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Electrochemical vaporization of SiO from Na_2O-SiO_2 slag by transferred argon plasma

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Plasma is partially ionized gas composed of ions, electrons and activated elements at high temperature. Some flying ash from incinerated municipal waste is melted to become glass by a transfer-type arc plasma furnace. As the glass is ionic silicate, when an electric current passes through anode to cathode, ions in molten slag electrochemically react with electron in plasma at the surface of molten slag. In case of molten Na_2O-SiO_2, sodium ions in the molten slag carry electric current and SiO_2 are reduced to evaporate as SiO gas by electron in plasma. The cases of Ag^+ in $NaNO_3$-KNO_3 molten salt and Fe^{2+} in FeO-SiO_2 slag were examined. The amount of cathodic reaction is larger than that of anodic reaction and not apparently according to the Faraday's law on the electrochemical reactions.

Introduction

About 80% of municipal solid waste of over 50 million tons per year is burned in incinerators in Japan. Some ash of incineration is melted to be glass for decreasing its volume and decomposing toxic materials at high temperature. A transfer-type plasma arc furnace is employed for vitrifying the ash and vaporizing heavy metals such as lead and zinc. Table I shows some elements in incineration ash and flying ash. The main compounds in incineration ash are SiO_2, CaO, Al_2O_3 and iron oxides. Flying ash is composed of the almost same compounds as incineration ash with less SiO_2 and more CaO because slack lime is added for desulfurization of exhaust gas. Fly ash also includes heavy metals such as lead, zinc and chromium because of exhaust gas including chlorine gas and sulfurous acid gas. In 1991, fly ash was prohibited being buried in the ground and obligated to melt in solid glass by law

Concept of plasma electrochemistry

Electron in transferred plasma has higher kinetic energy than that in metal electrode of aqueous solution. The electrons are accelerated under electric field near the surface of molten slag and react with cations in the slag. When ionic material is heated by thermal plasma, light electrons arrive faster than heavy ions at the surface of material and the surface is negatively charged. The charging is accelerated under electric field by transferred plasma. Electric current through molten ionic material is carried by mobile ions. For example, in CaO-SiO_2-Al_2O_3 molten silicate slag, calcium ion is the most mobile ion of the other cations and oxygen anion, that is, the transference number of calcium ion is almost unity. At the surface of molten silicate, the most reactive ions, such as lead ion or zinc ion, are reduced by electron in plasma. Without lead ion or zinc ion in molten silicate, SiO_2 will be reduced to be

Table I
The composition of incineration ash and fly ash

elements	incineration ash		flying ash	
	cooled by water	cooled by air	cooled by water	cooled by air
SiO_2 %	36.1~57.2	35~49.4	30.5~35.4	19~48.4
Al_2O_3 %	15.3~26.2	16.2~26.8	18.3~18.7	7.3~18.4
CaO %	10.4~32.49	13.1~22	27.1~37.5	27.7~41.8
Fe_2O_3 %	0.71~10.2	<0.01~13	0.37~5.41	0.61~10.4
MgO %	1.3~5.22	3.07~4.5	4.37~5.5	1.99~5.5
Na_2O %	2.66~7.8	2.9~7.13	0.38~3.74	0.27~3.3
K_2O %	0.57~1.7	0.48~2.8	0.12~1.7	0.14~1.5
Cu %	0.02~0.09	<0.01~1.4	0.02~0.16	<0.01~0.03
Pb %	<0.01~0.06	0.0042~0.022	0.0008~0.004	0.0005~0.003
Zn %	0.01~0.67	<0.01~0.15	0.04~0.15	0.01~0.55
Cl %	0.03~1.1	<0.1~0.4	0.002~0.64	0.15~8.6
小計 %	72.03~98.8	88.78~99.4	93.46~95.48	87.62~95.75
Cd mg/kg	<0.005~5	<5	<0.4	<0.001~5.51
As mg/kg	<0.5~10	<0.05~3.4	<0.5	<0.001~1.45
Hg mg/kg	<0.005~0.5	<0.01~0.072	<0.01	<0.01~0.43

SiO gas. On the other hand, as the electron polarizability of oxygen ion in molten silicate increases with increasing temperature, electron at the surface of molten silicate is easy to emit into plasma. From the analogy of electrochemical reactions in aqueous solutions, when the electric potential at the surface of molten silicate is fixed, the kind of redox reactions could be controlled.

When the surface is negatively charged by electron and ion is drawn to the surface under electric potential gradient. The layer of electric potential gradient is called as sheath. The fluxes of electron and ion become to be equal and then the potential at surface becomes constant. The potential can be described as the floating potential against the plasma potential;

$$\Phi_F = (k_B T_e / e)\ln(v_e / v_i) = (k_B T_e / 2e)\ln(m_i T_e / m_e T_i) \quad [1]$$

where T is temperature, v is velocity and m is mass. The subscriptions of e and i mean electron and ion, respectively. kB is Boltzman s constant and e is unit charge. When electric field is applied through the surface of molten silicate, the velocity of electron increases and the potential at the surface deviates from the floating potential. The potential difference, Δφ, is the driving force to promote the electrochemical reactions. The net flux of electron through sheath can be described as;

$$J_e = (n_e v_e / 4)\exp(-e|\Delta\varphi|k_B T_e) \quad [2]$$

In the present works, it is clear that the kind of electrochemical reactions takes place between molten ionic melt and transferred plasma.

Reduction of silver ions in molten salts

Ito *et al.*[1] studied the reduction of nickel ion in LiCl-KCl eutectic melt including 0.10–1.50mole% $NiCl_2$ by transferred argon plasma at 673–823K and made nickel powder. They used the plasma and reduced silver ion in the same solvent including AgCl. Then they produced silver powder.

Tsuji and Nagata[2,3] reduced silver ion in 54mole%$NaNO_3$-46mole%KNO_3 eutectic melt including 0.01mole%AgNO3 by transferred argon plasma at 673K and produced silver powder. The melt in a silica crucible was heated using a resistance furnace. The plasma electrode was tungsten rod as cathode and silver rod was dipped in the molten salt as anode. Electric current through the melt is curried by sodium ion and potassium ion. After passing electric current, silver particles are dispersed near the surface of molten salt and are collected to be weighed. The anode electrode of silver rod was also weighed to determine the weight decrease by electrolysis. Table II shows the results that the weight of silver anode rod decreases, while the weight of silver particles precipitated near the surface of melt increased by 2 to 6 mass% more than the weight decrease of anode. The electrode reactions are described as;

Table II
The amounts of silver precipitated as particles by plasma and dissolved at anode

Run no.	Preciptated silver by plasma (g)	Dissolved silver at anode (g)
1	8.12	8.13
2	3.6	3.39
3	1.9	1.87

$$\begin{aligned} &Cathode:\ Ag^{+}(melt) + e(plasma) \\ &Ag(particles\ dispersed\ in\ melt) \end{aligned} \quad [3]$$

$$Anode:\ Ag(silver\ rod)\ Ag^{+}(melt)\ + \mathrm{e}(silver\ rod) \quad [4]$$

Vaporization of SiO gas from FeO-SiO_2 melts

Matsumaru and Nagata[4] have applied transferred argon plasma to FeO-more than 30mole%SiO_2 melt which has over 90% of ionic conduction. The spot with about 10mm diameter on the surface of melt under transferred Argon plasma was heated at 1800 to 1830K. The electric conductivity of this melt is over $0.1\Omega^{-1}cm^{-1}$ and transfer plasma ignites. Figure 1 shows the melt under the plasma. There is a cavity at the spot of plasma and strong convection is observed on the surface. The vaporized sample oxides were analyzed to determine the ratio of silicon to iron. Figure 2 shows the ratio as a function of SiO2 content in the melt. The solid lines in the figure are the ratios at various temperatures estimated thermodynamically and kinetically using vapor pressures and diffusion coefficients of elements near the melt surface. The ratio of silicon to iron is higher than the estimated

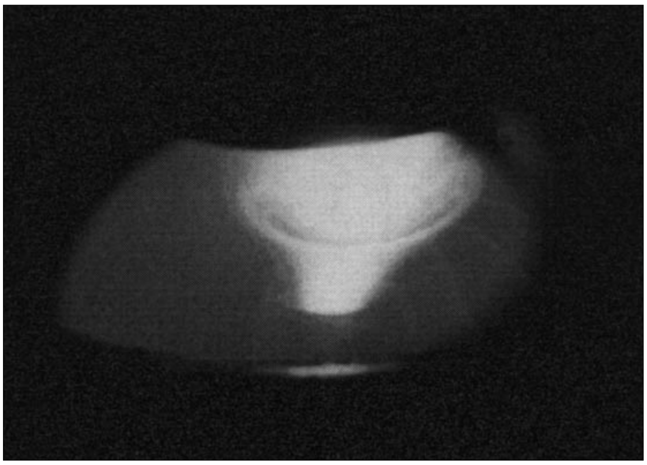

Figure 1. Melt under transferred argon plasma

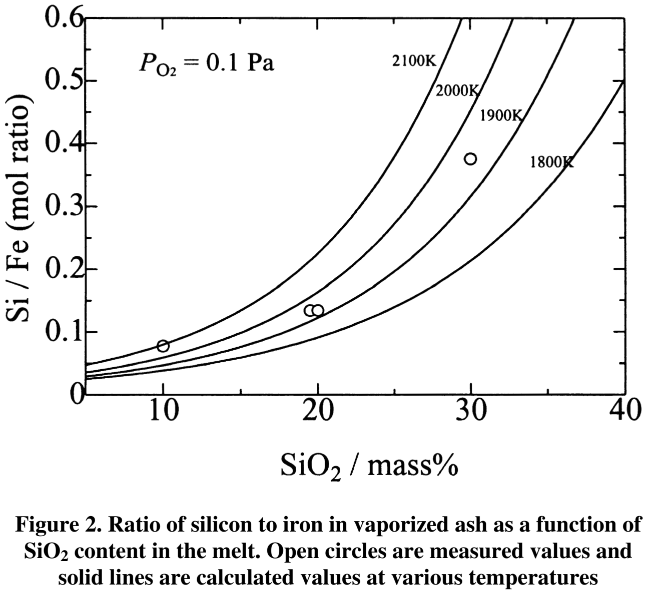

Figure 2. Ratio of silicon to iron in vaporized ash as a function of SiO_2 content in the melt. Open circles are measured values and solid lines are calculated values at various temperatures

value at 1800K. This means that SiO gas was accelerated to vaporize by transferred argon plasma. Electric current through the melt is carried by Fe^{3+} and Fe^{2+} ions and the electrode reactions are considered as following;

$$Cathode:\ SiO_2(melt)\ + 2e(plasma)\ SiO(g) + O^{2-} \quad [5]$$

$$Anode:\ Fe^{2+}(melt)\ Fe^{3+}(melt) + e(anode) \quad [6]$$

Vaporization of SiO gas from Na_2O-SiO_2 molten slag

25mole%Na_2O-75mole%SiO_2 molten slag is an ionic conductor of sodium ion. The melting point is 1072K and the electric conductivity is about $0.1\Omega^{-1}cm^{-1}$. The slag was set in a alumina crucible which had an iron plate as anode at the bottom. The slag was heated to melt at about 1173K by a resistance furnace, as shown in Figure 3. When transferred argon plasma was applied to the molten slag, the plasma flame overspreads the surface of slag. The constant electric current between 10 and 1000mA was passed through the molten slag during 2 to 30 minutes. After passing electric current, the penetration curve of iron oxide in slag near the anode electrode was detected. Thus, the iron anode was oxidized and the iron ion of Fe^{2+} diffused into the slag. The amount of iron ion in the slag exactly agreed with that estimated from the quantity of electricity according to the Faraday's law. The anode reaction is described as

$$Anode:\ Fe(anode)\ Fe^{2+}(slag) + 2e(anode) \quad [7]$$

The electric current in the slag is carried by sodium ion because of the transference number of sodium ion is unity.

The content of Na_2O in the slag increased and that of SiO_2 decreased. The thermodynamic calculations show that the equilibrium vapor pressure of Na gas is about $1x10^{-5}$ atm and that of SiO gas is about $1x10^{-10}$ atm at 1173K. The former is 10 times larger than the later. Thus, if these vaporizations take place according to the vapor pressures, the content of Na_2O could decrease and that of SiO_2 could increase. The vapor was condensed on the upper plate of furnace. The condensed powder was white and composed of sodium and silicon oxides. The analysis by ICP-AES showed Na was about 5% and Si 95%. The composition change of slag shows that SiO gas was electrochemically produced by the reaction of SiO_2 in slag with electron in plasma at the surface of slag. Then, the cathode reaction can be described as;

$$Cathode:\ SiO_2(slag)\ + 2e(plasma)\ SiO_2(gas) + O^{2-}(slag) \quad [8]$$

Figure 4 shows the relations between the quantity of electricity passed through slag and the amounts of anodic and cathodic reactions, respectively. The amount of anodic reaction follows the Faraday s law but that of cathodic reaction does not follow the law apparently. The amount of vaporized SiO gas was always more than 10 times larger than that estimated from the quantity of electricity.

Discussions

The above three cases show that the electrochemical reactions take place between transferred argon plasma and ionic melts at the surfaces of melts. The anodic reactions were the oxidation of silver, the oxidation of Fe^{2+} in slag and the oxidation of iron at the interface between slag and metal. The cathodic reactions by plasma were the reduction of Ag^+ to produce silver particles and the reduction of SiO_2 to vaporize SiO gas.

In the case of the reduction of silver ion, the amount of precipitated silver particles as cathodic reaction was 2 to 6% over that of dissolved silver as anodic reaction. As the anodic reaction follows the Faraday's law, the cathodic reaction does not follow the law apparently. In order to keep electroneutrality, the following reaction could take place on the surface;

$$Cl^- + Ar^+\ 1/2\,Cl_2 + Ar \quad [9]$$

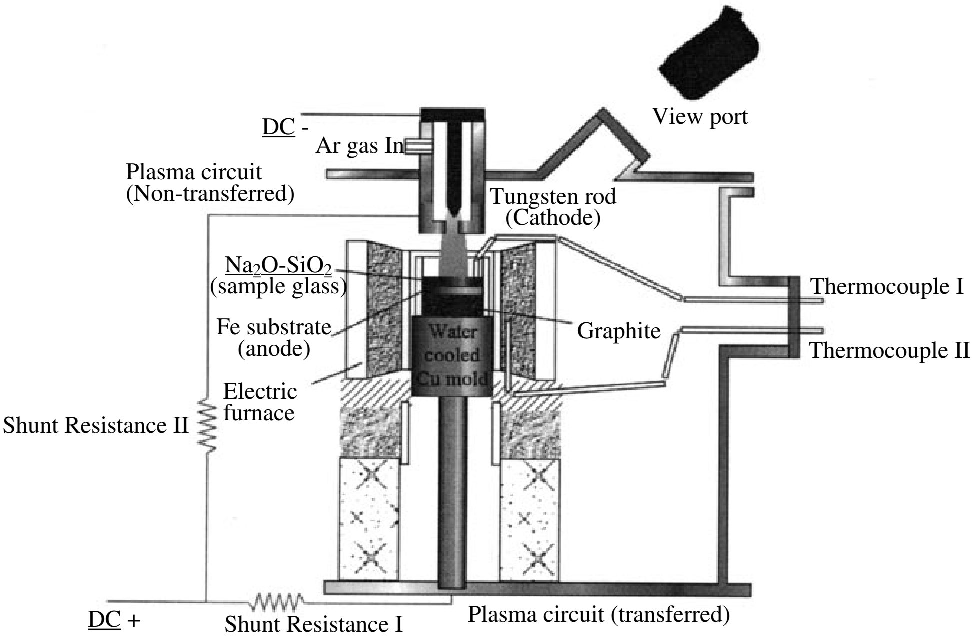

Figure 3. Transferred argon plasma furnace including a resistance furnace for melting slag

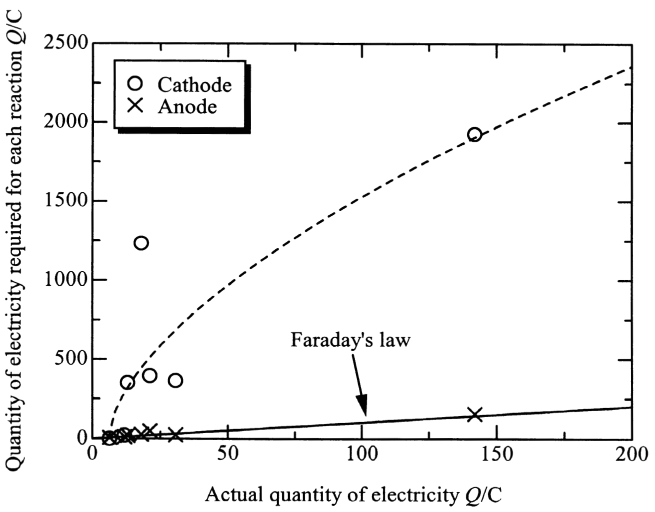

Figure 4. The comparison of actual quantity of electricity with that required for each reaction

or

$$NO_3^- + Ar^+ \; NO_2 + Ar + 1/2O_2 \qquad [10]$$

In the case of the reaction of SiO_2 to evaporate SiO gas for Na_2O-SiO_2 slag, the current efficiency of cathodic reaction was apparently over unity. This means that the cathodic reaction is not apparently according to the Faraday's law. The density of electron in plasma is larger than that in electric current and the electroneutrality is kept by Ar^+ ions in plasma. Electrons in plasma transfer to the surface of ionic melt under electric field and discharge cations in the melt. Electric current in ionic melt is carried by the most mobile ion of Na+. Because the surface of ionic melt is strongly charged negative with excess electron, Ar^+ in plasma is induced to the surface and oxygen ion in the melt is released from the surface to plasma. In order to keep electroneutrality, the following reaction could take place on the surface;

$$O^{2-} + 2Ar^+ \; 1/2O_2 + 2Ar \qquad [11]$$

Conclusions

Transferred argon plasma electrochemically reacts with ionic melts. Silver particles were produced by the reduction of silver ions in 54mole%$NaNO_3$-46mole%KNO_3 eutectic melt. SiO_2 in FeO-SiO_2 and Na_2O-SiO_2 melts was reduced to SiO gas. The amount of precipitated silver particles was 2 to 6% more than that of dissolved silver at the anode of silver rod. The ratio of silicon to iron in FeO-SiO_2 slag was higher than the estimated value. The amount of vaporized SiO gas from Na_2O-SiO2 melt was always more than 10 times larger than that estimated from the quantity of electricity. These phenomena indicate that the cathodic reactions are not apparently according to the Faraday's law. In order to keep electroneutrality, anion at the surface could emit and react with Ar+ in plasma.

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