Ionic Behavior of Oxygen in Slag

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ABSTRACT

As an endeavor to clarify the fundamental properties of slags, structural aspect of slag was approached. Binding states of oxygens were investigated using X-ray photoelectron spectroscopy (XPS) which allowed to measure the contents of four kinds of oxygen (free, non-bridging , bridging and associated oxygen) in the slag systems, $CaO-SiO_2$ and $CaO-AlO_{1.5}$ melts.

Experimental results indicate that the dissociation ratio of CaO is a function of slag composition and the ratio of CaO in $CaO-AlO_{1.5}$ is estimated to be smaller than in $CaO-SiO_2$ melt at the same CaO content at 1600 . For a polymerization index of slags $\dfrac{X_{O^0}}{X_{O^-}^2}$ or $\dfrac{1}{X_{O^{2-}}}$ may be considered.

INTRODUCTION

Traditionally, process metallurgists have studied macroscopic properties of slags, such as activities of components and viscosities, and have interpreted them in terms of the "basic", "acidic" or "amphoteric" oxide components of the slags. More recent investigations indicated that the slags have characteristics of ionic melts. Although the structure of slags is crucial to

the properties of slag, the reported results are rather scarce.

Oxygen must be one of the most important elements in slags. The concept of free oxygen in a slag was proposed by Fincham and Richardson [1] in order to explain the desulphurization phenomena in iron- and steelmaking. After the first theoretical estimation of free oxygen content by Toop and Samis [2], various approaches based on polymer theories [3~5] and statistical models [6] were reported; most of the reports being theoretical modeling approaches.

In this study, binding states of oxygens in slags were investigated by experimental measuring, and sulfide capacity was discussed by using experimental results.

EXPERIMENTS

Slags were prepared from reagent grade SiO_2, $AlO_{1.5}$ and CaO. The reagents were dried at 400 and CaO was calcined at 1000 . Accurately weighed mixtures were melted in platinum crucible at 1600 in an electric furnace. After being held for 12 hours, they were quenched on steel plate in contact with liquid nitrogen. The glass samples were polished using SiC powder and diamond suspension. Samples were kept in well-dried desiccators, before they were analyzed by XPS (X-ray Photoelectron Spectroscopy) spectrum. It was assumed that the binding states of oxygen are maintained by the quenching.

The XPS spectra of O_{1s} were measured by spectrometer of PHI-5700 type, using Al-mono X-ray. The spectrometer was operated under vacuum (~2.8×10^{-10} Torr range). In order to remove the surface contamination, all measurements were performed after lightly etching the surface of the specimen by Ar ion sputtering for 1 minute. The Au_{4f} and C_{1s} spectrum was used as a standard.

DATA ANAYSIS

All spectra were calibrated by gold and carbon. Au_{4f} as standard peak is shown in Figure 1. Spectrum data were deconvoluted by use of Gaussian Area Function as shown in Eq. (1). The binding states of oxygen in slag were obtained quantitatively by method of Toop and Samis [2]. Measured concentrations of oxygens-bridging oxygen, non-bridging oxygen and sum of

free oxygen and associated oxygen in CaO were used to evaluate the dissociation ratio of basic oxide.

$$y = \frac{a_0}{\sqrt{2\boldsymbol{p}}\, a_2} \exp\left\{ -\frac{1}{2}\left(\frac{x - a_1}{a_2} \right)^2 \right\} \tag{1}$$

where y and x is intensity and binding energy, respectively, a_0 is area of peak, a_1 center and a_2 FWHM(Full Width Half Maximum).

CaO-SiO$_2$ Binary Slag

Oxygens in CaO-SiO$_2$ melt have the following equilibrium reaction:

$$2O^- = O^0 + O^{2-} \tag{2}$$

with equilibrium constant $k_{(2)}$

$$k_{(2)} = \frac{\left(O^{2-}\right)\left(O^0\right)}{\left(O^-\right)^2} \tag{3}$$

where $\left(O^-\right)$, $\left(O^0\right)$ and $\left(O^{2-}\right)$ are the equilibrium number of moles of non-bridging oxygen, bridging oxygen and free oxygen ions per mole of slag.

Let the dissociation ratio of CaO be $x\left(0 < x \le 1\right)$, for 1 mole of melt it may be shown that, X_{SiO_2} moles of silica and $x\left(1 - X_{SiO_2}\right)$ moles of O^{2-} ions combine to form the anions of the melt plus free oxygen ions. A charge balance can be expressed as follows:

$$2\left(O^0\right) + \left(O^-\right) = 4X_{SiO_2} \tag{4}$$

Material balance considerations give the number of free oxygen ions per mole of slag,

$$\left(O^{2-}\right) = x\left(1 - X_{SiO_2}\right) - \frac{1}{2}\left(O^-\right) = \frac{1}{2}\left\{ 2x\left(1 - X_{SiO_2}\right) - \left(O^-\right) \right\} \tag{5}$$

Eq. (4) and Eq. (5) may be inserted into Eq. (3) to obtain an equation for (O^-) in terms of $k_{(2)}$ and X_{SiO_2},

$$4k_{(2)} = \frac{\{4X_{SiO_2} - (O^-)\}\{2x(1 - X_{SiO_2}) - (O^-)\}}{(O^-)} \tag{6}$$

The solution of Eq. (6) regarding (O⁻) may be expressed as follows:

$$(O^-) = \frac{(2X_{SiO_2} + x - xX_{SiO_2}) - \sqrt{(2X_{SiO_2} + x - xX_{SiO_2})^2 - (1 - 4k)8xX_{SiO_2}(1 - X_{SiO_2})}}{(1 - 4k_{(2)})} \tag{7}$$

The content of oxygen associated to CaO may be obtained as follows:

$$(O^{ass.}) = (1 - x)(1 - X_{SiO_2}) \tag{8}$$

The contents of four different types of oxygens with variation of dissociation ratio (x) of CaO can be calculated by Eq. (4), Eq. (5), Eq. (7) and Eq. (8).

On the other hand, dissociation ratio of CaO in CaO-SiO$_2$ at 1600 can be estimated from the measured values of $\dfrac{O^-}{O^0}$ and material balance for oxygen.

The equilibrium constant ($k_{(2)}$) for CaO-SiO$_2$ 0.0017 at 1600 is taken from Toop and Samis [2].

CaO-AlO$_{1.5}$ Binary Slag

The similar treatment can be applied for the system of CaO-AlO$_{1.5}$ binary system, a mixture of CaO and trivalent oxide.

Charge balance: $(O^0) = \dfrac{1}{2}\{3X_{AlO_{1.5}} - (O^-)\}$ (9)

Material balance: $(O^{2-}) = x(1 - X_{AlO_{1.5}}) - \dfrac{1}{2}(O^-)$ (10)

Eq. (3), Eq. (9) and Eq. (10) combine to make an equation for $\left(O^-\right)$ in terms of $k_{(2)}$ and $X_{AlO_{1.5}}$ as follows:

$$\left(O^-\right)=\frac{\left(\frac{3}{2}X_{AlO_{1.5}}+x-xX_{AlO_{1.5}}\right)-\sqrt{\left(\frac{3}{2}X_{AlO_{1.5}}+x-xX_{AlO_{1.5}}\right)^2-(1-4k)6xX_{AlO_{1.5}}\left(1-N_{AlO_{1.5}}\right)}}{(1-4k_2)} \qquad (11)$$

The content of oxygen associated to CaO in CaO-AlO$_{1.5}$ may be obtained as follows:

$$\left(O^{ass.}\right)=(1-x)\left(1-X_{AlO_{1.5}}\right) \qquad (12)$$

The equilibrium constant $(k_{(2)})$ for CaO-AlO$_{1.5}$ is estimated 0.15 at 1600 based upon thermodynamic data.

RESULTS AND DISCUSSION

O_{1s} binding energy of SiO_2 is shown in Figure 2. The binding energy, 532.12 eV coincides with the recommended value, 532.4 eV [7]. The process of analysis is also shown. The process was composed with smoothing, baseline-subtraction and deconvolution, and it was applied the entire spectrum measured. The deconvoluted peaks of CaO-0.648SiO$_2$ are shown in Figure 3. The amounts of oxygens can be obtained from the areas of peaks.

The contents of four kinds of oxygens -free oxygen, bridging oxygen, non-bridging oxygen and associated oxygen in CaO were shown in Figure 4 when the dissociation ratio of CaO is 0.97. It shows that the deviation from calculated lines in acidic slag is larger than that in basic slag. This phenomenon can be considered the dissociation ratio change with the variation of slag composition. The dissociation ratios of CaO in each composition are estimated by trial and error method. The same method is introduced to CaO-AlO1.5 slag, and the results are shown in Figure 5. It indicates that the ratio of CaO at 48mole%SiO$_2$ is 0.97(Figure 4). The same method was introduced to other composition in CaO-SiO$_2$ and CaO-AlO$_{1.5}$. The dissociation behaviors of CaO in CaO-SiO$_2$ and CaO-AlO$_{1.5}$ are shown in Figure 5. As shown in Figure 5 the dissociation ratio of CaO is not constant, but has dependence on slag composition. It is observed that dissociation of CaO changes markedly between 55mole% and

60mole% of SiO_2 for CaO-SiO_2 system. It means that there are different regions of solution behavior having boundary between 55mole% and 60mole% of SiO_2. The similar phenomenon is observed in viscosity change shown in Figure 6. The viscosity of CaO-SiO_2 at 1600 [8] seems to have two mechanisms (Region and Region) with the boundary at X_{SiO_2} about 0.57. These phenomena indirectly indicate that not only free oxygen but also non-bridging oxygen and bridging oxygen affect the properties of slag as a measure of slag structure. The dependence of viscosity on $\dfrac{X_{O^0}}{X_{O^-}^2}\left(\propto \dfrac{1}{X_{O^{2-}}}\right)$ is shown in Figure 7. The linear relationship between the viscosity and $\dfrac{X_{O^0}}{X_{O^-}^2}$ indicates that $\dfrac{X_{O^0}}{X_{O^-}^2}$ or $\dfrac{1}{X_{O^{2-}}}$ may be an index of degree of polymerization in slags.

Sulfide capacity is a function of the activity of oxygen ion as indicated in the reaction:

$$\frac{1}{2}S_2 + O^{2-} = S^{2-} + \frac{1}{2}O_2 \tag{13}$$

Based upon the Eq. (13), the sulfide capacity is defined as Eq. (14) and Eq. (15).

$$C_{S^{2-}} = \left(\% S^{2-}\right)\cdot\left(\frac{P_{O_2}}{P_{S_2}}\right)^{\frac{1}{2}} = K_{(13)}\frac{g_{O^{2-}}}{f_{S^{2-}}}X_{O^{2-}} \tag{14}$$

$$\log C_{S^{2-}} = \log\left\{K_{(13)}\frac{g_{O^{2-}}}{f_{S^{2-}}}\right\} + \log X_{O^{2-}} \tag{15}$$

Sulfide capacities of CaO-SiO_2 and CaO-$AlO_{1.5}$ [9] are shown in Figure 8 with respect to the mole fraction of free oxygen ion. Sulfide capacity of CaO-$AlO_{1.5}$ is larger than that of CaO-SiO_2, probably due to difference in free oxygen contents, which is dependent of the dissociation ratio of CaO with different kinds of acidic oxide.

SUMMARY

Ionic behavior of oxygen in CaO-SiO_2 and CaO-$AlO_{1.5}$ melts at 1600 was investigated. The contents of four kinds of oxygen (free oxygen, non-bridging oxygen, bridging oxygen and

associated oxygen) in liquid slags were measured quantitatively. Based upon the results it may be concluded that:

In CaO-SiO$_2$ melt,

- there are two regions(I and II) where ionic behavior of oxygen is different from each other. Boundary is about CaO-57mole%SiO$_2$.

- $\dfrac{X_{O^0}}{X_{O^-}^2}$ or $\dfrac{1}{X_{O^{2-}}}$ is introduced as a polymerization index of slags

- sulfide capacity of CaO-SiO$_2$ in more basic region   – was analyzed with free oxygen

In CaO-AlO$_{1.5}$ melt,

- dissociation ratio of CaO is smaller than in CaO-SiO$_2$ melt at the same CaO content.

- sulfide capacity is larger than that of CaO-SiO$_2$, because free oxygen content is more than in CaO-SiO$_2$ melt in liquid region.

ACKNOWLEDGEMENTS

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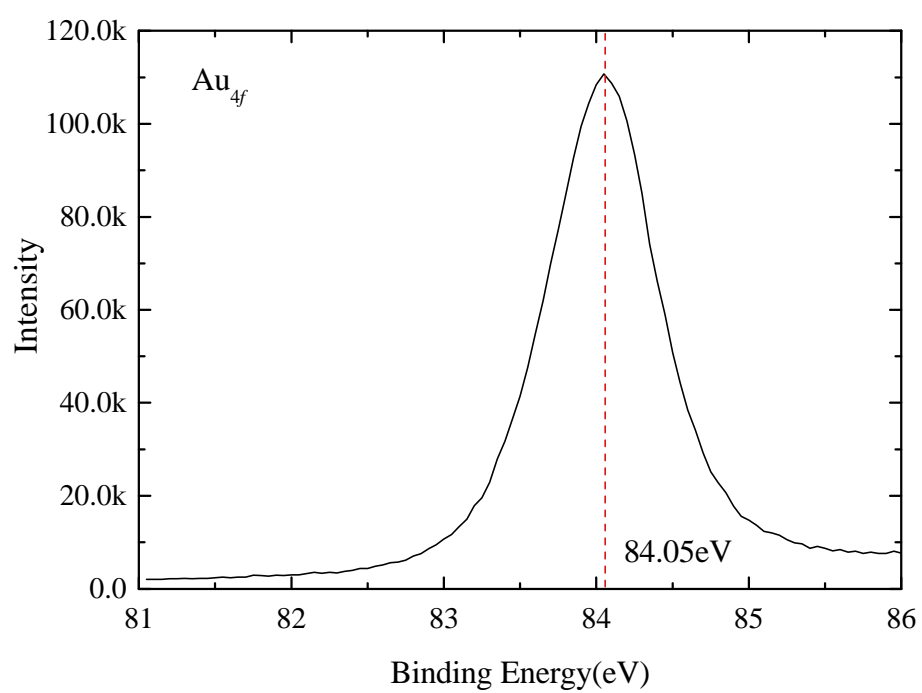[9] I.P. Rachev, F. Tsukihashi and N. Sano, Matall. Trans., 22B (1991) 333-338

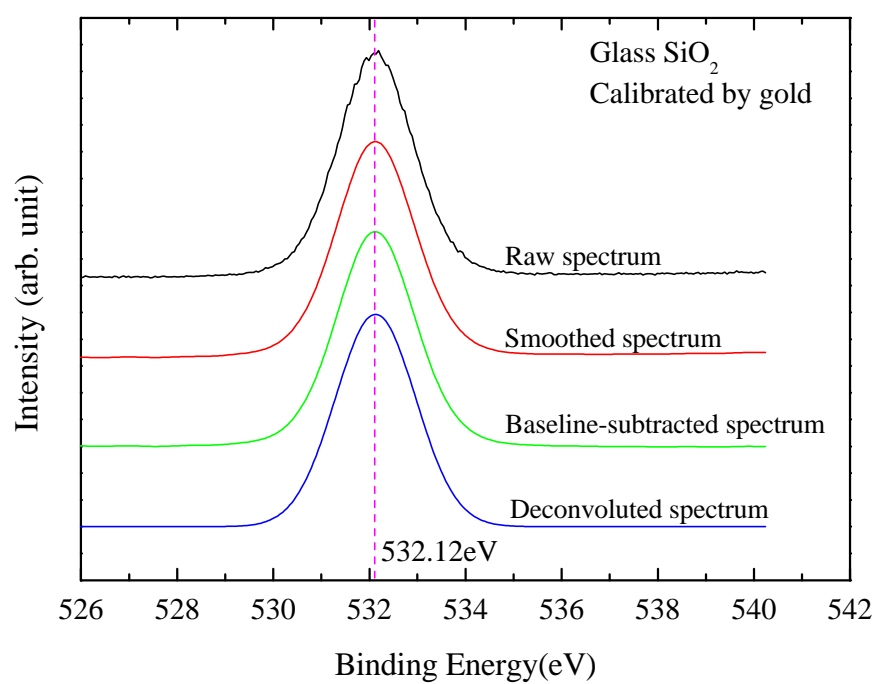Figure 1: Binding energy of Au$_{4f}$ as standard peak for calibration

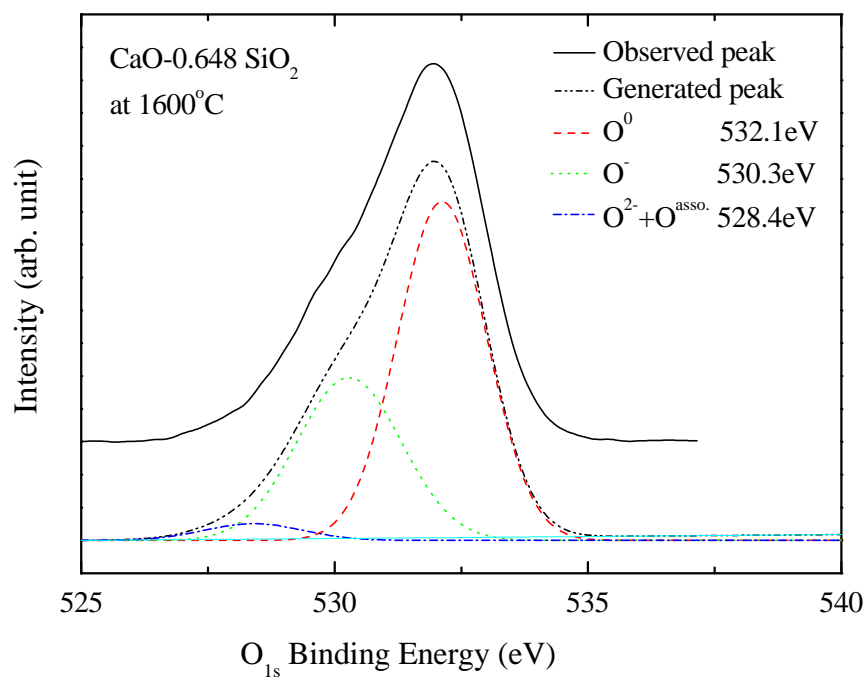Figure 2: Binding energy of oxygen in glass-SiO$_2$ showing the process of data analysis.

Figure 3: Deconvoluted O_{1s} binding energy of CaO-0.648SiO$_2$.
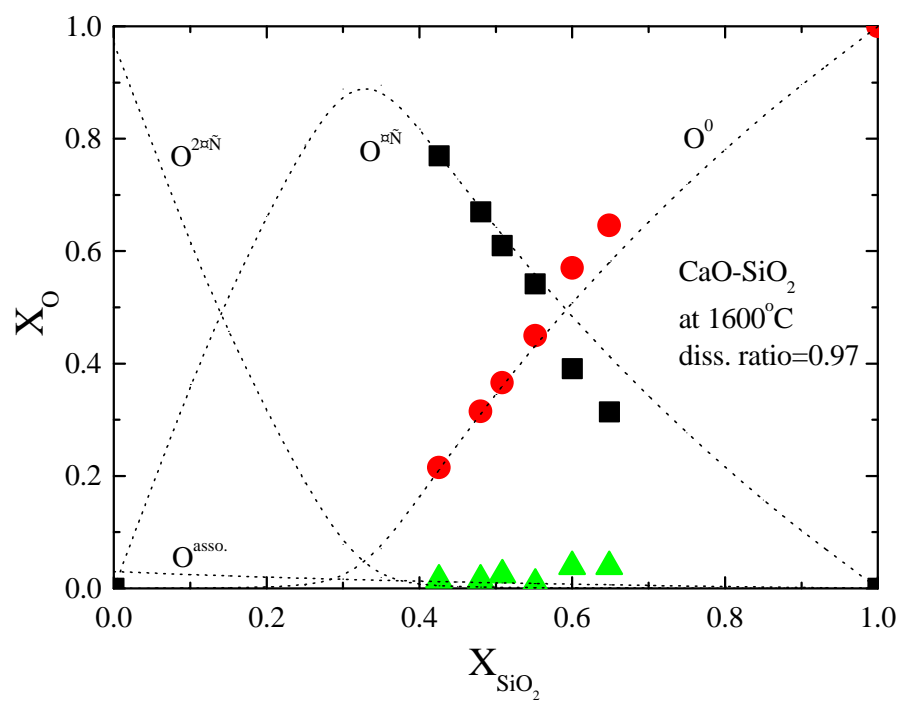
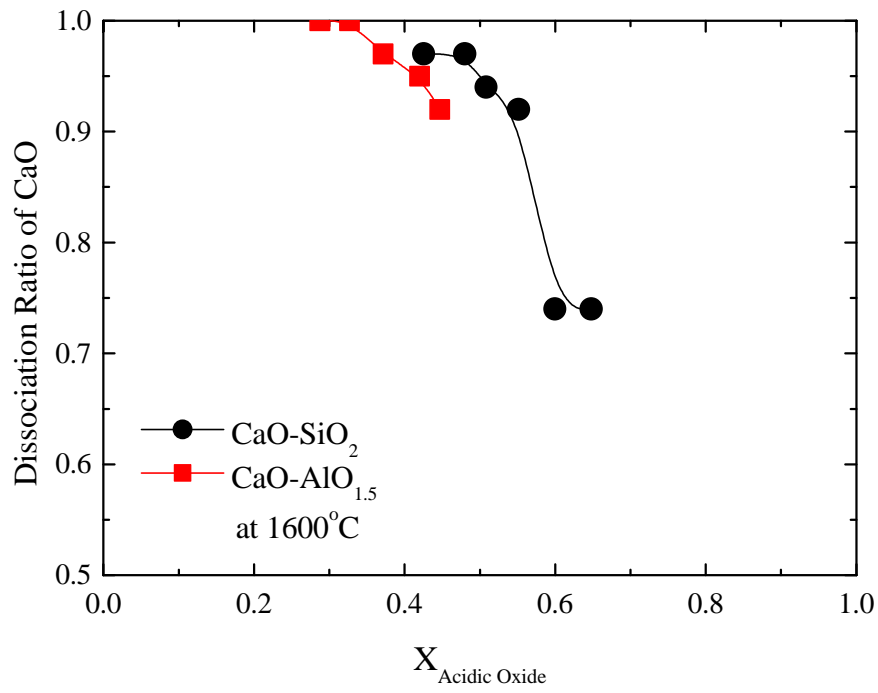Figure 4: Oxygens in CaO-SiO$_2$ at 1600 when the dissociation ratio of CaO is 0.97.

Figure 5: Dissociation ratio of CaO with variation of mole fraction of acidic oxides in CaO-SiO$_2$ and CaO-AlO$_{1.5}$ slag at 1600 .
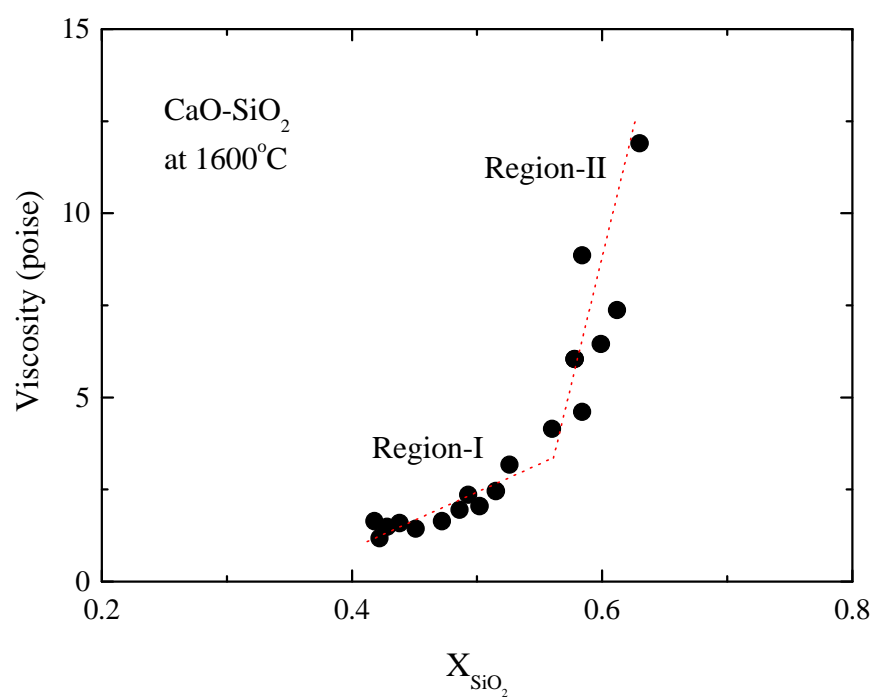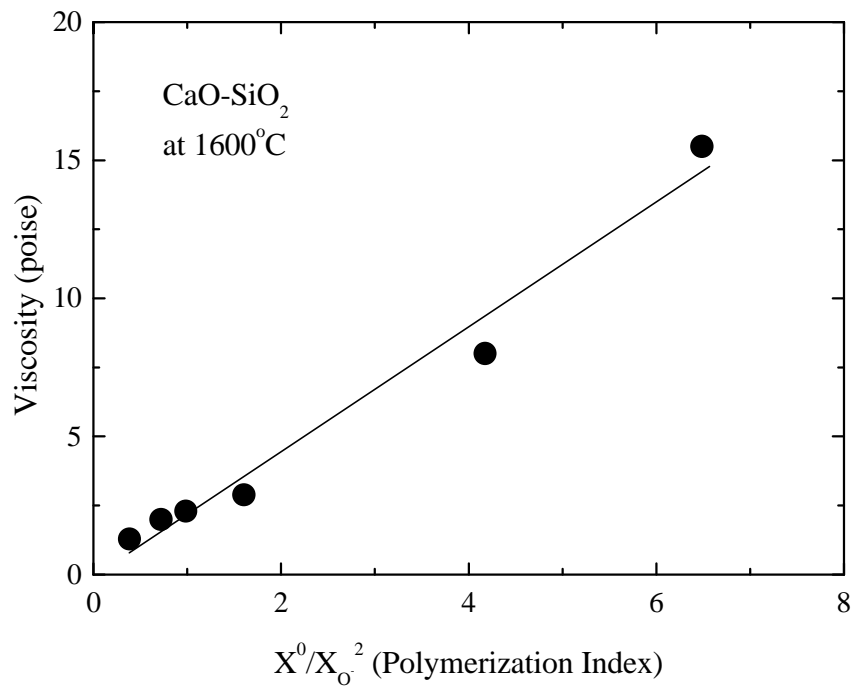
Figure 6: Viscosity of CaO-SiO$_2$ melts at 1600

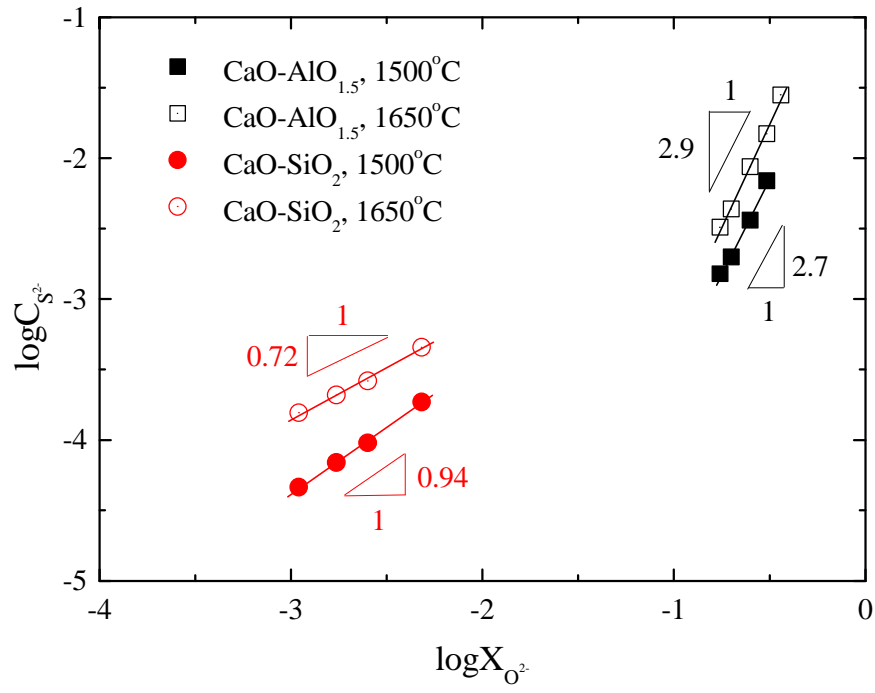Figure 7: Relationship between viscosity and $\dfrac{X_{O^0}}{X_{O^-}^2}$ in CaO-SiO2 at 1600 .

Figure 8: Sulfide capacities of slags with respect to $\log X_{O^{2-}}$.