The Oxygen Partial Pressure on the Surface of $\text{Na}_2\text{O-SiO}_2$ Molten Glass Heated by Thermal Plasma of Ar

Keiichiro Kashimura* and Kazuhiro Nagata

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8552, Japan

Transfer thermal plasma of Ar was deposited on the surface of $\text{Na}_2\text{O-SiO}_2$ molten slag at about 1200 to 1350°C using a hybrid plasma furnace composed of transfer- and non-transfer plasma. The dependence of the transferred-type thermal plasma current on oxygen potential of the glass has been studied using an oxygen sensor made of solid electrolyte. During application of the transfer plasma with current less than 0.4 A, the oxygen partial pressure at the slag surface increased to 1×10^{-3} from 1×10^{-16} atm and that in the out gas of Ar was decreased from 1×10^{-4} to 1×10^{-12} or 1×10^{-14} atm. This paper describes a physical model aimed at studying the most dominant parameter for sheath forming from the above mentioned. [doi:10.2320/matertrans.MRA2008353]

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1. Introduction

Thermal plasma is a very useful heating source in several industries such as ore refining, garbage incinerators and chemical synthesis. Due to many applications of plasma, plasma processing has been extensively studied. Generally atmospheric plasma is called as thermal plasma and is thermodynamically situated in the local equilibrium state. The plasma is recognized as a heat reservoir in the vast metallurgical processes and has been applied in the refining of titanium, heating a tundish in the continuous-casting process and smelting iron in a cupola.¹⁾

The amount of vaporization is very important from the standpoint of plasma processing. We have applied thermal transferred type plasma onto molten 25 mol% $\text{Na}_2\text{O-SiO}_2$ glass²⁾ and tried to reduce the slag by the electrochemical reaction. The glass sample is used as a slag which is an unavoidable by-product in the iron smelting process. The report showed that the evaporated amount of SiO_2 is greater than the calculated value. For this system, there was little vaporization of SiO_2 according to thermodynamics.³⁾

Authors assumed that a floating potential could be electrochemical driving force at plasma-slag interface. The potential of the sample was dependant on the plasma current, increasing with an increase in plasma current. It was found that there was discontinuous change point of the potential in the system.⁴⁾ When the plasma current changed, the mechanism of the electrochemical reaction on the surface varied.

In the present study an oxygen potential on the surface of molten $\text{Na}_2\text{O-SiO}_2$ glass heated by the transfer-type thermal plasma is measured using a solid electrolyte. The aim of the present experiment is to investigate differences of the pressure for each transfer current. The reaction mechanism on the slag surface is discussed based on the results of this study and of the references 3) and 4). An analytical model is handed in to describe the plasma sheath forming.

Fig. 1 Schematic illustration of hybrid plasma furnace. Transferred plasma was generated by the potentiostat (DC2). DC1 is a direct current generator with 150 to 200 A.

2. Experimental

2.1 Preparation of slag sample

A hybrid plasma arc furnace 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%) blown from a plasma gun and transfer plasma 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 iron plate with a 5 mm thickness to make a crucible. A 18.1–25.8 mol% $\text{Na}_2\text{O-SiO}_2$ slag was prepared from the mixture of NaCO_3 and SiO_2 reagent powders. The slag was pre-melted in a platinum crucible in air, quenched on a water cooled copper plate and then crushed. The slag was melted in an alumina crucible under Ar gas atmosphere for 2 h and then cooled to room temperature. The depth of the molten slag was about

*Present address: National Institute for Fusion Science, Toki 509-5292, Japan

The sensor might have a problem in the case that it was in plasma phase. An oxygen sensor feels a chemical potential difference between a reference electrode and a probe. There are many electrons in plasma phase and these electrons make large potential difference on the surface of the sample. The potential difference is called a floating potential.⁵⁾ Since the potential difference of this system is estimated as 2~3 (V),

Fig. 4 Oxygen partial pressure on a molten slag surface during applying transfer plasma in addition to non-transfer plasma and transfer plasma current.

Fig. 5 Oxygen partial pressure in out gas of Ar from a plasma chamber during applying transfer plasma on molten slag in addition to non-transfer plasma.

we had thought the uncertainties of the measurement to be large before this experiment.⁴⁾ But the result of the Fig. 4 was only mA values. The result indicated that the sensor did not feel an uncertainty from the floating potential. The error caused by plasma was not observed in this experiment.

4.2 Reducing ability of thermal Ar plasma

The transfer plasma irradiation decreased Si element in the slag, as shown in Table 1. A type in the table means a circuit type of hybrid plasma apparatus; type I: automatic and

Table 1 Composition of slag before and after reaction using low current plasma.

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

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Fig. 6 Comparison of the measured quantity of electricity with the calculated ones from the decreased amount of SiO₂ (cathode) and the dissolved FeO (anode) in molten silicate slag according to the Faraday's law.

type II: controlled using DC 2. Type II apparatus was used in this study. We assumed that thermal transferred plasma of Ar had reducing ability from the result of the Table 1. The oxygen partial pressure on the slag surface increased during the plasma irradiation as shown in Fig. 4. Since the oxygen was emitted from the molten slag, the assumption was right. The amount of the reaction in the slag did not follow the Faraday's Law, as shown in Fig. 6. An electrochemical model that the slag was electrolyte was inadequate to account for the reaction mechanism.^{2,3)}

In this system, an anode electrode was molten slag that was high electric resistance. The main carrier of the current was

Fig. 7 Voltage-Current curve of Langmuir probe at the molten slag surface during applying transfer plasma.

Na ion in the slag phase and an electron in the plasma phase. The mobility of the electron is much larger than that of Na ion and there was floating potential at the plasma-slag interface. Figure 7 shows a current-voltage curve of the surface in the system. In Fig. 7 the curves for $I_{pl} = 4$ and 5 A have rate-determining steps at around $V_{pr} = 0$ V. These steps are a result of the sheath formation at the sample surface. On the other hand, the curve for $I_{pl} = 3$ A is anomalous as the curve has no rate-determining step and the probe current was obtained when the negative probe voltage was applied. The anomalous curve was observed only in the low plasma current (≤ 3 A) experiment. It is noticeable that the values of the floating potential calculated from the figure did not agree with the reported values for Ar plasma.

To account the anomalous curve, we assumed that there was another electrochemical mechanism at the plasma-slag interface to account for these results. The reaction was caused by the floating potential and the chemical potential difference of the reaction changed the measured values of the floating potential. The concept of the chemical reaction was described as follows.⁴⁾

$$\phi_f = \frac{kT_e}{2e} \ln \left[\frac{m_i T_e}{m_e T_i} \right] - \alpha_{rea} \quad (1)$$

Where, ϕ_f : floating potential, m_i : mass of ion, m_e : mass of electron, α_{rea} : a compensation term of a reaction. α_{rea} can be the potential difference of the reaction.

$$\alpha_{rea} = \sum_k \mu_k dN_k = N_A \sum_k \mu_k d\xi_k \quad (2)$$

μ_k : chemical potential for k particles, ξ : extent of reaction, N_A : Avogadro's number. A compensation term corresponds to equilibrium electrode potential of the reaction. The reaction described by eq. (2) controlled the oxygen potential of the system. If one assumed that the compensation term is equal to the chemical potential, we can estimate that α_{rea} is 2.08 V at 1400 K. The results of the Fig. 7 are well described by the estimation. The data and chemical formula to calculate the α_{rea} was from references 3, 6–8).

4.3 Mechanism of sheath formation

A mechanism of the reaction on the slag surface changes

Fig. 8 A model for distribution of voltage near ion sheath and the conditions.

in response to the plasma current. We can observe the feature as the current-voltage curve was different in Fig. 7. Meanwhile, Fig. 5 shows that the oxygen potential of 4 A was different from the others'. These results indicate that the plasma current changes the sheath structure in this system. But eq. (2) can't describe the sheath forming.

Let us consider two states of a particle to describe the mechanism change of the sheath formation— A: a state before a particle feels a floating potential and B: a state after a particle receives all potential energy. The conditions of the model are shown in Fig. 8. The equation of continuity is as follows.

$$n_i(x)u_i(x)m_i = n_i(0)u_i(0)m_i \quad (3)$$

Where, $n(x)$: number density, $u(x)$: velocity of ions, m : mass of a particle. The subscript i refer to the particles— i : ion and e : electron. We have deduced an equation of the following form by extending Bohm's treatment of the Newton's motion equation.⁹⁾

$$m_i \dot{u}_i(x) = eE(x) + A \quad (4)$$

The term A describes the force that breaks the sheath out. We will give our conclusion with respect to the force A . The integral from 0 to x of the eq. (4) gives the next expression.

$$\left[\frac{m_i u(x)^2}{2} \right]_d^0 = [-eV(x) + Ax]_d^0 \quad (5)$$

$$u(d) = \left(u_i(0)^2 - 2 \frac{e(V(d) - V(0)) - Ad}{m_i} \right)^{\frac{1}{2}}$$

Elimination of $u(x)$ between eq. (3) and eq. (5) gives the following equation.

$$n_i(d) = n_i(0) \left(1 - 2 \frac{e(V(d) - V(0)) - Ad}{m_i u_i(0)^2} \right) \quad (6)$$

Meanwhile, Maxwell-Distribution gives an electron density as follows.

$$n_e(x) = n_e(0) \exp \left[- \frac{e(V(x) - V(0))}{kT_e} \right] \quad (7)$$

Densities of the ion must be larger than that of the electron to form the ion sheath.

$$\left(1 - 2 \frac{e(V(d) - V(0)) - Ad}{mu_i(0)^2}\right) > \left[1 - 2 \frac{e(V(d) - V(0))}{kT_e}\right] \quad (8)$$

Where, we used the Maclaurin approximation to simplify the equation.

Finally, combining eq. (8) and Bohm's condition,⁹⁾ we obtain eq. (9).

$$A < \frac{(V(d) - V(0))}{d} \left(1 - \frac{mu_i(0)^2}{kT_e}\right) = e \left(\frac{\frac{1}{2}mu_i(0)^2 - \frac{1}{2}kT_e}{\frac{1}{2}kT_e}\right) E(d) \quad (9)$$

If one assumes a force that gives energy an ion in the sheath, the change of the sheath structure is described well as shown as eq. (9). The equation (9) indicates that subtraction between a kinetic energy of an ion and the energy of an electron makes the sheath stronger. When the force A was larger than that of non-equilibrium plasma on the slag surface, the sheath structure was broken.

Because the right term of the eq. (5) is equals to electrochemical potential, we conclude that A is the chemical force of the reaction of the surface. According to Saha's equation, the electron density of the system is about $10^{18} \text{ (cm}^{-3}\text{)}$ at 3000 (K) .⁴⁾ The debye length of the plasma phase is almost 10^{-7} cm when the energy of the electron is 1 eV . The result indicates that the assumption is possible in viewpoint of space. This model can describe the mechanism of the sheath forming and fit the result of Fig. 7, too.

Because the ionization degree of this plasma was very low and the current was very little,⁴⁾ the model did not consider the heating effect of the anode voltage drop. However, the further study is needed to understand the order of the effect.

5. Conclusion

The oxygen potential of the transferred-type thermal plasma current at the slag surface has been studied using an oxygen sensor made of a solid electrolyte. The oxygen partial pressure increased and then gradually decreased during applying transfer plasma and the plasma irradiation changed the pressure in out gas. It was found that the sheath structure changes in response to the plasma current.

Furthermore, the physical model was handed in to explain the change of sheath structure. This change of the potential can be explained by the chemical reaction of the surface.

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