Effect of CaO, Al₂O₃, MgO and ZnO on the Activity of PbO in the Molten PbO–SiO₂ System*

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The e.m.f. measurements were carried out in the temperature range of 1173~1323 K by means of the following galvanic cells employing solid electrolytes:

\[ \text{Ni.NiO(s)/ZrO₂+CaO/Pb.PbO–SiO₂–MeO(1)} \]

where MeO is CaO, Al₂O₃, MgO and ZnO.

From these experimental results, it was found that the activity of PbO in the molten PbO–SiO₂ system was increased remarkably by the addition of CaO or MgO, considerably by ZnO and slightly by Al₂O₃.

These experimental results were found to be in good agreement with the results of Richardson and Pillay on the PbO–SiO₂–CaO, PbO–SiO₂–MgO and PbO–SiO₂–ZnO systems.

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I. Introduction

The present study has been undertaken for determination of the activities of components in the molten ternary silicates. Many investigators have determined the activity of PbO in the molten PbO–SiO₂ system by the e.m.f. method using stabilized zirconia as a solid electrolyte.

In our study, e.m.f. measurements were carried out for the PbO–SiO₂ binary system, followed by those on the PbO–SiO₂–CaO (Al₂O₃, MgO and ZnO) ternary system, and the effect of these metallic oxides on the activity of PbO in the molten PbO–SiO₂ system was investigated.

Such ternary systems are the basic slag systems in the field of lead smelting, but no thermodynamic studies on such systems have been reported except only the paper of Richardson and Pillay. Their investigation was based on the experiment that the oxygen content in liquid lead in equilibrium with the molten silicate via the gaseous atmosphere was determined.

II. Experimental Principle and Methods

In the present investigation, e.m.f. measurements were carried out in the temperature range of 1173~1323 K by means of the following cell (I):

\[ \text{Ni.NiO(s)/ZrO₂+CaO/Pb.PbO–SiO₂–MeO(1)} \]

where MeO is CaO, Al₂O₃, MgO and ZnO.

As a reference electrode, Ni·NiO electrode was used instead of Pb·PbO which had been used in the previous study by the one of authors because the vapor pressure of PbO is considerably high and the corrosion of crucible and lead wire by PbO is remarkable and the e.m.f. measurements for many hours is very difficult. Based on the equilibrium e.m.f. values, the activity of PbO in the molten silicate was calculated according to the following eq. (1):

\[ \log a_{\text{PbO}} = \frac{1}{4.575T} (2EF + \Delta G_{\text{NIO}} - \Delta G_{\text{PbO}}) \]  (1)

where \( a_{\text{PbO}} \) is the activity of PbO,

\( T \) is the temperature in degree K,

\( F \) is Faraday's constant,

\( E \) is e.m.f. of the cell,
\( \Delta G_{\text{NiO}}^0 \) and \( \Delta G_{\text{PbO}}^0 \) are the standard formation free energy of NiO and PbO. The experimental apparatus and cell used in the present study are schematically shown in Fig. 1(a) and (b).

The furnace used was the silicon carbide resistance type and its temperature was controlled automatically in the range \( \pm 1 \) K.

The crucible consisted of stabilized zirconia containing 11 mol\% CaO (19 mm OD, 16 mm ID and 38 mm depth) and was employed as a solid electrolyte.

Ni·NiO reference electrode was prepared by pressing an intimate mixture of Ni(99.5\% up) and NiO(chemical extra pure) powder under a load 3~4 t/cm\(^2\) and subsequently sintering its disk at 1473 K for 6 h in argon atmosphere.

Every silicate mixtures were made by the following procedure.

The mixtures of each powder of metallic oxides (chemical reagent grade) in the desired ratio were pressed to the form of a disk and its disk was charged in the cell.

The iron wire was used as a lead wire for the molten PbO-SiO\(_2\)-CaO and PbO-SiO\(_2\)-Al\(_2\)O\(_3\) systems and the iridium wire was used for PbO-SiO\(_2\)-MgO and PbO-SiO\(_2\)-ZnO systems. The iron lead wire could not be kept in direct contact with the molten silicate, but the iridium lead wire could be dipped directly in the liquid lead in the presence of the molten silicate. Therefore, the use of the iridium lead wire was more convenient than iron.

In both cases the lead wire was kept above the surface of the molten silicates except for the e.m.f. measurement and the steady e.m.f. could be measured for a longer time.

The iridium lead wire was held with a zirconia small plate which was used for stirring a molten electrode as shown in Fig. 1(b).

All materials used were charged into the cell as shown in Fig. 1 and kept for 2 h in vacuum at about 573 K to ensure dehydration.

Purified argon gas was introduced into the cell and the pressure was kept above atmospheric pressure.

The equilibrium e.m.f. was read after maintaining the cell at a constant temperature at the first measurement for 2 h, and the latter was kept at a constant temperature for 1 h.

The temperature change was made by an alternate increase and decrease.

### III. Experimental Results and Discussion

Before the experiments of the four ternary systems, several supplemental experiments were carried out on the PbO-SiO\(_2\) binary system and the following were confirmed.

1. Composition change in the molten silicates was less than 1\% during all e.m.f. measurements and its effect on the e.m.f. measurement was negligibly small.

2. The difference of lead wire for the molten silicates, iron and iridium, had not such a large effect on the e.m.f. measurement that the activity of PbO was in approximate agreement with each other except the high PbO composition range than \( N_{\text{PbO}} = 0.7 \) in
which the activity of PbO calculated from the e.m.f. measurements with the iridium lead wire was a little large than with iron lead wire.

1. PbO–SiO₂–CaO system

Since the relevant equilibrium phase diagram of this ternary system is not available, a preliminary experiment was carried out in order to determine the composition range of homogeneous liquid state at 1273 K. Based on the results of the preliminary experiment, the compositions of samples were selected as shown in Fig. 2.

The compositions of the samples selected were in two quasi-binary systems with SiO₂: CaO ratios of 4: 1 and 7: 3.

The galvanic cells consist of the NiNiO reference electrode and the Pb, PbO–SiO₂–CaO electrodes were constructed. The equilibrium e.m.f. of the cell were measured at several temperatures.

Figure 3 shows the e.m.f. for the quasi-binary system with the ratios of SiO₂/CaO = 4 and 7/3, respectively.

The e.m.f. plots against T were found to be nearly linear, and any irreversible reaction in the cell was confirmed to be negligibly small. From the values of e.m.f. at 1273 K, the activities of PbO were calculated and are shown in Fig. 4 as an isoactivity lines.

![Fig. 2](image1)

Fig. 2 The composition range of homogeneous liquid state in the PbO–SiO₂–CaO system at 1273 K. Digits indicate the number of samples.

![Fig. 3](image2)

Fig. 3 Relation between e.m.f. and temperature of the cell: NiNiNiO/ZrO₂+CaO/PbPbO–SiO₂–CaO,Fe Full and dot-dash lines show the e.m.f. for the quasi-binary system with the ratios of SiO₂/CaO = 4 and 7/3. Concentrations are in mole fractions.

![Fig. 4](image3)

Fig. 4 Iso-activity curves for PbO in PbO–SiO₂–CaO melts at 1273 K.

In this figure the result of Richardson and Pillay(2) is also shown with the present result.

The present result was nearly consistent with that of Richardson and Pillay, both of which showed that the activity of PbO was remarkably increased by the addition of CaO.

2. PbO–SiO₂–Al₂O₃ system

In order to investigate the effect of Al₂O₃ on the activity of PbO in the molten PbO–SiO₂ system, the e.m.f. measurements were carried out for the PbO–SiO₂–Al₂O₃ system according to the same procedure as that for the PbO–
SiO₂-CaO system. The compositions of samples are shown in Fig. 5.

The measured e.m.f. values were plotted as a function of temperature as shown in Fig. 6 for the samples of the three quasi-binary systems with SiO₂/Al₂O₃ = 4, 3/2 and 1.

The activities of PbO at 1273 K are shown in Fig. 7 as an isoactivity lines. From this figure it was found that the activity of PbO was slightly increased by the addition of Al₂O₃.

3. PbO-SiO₂-MgO system

The compositions of samples are shown in Fig. 8.

The measured e.m.f. were plotted as a function of temperature in Fig. 9 for the samples of the two quasi-binary systems with SiO₂/MgO = 4 and 3/2.

The activities of PbO at 1273 K are shown in Fig. 10 as an isoactivity lines. The result of Richardson and Pillay is shown in this figure. It was found that both results were in excellent agreement with each other and the activity of PbO was remarkably increased by the addition of MgO as was the case with CaO addition.

4. PbO-SiO₂-ZnO system

The compositions of samples are shown in Fig. 11.

The measured e.m.f. are plotted as a function of temperature in Fig. 12 for the samples of the three quasi-binary systems with SiO₂/ZnO = 4, 3/2 and 2/3, respectively.

The activity of PbO at 1273 K are shown in
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IV. Conclusion

Activities of PbO in the molten PbO–SiO₂–CaO, PbO–SiO₂–Al₂O₃, PbO–SiO₂–MgO and PbO–SiO₂–ZnO ternary systems at 1273 K were determined by e.m.f. measurements employing a solid electrolyte.

From the present experiments, the following conclusions were obtained.

1. The activity of PbO in the molten PbO–SiO₂ system increased remarkably by the addition of CaO.
2. It increased slightly by the addition of Al₂O₃.
3. It increased remarkably by the addition of MgO as in the case of CaO addition.
4. It increased considerably by the ad-
Fig. 12 Relation between e.m.f. and temperature of the cell:
Ni, Ni, NiO/ZrO₂ + CaO/Pb, PbO – SiO₂ – ZnO, Ir – Pt. Full, dot-dash and dashed lines show the e.m.f. for the quasi-binary system with the ratios of SiO₂/ZnO = 4, 3/2 and 2/3. Concentrations are in mole fractions.

Addition of ZnO and its extent was an intermediate level among the results of CaO, MgO and Al₂O₃ additions.

REFERENCES

Fig. 13 Iso-activity curves for PbO in PbO–SiO₂–ZnO melts at 1273 K.