible.

A result of Fig. 5 did not agree with the results calculated by reported values. This discrepancy may have been attributed to the existence of another mechanism, and that other mechanism controlled the reaction amount at the slag-plasma interface.

4.3 Selective evaporation by plasma current
The slag of Run 7 was heated only by the non-transfer plasma. The composition of Na$_2$O in the slag slightly decreased as a result of thermal vaporization. For the transfer plasma currents less than 1.0 A, the concentration of Fe gradually decreased as a result of diffusion from the anode.
Table 2 Composition of slag before and after reaction using low current plasma.

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial composition (mol%)</th>
<th>Final composition (mol%)</th>
<th>Voltage* (V) (Type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.573 22.27 77.73 0.689 25.61 74.39 — (I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.573 22.27 77.73 0.727 26.59 73.41 — (I)</td>
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<tr>
<td>3</td>
<td>0.575 22.33 77.67 0.646 24.41 75.59 — (I)</td>
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</tr>
<tr>
<td>4</td>
<td>0.575 22.33 77.67 0.678 25.32 74.68 — (I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.575 22.33 77.67 0.592 22.85 77.15 — (I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.575 22.33 77.67 0.660 24.82 75.18 — (I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.575 22.33 77.67 0.653 24.62 75.38 — (I)</td>
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<tr>
<td>8</td>
<td>0.639 24.20 75.80 0.592 22.84 77.16 0 (II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.639 24.20 75.80 0.603 23.16 76.84 0 (II)</td>
<td></td>
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</tr>
<tr>
<td>10</td>
<td>0.639 24.20 75.80 0.636 24.20 75.80 50 (II)</td>
<td></td>
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<tr>
<td>11</td>
<td>0.649 24.50 75.50 0.663 24.90 75.10 70 (II)</td>
<td></td>
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<tr>
<td>12</td>
<td>0.592 22.83 77.17 0.443 18.14 81.86 90 (II)</td>
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<tr>
<td>13</td>
<td>0.580 22.49 77.51 0.515 20.48 79.52 90 (II)</td>
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<tr>
<td>14</td>
<td>0.580 22.49 77.51 0.544 21.38 78.62 90 (II)</td>
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<td>15</td>
<td>0.580 22.49 77.51 0.544 21.38 78.62 90 (II)</td>
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</tr>
<tr>
<td>16</td>
<td>0.558 21.80 78.20 0.558 21.82 78.18 40 (II)</td>
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<tr>
<td>17</td>
<td>0.592 22.87 77.13 0.616 23.56 76.44 80 (II)</td>
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</tr>
</tbody>
</table>


The electrochemical reaction at the interface, and the electrochemical reaction was driven by a floating potential. When the plasma current is high, this caused the reaction to remove the Na2O from the glass sample.

The analytical models and data in this study are insufficient, and further exploration needs to be carried out.

5. Conclusion

The transfer thermal plasma of argon (Ar) was applied onto the surface of Na2O-SiO2 molten slag at about 1200 to 1350°C using a hybrid plasma furnace composed of transfer- and non-transfer plasma. The results are as follows:

(1) The amount of evaporated Na was about seven times more than that calculated from the quantity of electricity, according to Faraday’s law for transfer plasma currents greater than 3 A.

(2) The species to be evaporated from the surface changed according to the plasma current.

It is concluded that an electrochemical reaction exists at the plasma-slag interface because a voltage on the surface changes according to the plasma current, and the reaction can be controlled by the plasma current.

REFERENCES