THE MECHANISMS OF ELECTROCHEMICAL VAPORIZATION FROM SODIUM SILICATE MELT HEATED BY TRANSFER THERMAL PLASMA OF Ar

Kazuhiro Nagata
Tokyo Institute of Technology, Japan

Kei-Ichiro Kashimura
National Institute for Fusion Science, Japan

ABSTRACT

The transfer thermal plasma of Ar was applied on the surface of 25mol%Na_2O-SiO_2 molten slag using a hybrid plasma furnace composed of non-transfer and transfer thermal plasma. The bottom of alumina crucible was closed with an iron plate as anode. For applying only non-transfer thermal plasma, there was little vaporization of Na from the slag surface according to thermodynamic calculations. For the transfer plasma current of less than 0.4A with or without additional non-transfer plasma, SiO electrochemically vaporized rather than Na from the surface. For the current more than 3A, Na vaporized more than SiO. The amounts of vaporized SiO and Na were about 50 and 100 times larger than those expected from the Faraday's law, respectively. On the other hand, the amount of dissolved Fe^{2+} *in the molten slag at the anode electrode was well according to Faraday's law. In order to keep the electro-neutrality for the excess of vaporization, oxygen ions were emitted from the surface. The model of electrochemical electrode as cathode at the surface of molten slag in contact with transfer thermal plasma has been proposed. The excess electrons in plasma bombard the surface, that is, the plasma phase acts as cathode, and the slag surface is polarized to negative. For the lower current density of transfer plasma,* SiO_2 *in slag is reduced by electron to be SiO gas and* O^{2-}*, and for the larger current density,* Na^+ *is additionally reduced to Na gas.*

Key Words: *Transfer thermal plasma, sodium silicate slag, vaporization, electrochemical polarization, electric double layer.*

INTRODUCTION

When incinerator ash is melted in a furnace of transfer thermal plasma, it is reported that lead and zinc selectively evaporate from molten slag. The evaporation of these metals is caused by high temperature plasma. The evaporation mechanisms are not clear but are known to be complicated due to physical aspects such as electromagnetic fields. Kashimura *et al*. [1] assumed that the selective vaporization is due to electrochemical reactions at the interface between the slag and plasma flame. The transfer plasma is composed of weakly dissociated gas ions and electrons. The electrons accelerated in large electric field bombard on the slag surface and act as cathode. The silicate slag is an electrolyte with mobile cations such as Ca^{2+}, Na^+ and K^+, while metal ions such as zinc and lead ions are predominantly reduced to metal vapors. This is an analogy with the aqueous electrochemical reactions. Electrons in transfer thermal plasma have low density and high kinetic energy, while electrons in metal electrode of an aqueous electrochemical cell have high density and low kinetic energy. This analogy indicates that lead and zinc ions in molten slag are electrochemically reduced by electrons in the transfer plasma at the slag/plasma interface.

In this study, the model has been examined using a simple system of 25mol% Na_2O-SiO_2 slag applied with transfer thermal plasma of Ar.

EXPERIMENT

Applying Transfer Plasma on Slag Surface

The hybrid plasma arc furnace of 20kW was employed, as shown in Figure 1. The hybrid thermal plasma was composed of non-transfer plasma of Ar gas (99.999%) blown from the plasma gun and transfer plasma between a tungsten electrode in the gun and a water-cooled copper stand. Ar gas was flowed from the plasma gun with the flow rate of 5 l/min under 1 atm. An auxiliary resistance furnace was set in the chamber of the furnace in order to heat samples. One end of alumina tube with 28mm inside diameter and 30mm length was closed with a polished iron plate with 5mm thickness. The alumina tube was used as a crucible.

25mol%Na_2O-SiO_2 slag was prepared from the mixture of Na_2CO_3 and SiO_2 reagent powders. The slag was premelted in a platinum crucible in air, quenched on a water-cooled copper plate and crashed. The slag was melted in the alumina crucible under Ar gas atmosphere for 2h. The depth of molten slag was about 5 mm in the center and about 8 mm near the wall. The temperature in the molten slag was measured using an R-type thermocouple near the crucible wall. The crucible with slag was set on the water-cooled copper stand and an iron plate with the length of 30 mm was sandwiched between them.

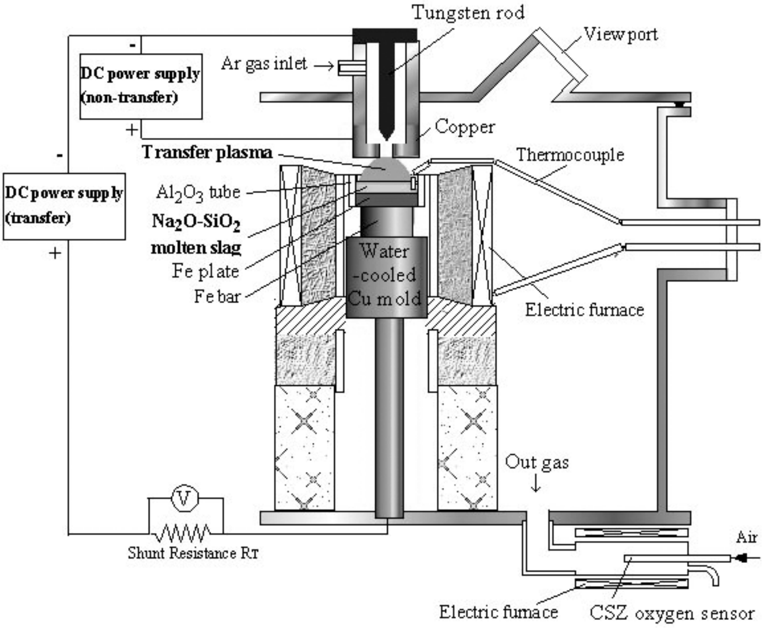

Figure 1: Schematic diagram of the hybrid plasma furnace composed of non-transfer and transfer plasma

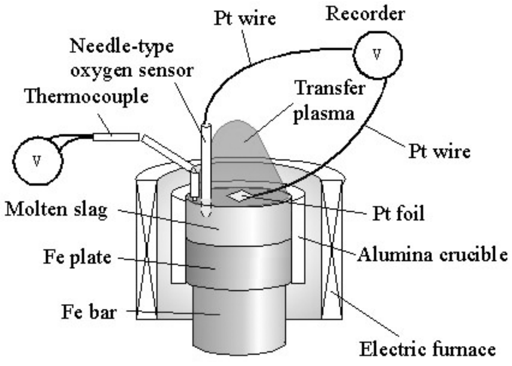

Figure 2: Measurement cell of the oxygen partial pressure at the surface of molten slag during applying transfer plasma in addition to non-transfer plasma by means of oxygen sensor; Pt/Cr•Cr_2O_3 / ZrO_2 (MgO)/slag / Pt foil

The chamber was evacuated three times and rinsed with Ar gas. When the slag was melted in the auxiliary resistance furnace at 1200°C, the copper stand was lifted and the distance between the tip of tungsten electrode in the plasma gun and slag surface was kept in 20 mm. Non-transfer plasma was ignited with the direct current of 150A and then the stable jet flame of non-transfer plasma was generated with the constant current of about 10A. After 30s, in addition to the non-transfer plasma, transfer thermal plasma was generated with the constant current of 3 to 5A using an electric power generator. The flame of transfer thermal plasma spreads over the slag surface. The current and voltage of transfer and non-transfer plasma were recorded using a computer. The plasma flame on the surface of molten slag was monitored by a video camera through the window of chamber.

Oxygen Potential Measurement at Slag Surface and In Out Gas

The oxygen concentration cell was dipped in the molten slag, as shown in Figure 2. A small platinum foil with 3x3 mm^2 was set on the center of slag surface. The cell was an one-end closed tube of ZrO_2 -9mol%MgO solid electrolyte with the outer diameter of 3.2 mm, the inner diameter of 2.5mm and the length of 30mm and the mixture of Cr and Cr_2O_3 powders was stamped with a platinum wire in the tube in order to fix the oxygen partial pressure, Po_2 (ref.), as a reference. The electrochemical cell equation is described as:

$$\text{Pt} / \text{Cr} \bullet \text{Cr}_2\text{O}_3 / \text{ZrO}_2\text{-9mol\%MgO/molten slag/Pt foil} \qquad (1)$$

As the transference number of Na^+ ions in the molten slag was unity, the oxygen partial pressure, Po_2, at the surface was determined by the following equation;

$$Po_2 = Po_2(\text{ref.}) \exp(RT/4\varepsilon F) \qquad (2)$$

where ε is the electromotive force of the cell and *R* and *F* are gas constant and Faraday constant, respectively. *T* is absolute temperature.

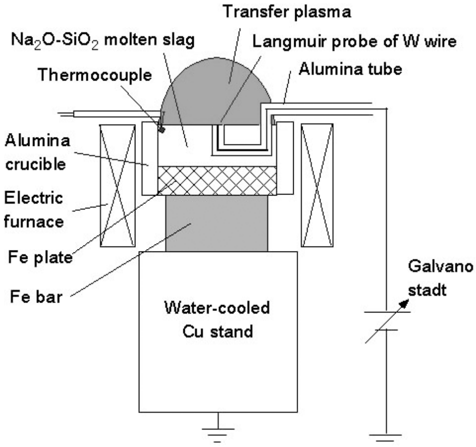

Figure 3: Measurement cell of electrochemical polarization at the surface of molten slag by means of probe during applying transfer plasma in addition to non-transfer plasma

The oxygen partial pressure in the out gas of Ar was measured by means of an oxygen concentration cell of a one-end closed tube of ZrO_2 -15mol%CaO solid electrolyte. Air was flowed into the tube in order to fix the oxygen partial pressure of 0.21 atm as a reference.

Surface Potential Measurement of Molten Slag

The probe of tungsten wire with 0.8mm diameter was set vertically in the center of the crucible. The wire was insulated with fine alumina tubes. After slag was melted in the crucible and cooled to room temperature in Ar gas, the wire was cut just at the surface, as shown in Figure 3. The probe was slightly wet with the slag. The probe was connected to a galvanostadt (HA-501, Hokuto Denko Ltd.). During applying transfer plasma of the current of 3 to 5A on the molten slag, a constant current was applied to the probe from the galvanostadt for about 10s. The stable electric potential of the probe in reference to the Cu stand was measured. The current was changed from –0.04 to 0.04A.

Measurement of Spectrum of Plasma and Analysis of Slag Samples

The spectrum of plasma was measured using the spectral analysis of fiber-optics type (USB2000, Ocean Optics). The slit width was 5 μm and the wavelength region was 250 to 800 nm.

The slag was analyzed by EPMA (Electron Probe Micro Analyzer, SHIMAZU XRF-1800). The compositions of Na, Si and Fe in the slag were also determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry, SPQ-9000, LEEMAN LABS). The compounds near the anode electrode were identified by XRD (X-ray Diffractometer, Rint-TTR-3C/PC, Rigaku Denki).

RESULTS

Electrochemical Decomposition of Slag by Transfer Plasma

As shown in Figure 4, for the voltage 30V, the current of transfer plasma initially increased to 0.8A and gradually decreased to about10mA. For the current of 3A, the voltage was unstable and vibrated around 60V. Generally, for the stable current over 1A, the voltage was unstable.

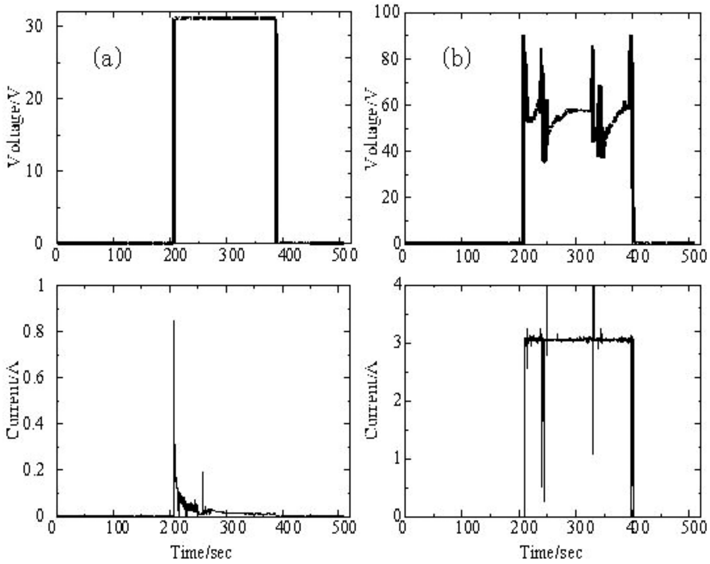

Figure 4: Voltage and current of transfer plasma of (a) less than 1 A and (b) 3 A in addition to non-transfer plasma

The color of non-transfer plasma of Ar was purple or blue. When transfer plasma was added, the color became yellow. From the spectrum of plasma, the activated species of Na, Ar, and Si and neutral oxygen were detected.

Table 1: Composition of slag before and after reaction for the transfer plasma current less than 1A

No.	Initial composition (mol%)			Final composition (mol%)			Voltage* (V)
	Na/Si	Na_2O	SiO_2	Na/Si	Na_2O	SiO_2	
1	0.573	22.27	77.73	0.689	25.61	74.39	—
2	0.573	22.27	77.73	0.727	26.59	73.41	—
3	0.575	22.33	77.67	0.646	24.41	75.59	—
4	0.575	22.33	77.67	0.678	25.32	74.68	—
5	0.575	22.33	77.67	0.592	22.85	77.15	—
6	0.575	22.33	77.67	0.660	24.82	75.18	—
7	0.575	22.33	77.67	0.653	24.62	75.38	—
9	0.639	24.20	75.80	0.592	22.84	77.16	0
10	0.639	24.20	75.80	0.617	23.58	76.42	0
11	0.639	24.20	75.80	0.603	23.16	76.84	0
12	0.639	24.20	75.80	0.636	24.20	75.80	50
13	0.572	22.25	77.75	0.588	22.71	77.29	50
14	0.649	24.50	75.50	0.663	24.90	75.10	70
15	0.592	22.83	77.17	0.443	18.14	81.86	90
17	0.580	22.49	77.51	0.515	20.48	79.52	90
18	0.580	22.49	77.51	0.544	21.38	78.62	90
20	0.558	21.80	78.20	0.558	21.82	78.18	40
21	0.593	22.87	77.13	0.616	23.56	76.44	80

Table 2: Quantity of electricity at cathode and anode reactions for the transfer plasma current less than 1A

No.	Cathode reaction		Anode reaction		Quantity of electricity$^+$/C	Voltage /V
	SiO/10^{-3}mol	Q*/C	Fe^{2+}/10^{-3}mol	Q#/C		
1	9.263	1788	0.4026	77.7	—	—
2	15.182	2930	0.3788	73.1	—	—
3	15.890	3067	0.4284	82.7	—	—
4	9.989	1928	0.7972	153.9	142.0	—
5	1.826	352	0.1015	19.6	13.0	—
6	6.378	1233	0.1387	26.8	18.0	—
7	8.100	1563	0.3796	73.3	—	—
12	0.000	0	0.0377	7.3	6.3	50
13	2.047	395	0.2514	48.5	21.2	50
14	1.885	364	0.1216	23.5	30.7	70
20	0.106	21	0.0635	12.3	11.8	40
21	3.877	748	0.1509	29.1	39.4	80

Note: Q* and Q# are obtained from the decrease of SiO_2 (cathode) and the dissolution of FeO (cathode) in molten slag according to Faraday's law, respectively. +:Quantity of electricity is obtained from the integration of electric current with reaction time.

Tables 1 and 2 show the compositions of slag samples before and after applying transfer plasma with less than 1 A and the quantities of electricity at anode and cathode, respectively. The composition ratio of Na to Si in slag increased after the experiments. For 0V, that is 0 A of the transfer plasma, the ratio a little decreased according to thermal vaporization. It did not change at 40V but increased at 50V and 70V, which corresponded to less than 1 A. For 90V, the ratio decreased. In Table 3, after applying the transfer plasma, the composition of Na_2O in slag decreased to 6.9 to 13.4 mol%Na_2O. In the current less than 1 A, SiO gas vaporized rather than Na gas[1)] and in 3 to 4 A, Na vaporized rather than SiO gas. For less than 1A, the concentration of Fe ion in slag gradually decreased from the anode electrode according to diffusion, as shown in Figure 5. For in 3 to 4 A slag produced some solid compounds such as the dendrite crystals of SiO_2 and $FeSiO_3$ near the anode electrode of iron pate, as shown in Figure 6.

Table 3: Composition of slag before and after reaction for the transfer plasma current more than 3A, the quantity of electricity and the composition calculated from Faraday's law

Run No.	Composition of Na_2O in slag (mol%)		Total quantity of electricity (C)	Calculated composition of Na_2O(mol%)	Current of transfer plasma (A)
	Before	After			
1	21.7	9.6	714.07	19.0	4
2	21.7	13.4	48.797	21.5	4
3	18.1	8.2	901.89	15.0	3
4	18.8	6.9	11.38	18.8	4
5	21.9	9.63	69.2	21.7	3
6	21.9	7.75	169.77	21.5	4
7	25.8	24.2	0	25.8	0

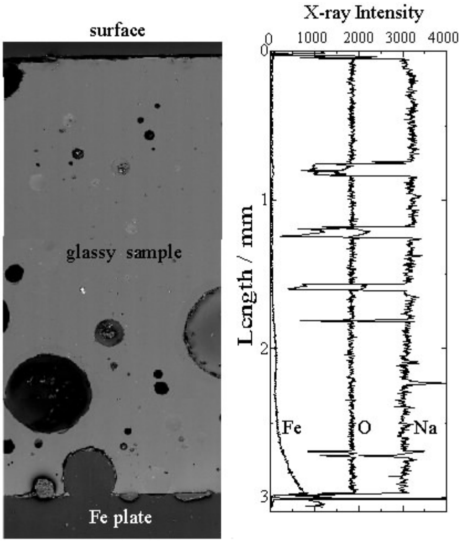

Figure 5: Cross-section of slag applied transfer plasma with the current of initially 0.8A and finally 0.01A at the voltage of 30V and the concentration profiles of iron, sodium and Oxygen in slag at the center of crucible

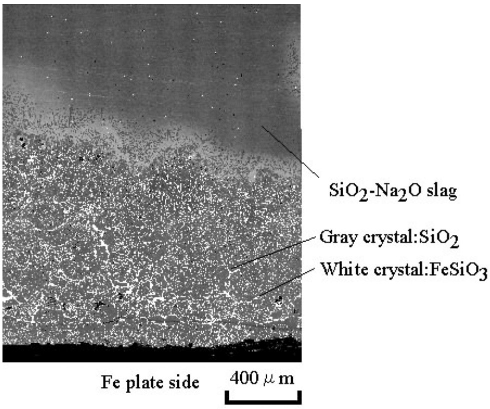

Figure 6: Cross-section of slag applied transfer plasma with the current of 4A at the voltage of 120 V and the compounds of SiO_2 and $FeSiO_3$ precipitated on the anode electrode of iron plate

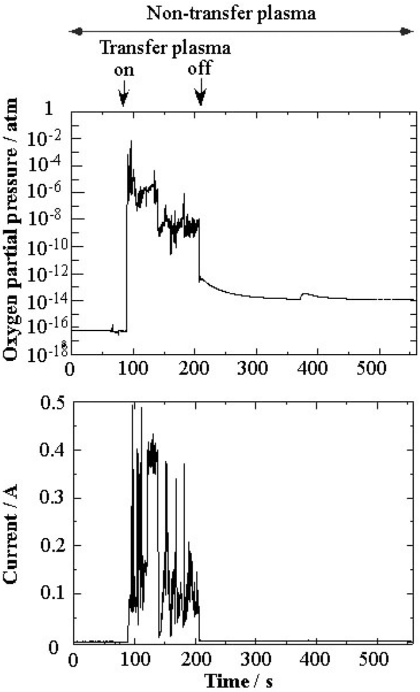

Figure 7: Oxygen partial pressure at the surface of molten slag during applying transfer plasma in addition to non-transfer plasma and the transfer plasma current

Oxygen Partial Pressure at the Slag Surface

The oxygen partial pressure at the slag surface was $1x10^{-16}$ atm during only applying non-transfer plasma. The oxygen partial pressure was near that in equilibrium with Fe and FeO in spite of no existence of FeO in the initial slag. When the transfer plasma with the current less than 0.4 A was applied, the oxygen partial pressure increased to $1x10^{-3}$ atm and gradually decreased to $1x10^{-9}$ atm, as shown in Figure 7. After the current of the transfer plasma was switched off, the oxygen partial pressure decreased and gradually backed to the original pressure.

At the same time, the oxygen partial pressure in the out gas of Ar was 1x10^{-4} to 1x10^{-5} atm during only applying non-transfer plasma. When the transfer plasma with the current of less than 1A, 2A or 4A was applied, the oxygen partial pressure decreased to 1x10^{-12} or 1x10^{-14} atm and then gradually increased to 1x10^{-9} or 1x10^{-12} atm, as shown in Figure 8. After the current of the transfer plasma was switched off, the oxygen partial pressure gradually backed to the original pressure.

Electrochemical Polarization at the Slag Surface

The electric potential of the probe was successfully measured under a constant current, while the current of the probe was unstable under a constant potential. The potential-current curves of the probe are shown in Figure 9. For the transfer plasma current of 4 or 5A, the current of the probe steeply increased with increasing the potential in lower and higher potentials and among the intermediate potential, it slowly increased. It was realized that in the intermediate potential region the resistant of the probe was higher than the other regions. The intermediate potential decreased to negative with increasing the transfer plasma current more than 4A. For the transfer plasma current of 3A, however, the potential-current curve appeared in positive potential and the current slowly increased with increasing the potential.

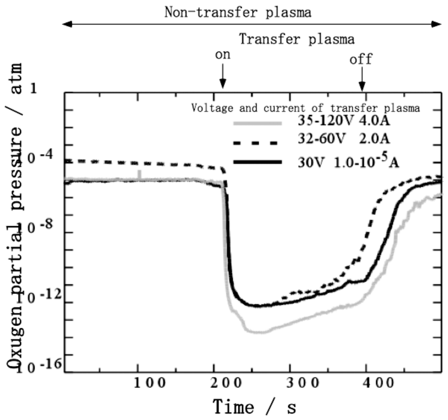

Figure 8: Oxygen partial pressure in the out gas of Ar from the plasma chamber during applying transfer plasma on molten slag in addition to non-transfer plasma

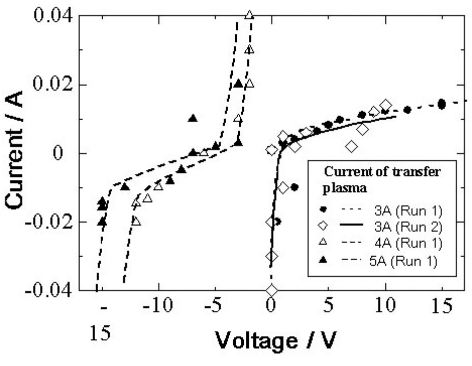

Figure 9: Voltage-current curve of probe at the molten slag surface during applying transfer plasma in addition to non-transfer plasma

DISCUSSIONS

Electrochemical Reactions at the Slag Surface

For the partial pressure of oxygen of $1\text{x}10^{-16}$ atm in equilibrium with Fe and FeO, the vapor pressures of Na and SiO on the molten slag were $2.7\text{x}10^{-6}$ atm and $2.6\text{x}10^{-18}$ atm, respectively. The vaporization rate of Na is larger than that of SiO and total fluxe of Na and SiO is small. For the transfer plasma current less than 1A at the voltage between 40 to 70V, the ratio of Na to Si in slag was increased, as shown in Table 1. It is realized that the flux of SiO is accelerated by transfer plasma. The following electrochemical reaction takes place at the molten slag surface;

$$SiO_2(\text{slag})+2e\ (\text{plasma})\rightarrow SiO(g)+O^{2}\text{-}(\text{slag}) \qquad (3)$$

Na^+ ions predominantly carry electric current through the molten slag from the anode electrode of iron plate to the slag surface.

For the transfer current of 3 or 4A at the voltage more than 90V, the composition of Na_2O in slag decreased rather than that of SiO_2, as shown in Table 2. It is realized that the vaporization of Na is accelerated by transfer plasma. The spectrum of transfer plasma flame showed the activated Na, Si, Ar and the neutral Oxygen. The following electrochemical reactions take place in addition to the reaction (1);

$$Na^+(\text{slag})+e(\text{plasma})\rightarrow Na \qquad (\text{gas}) \qquad (4)$$

$$SiO_2(\text{slag}) + 4e(\text{plasma}) \rightarrow Si\,(\text{gas})+ 2O^{2}\text{-}(\text{slag}) \qquad (5)$$

These aspects show that the transfer plasma acts as cathode electrode because electrons accelerated under electric field bombard on the slag surface.

At the anode electrode of iron plate, iron electrochemically solved and diffused into molten slag as Fe^{2+} for the transfer plasma current of less than 1A, as shown in Figure 5.

$$Fe(\text{electrode})\rightarrow Fe^{2+}(\text{slag})+2e(\text{electrode}) \qquad (6)$$

For the current of more than 1.7A, oxygen gas additionally evolved 1).

$$O^{2}\text{-}(\text{slag})\rightarrow 1/2O_2(\text{gas})+2e(\text{electrode}) \qquad (7)$$

For the large current of transfer plasma more than 3A, SiO_2 and $FeSiO_3$ were precipitated on the anode electrode, as shown in Figure 6. According to the migration of Na^+ ions to the slag surface, the oxidation of iron produced these compounds near the anode.

Excess Evaporation of SiO and Na from that According to the Faraday's law

The amount of dissolved Fe^{2+} in the molten slag at the anode electrode agreed with that calculated from the quantity of electricity according to Faraday's law. In Figure 10, the quantity of electricity calculated from the amount of dissolved Fe^{2+} is compared to the integrated electric current with reaction time. At the transfer plasma voltage between 40 and 50V, the calculated quantity of electricity was slightly larger than the integrated electric current. This error is due to the unstable electric current as shown in Figure 4. At 70 and 80V, the calculated quantity of electricity was smaller than the integrated electric current because of the additional reaction due to oxygen gas evolution.

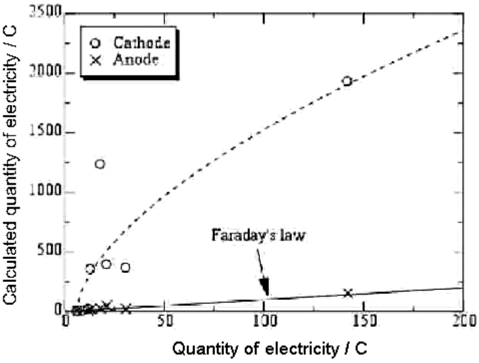

Figure 10: Comparison of the quantities of electricity calculated from the decreased amount of SiO_2 (cathode) and the dissolved amount of FeO (anode) in molten slag according to the Faraday's law, respectively, for the transfer plasma current of 1A

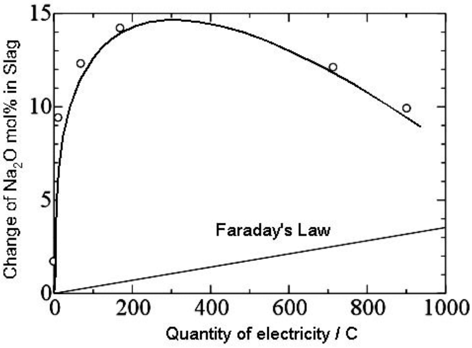

Figure 11: Relation of the composition change of Na_2O mol% in molten slag to the quantity of electricity for the transfer plasma current more than 3A

On the other hand, for the transfer plasma current of less than 1A, the quantity of electricity calculated from the decrease of SiO_2 in slag according to Faraday's law was 10 to 100 times more than the integrated electric current, as shown in Table 2 and Figure 10. The excess cathodic reaction at the slag surface was caused by bombardment of excess electrons in the transfer plasma. For the transfer plasma current more than 3A, the transfer plasma accelerated the vaporization of Na from the slag surface and the amount of vaporized Na was about 7 times more than the calculated one according to the Faraday's law, as shown in Figure 11.

Emission of O^{2-} ions for Keeping the Electrical Neutrality of Excess Vaporization

In order to keep the electro-neutrality at the slag surface, the excess oxygen ions should emit from the surface to plasma.

$$O^{2-}(\text{slag}) \rightarrow O^{2-}(\text{plasma}) \qquad (8)$$

Then, oxygen ions react with Ar^+ ions in plasma to produce oxygen gas near the slag surface.

$$O^{2-}+2Ar^{+}\rightarrow 1/2O_2+2Ar \tag{9}$$

As shown in Figure 7, the oxygen partial pressure at the slag surface increased to about $1x10^{-3}$ atm from $1x10^{-16}$ atm during applying the transfer plasma of Ar with the current of less than 1A. This evidence indicates the emission of oxygen ions from the slag surface.

At the same time, the oxygen partial pressure in the out gas of Ar decreased from about $1x10^{-4}$ to 10^{-12} atm during applying transfer thermal plasma. From the spectrum of plasma flame, SiO, Si and Na gases electrochemically vaporized and was oxidized to be SiO_2 and Na_2O by oxygen gas produced by the equation (7). Thus, the oxygen partial pressure in the out gas decreased.

Electrochemical Polarization at the Slag Surface

Electrons were emitted to plasma phase when minus electric current passed through the probe. On the other hand, electrons were absorbed from plasma when plus current passed. There were two break points on the potential-current curve at -12 and -4V for the transfer plasma current of 4A. Between the two break points, the electric resistance of the probe was higher than those out side of both break points. This indicates the existence of barrier with negative potential such as O^{2-} ions. At lower than -12V, electrons broke the barrier and were emitted to plasma phase. At higher than -4V, electrons also broke the barrier and were absorbed from plasma phase to the probe.

The barrier is probably the electric double layer composed of O^{2-} ions in plasma phase and Na^{+} ions at the slag surface. The potential difference of the electric double layer was about 8V for the transfer plasma current of 4 A. For 5A, the potential difference was about 10V. However, for 3A, the potential-current curve of the probe appeared in positive potential. The current of the probe decreased to negative near zero potential and gradually increased with increasing the potential. This indicates that O^{2-} ions diffuse into plasma phase from the slag surface.

CONCLUSIONS

The transfer thermal plasma of Ar as cathode electrochemically reduced Na_2O -SiO_2 molten slag to evaporate SiO and Na according to the surface potential of slag. The amounts of evaporated SiO and Na were more than the calculated ones according to the Faraday's law. For keeping the electrictro-neutrality, O^{2-} ions were emitted from the surface. The electric double layer was composed of O^{2-} in plasma and Na^{+} at the slag surface.

REFERENCES

Kashimura, K., Nakada, K. & Nagata, K. (2008). *Excess Electrochemical Vaporization of SiO from Na_2O - SiO_2 Molten Slag by Transfer Thermal Plasma of Ar.* Mater.Trans. 49 (6), pp. 1327-1332. [1]