Phase Diagram for the Pb-Cr-O system

Hiroko Miyagawa, *Masayuki Miyagawa,
Masahiro Susa and Kazuhiro Nagata

Department of Metallurgical Engineering
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152 Japan
Phone: +81-3-5734-3141
*SONY Corp.
Osaki, Shinagawa-ku, Tokyo 141 Japan
Phone: +81-3-3495-3892

ABSTRACT

The activity of PbO in Pb-Cr-O melts equilibrated with liquid Pb has been measured and the phase diagram for the Pb-Cr-O system has been determined partly. The activity of PbO was measured over the temperature range between 1173 and 1373 K by means of the emf method using MgO-stabilized ZrO_2 as a solid electrolyte. The activity of PbO showed negative deviation from Raoult's law in the mole fraction range of PbO lower than 0.8 and positive deviation in the higher concentration of PbO. The ratio of Cr^{2+}/Cr^{3+} increased with increasing the PbO concentration. This means that CrO acts as a base and Cr_2O_3 acts as an acid.

1. INTRODUCTION

The development of the smelting reduction technology is one of the most important projects, since it leads to the conservation of energy as well as the simplification of metallurgical processes. Some studies on the smelting reduction of chromite ores have concentrated on the optimization of the slag composition,[1,2] the application of plasma arc,[2] the use of coke[3,4,5] and so on.[6] It is also inevitable in practice to know the thermodynamic properties and the phase diagrams of slags for the smelting reduction of chromium ores.

Chromite($FeCr_2O_4$), Crocoite($PbCrO_4$) and Phoenicochroite($3PbO{\cdot}2Cr_2O_3$) are natural ores for chromium-making, the first being very well known. However, this study concentrates on the Pb-Cr-O system, since this system can also be involved in the smelting reduction process in the optimization of the slag composition.

Several studies have been carried out about the measurement of the activity of PbO in slags such as $PbO-SiO_2$[7,8,9,10] and $PbO-GeO_2$ systems.[11] However, there has been a few reports on the activity of constituent oxides in slags containing chromium.[12,13] On the other hand, with respect to the phase diagram for Pb-Cr-O system, the data available[14,15,16,17] are only those for the phase relation between PbO and CrO_3, and further data are required.

There is also considerable scientific interest in the measurement of the activity of PbO in Pb-Cr-O melts. It is generally said that the activity of an oxide is affected most strongly by another oxide having the most different basicity. In Pb-Cr-O melts, Pb exists as Pb^{2+}. In Contrast, Cr can be in the form of Cr^{2+}, Cr^{3+}, Cr^{4+}, Cr^{5+} and Cr^{6+}, which correspond to the oxides CrO, Cr_2O_3, CrO_2, Cr_2O_5 and CrO_3, respectively. These oxides have different basicities and affect thermodynamic properties of the whole system in the different way. Accordingly, it is very interesting to discuss factors affecting the activity of PbO in the melts from the viewpoint of the basicity.

Consequently, the aim of this study is to measure the activity of PbO in Pb-Cr-O melts equilibrated with liquid Pb using the emf method, and to give new data to the phase diagram for the Pb-Cr-O system by the determination of chemical compositions of the melts, since these are relevant to the smelting reduction process.

2. EXPERIMENTAL

2.1 Samples

Powders of reagent grade PbO and Cr_2O_3 were dried in mullite crucibles in air at 200℃ for 24 h. The reagents were weighed to the required compositions and mixed in an alumina mortar. The mole fraction of PbO ranged between 0.7 and 1. Grains of Pb of 99.9% purity were prepared to be equilibrated with the slag.

2.2 Determination of slag compositions equilibrated with liquid Pb

After weighing a PbO and Cr_2O_3 mixture and Pb grains, the Pb grains were put in the bottom of a crucible(13 mm in outer diameter × 9 mm in inner diameter × 50 mm in height) of 15 mol% MgO-stabilized ZrO_2 solid electrolyte, and then the mixture was placed on the Pb grains. Finally, the crucible was closed by an Al_2O_3 disc sealed by Al_2O_3 cement and water glass. A mullite pipe of 0.8 mm in inner diameter was set as a vent to keep atmospheric pressure in the crucible as shown in Fig.1(a). After assembling, the crucible was heated at 200℃ to remove water.

The crucible containing the sample was heated at 800℃ in a flow of Ar gas which was dried and deoxidized using sponge Ti at 900℃, and it was confirmed that the oxygen partial pressure was less than 10^{-15} atm by the oxygen sensor. The crucible was heated for 1 h to realize equilibrium between the Pb metal and the slag at temperatures between

1173 K and 1373 K. After equilibrium, the crucible was quenched to room temperature.

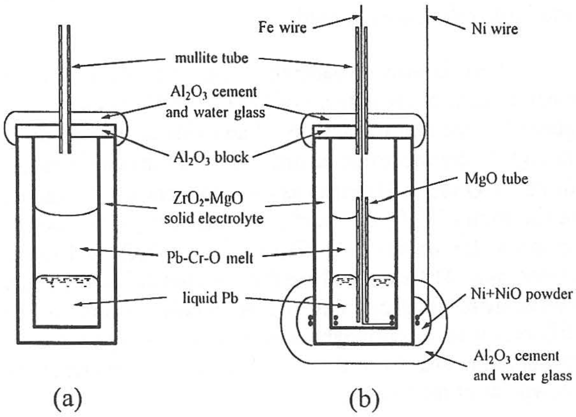

Fig.1 Schematic diagram of a cell for determining the slag compositions equilibrated with liquid Pb(a) and a Galvanic cell for activity measurements(b).

The sample was taken off from the solid electrolyte crucible, and the metal was separated from the slag. A little of slag stuck on the metal was removed by dipping in $20HClO_4+1H_3PO_4$ solution at 250℃ for 10 min. Weighing of the metal showed the decrease of masses of Pb, which was caused by the reaction of Pb with Cr_2O_3 in slag as the following reaction;

$$Pb + Cr_2O_3 \rightarrow PbO + 2CrO.$$

The cell was weighed continuously using a thermo-balance for 6 h in the temperature range between 1173 and 1373 K, resulting in no mass change. This indicates that the inside of the cell was a quasi-closed system.

Thus, the composition of $PbO-Cr_2O_3-CrO$ slags was determined from the mass change of Pb and the starting composition of $PbO-Cr_2O_3$ mixtures.

2.3 Activity measurements by a Galvanic cell

Fig.1(b) shows a schematic diagram of an assembled Galvanic cell as an oxygen concentration cell. The cell assembly was almost the same as that for the determination of slag compositions except for the electrodes of the cell. Fe lead wire as inner electrode was protected by a MgO tube in order to prevent the lead wire from reacting with the slag. Ni wire as outer electrode was covered with the mixture of Ni and NiO powder (1:1 in volume), which was sealed by Al_2O_3 cement and water glass. Accordingly, the oxygen pressure of outer electrode as reference was determined by the equilibrium reaction of $Ni(s) + 1/2O_2 (g) = NiO(s)$.

The construction of the cell is expressed by the following equation;

$$Ni,\ Ni+NiO \mid ZrO_2\text{-}MgO \mid Pb+(PbO\text{-}Cr_2O_3\text{-}CrO),\ Fe$$

and the emf of this cell is given by the Eq.(1).

$$E = -\{\Delta G^0(NiO) - \Delta G^0(PbO)\}/2F + (RT/2F)\ln a_{PbO}, \quad (1)$$

where $\Delta G^0(NiO)$ and $\Delta G^0(PbO)$ are the standard Gibbs energies of formation for NiO and PbO, respectively, F the Faraday constant, R the gas constant, T the temperature and a_{PbO} is the activity of PbO.

On the other hand, when only PbO and Pb are contained in the cell, the emf of this cell is given by the following equation.

$$E_0 = -\{\Delta G^0(NiO) - \Delta G^0(PbO)\}/2F. \quad (2)$$

Combination of Eqs.(1) and (2) leads to

$$E = E_0 + RT/2F \ln a_{PbO}. \quad (3)$$

Consequently, the activity of PbO can be calculated from Eq.(3).

The Galvanic cell was heated in a gas flow of deoxidized Ar. After the temperature reached 1173 K which was higher than the melting point of the sample, the emf measurement was started. When the emf showed a constant voltage for 30 min, the voltage was considered as the emf value in equilibrium. Measurements were made during the heating cycle at intervals of about 50 K up to 1373 K and also during the cooling cycle to confirm the reproducibility of data. Thermo-electromotive force between the Ni and Fe wires was measured and taken off from the measured emf.

Observation of the cell after experiment showed that there was no chemical attack to the electrolyte and the Fe wire from the slag.

3. RESULTS

3.1 Slag compositions

Fig.2 shows slag compositions at various temperatures plotted in the quasi-ternary $PbO-Cr_2O_3-CrO$ phase diagram. The solid lines indicate liquidus lines which are equilibrated with liquid Pb.

3.2 Electromotive force of Galvanic cells

Fig.3 shows emf values from the Galvanic cell as a function of temperature. The open and closed circles in these plots represent the values for two different cells. The overlapped open circles represents the values during the heating and cooling cycles. It can be seen from this figure that the reproducibility of these measurements was good.

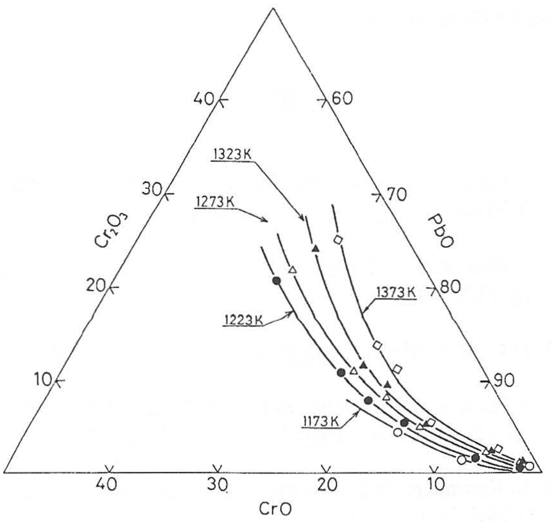

Fig.2 Compositions of slags equilibrated with liquid Pb.

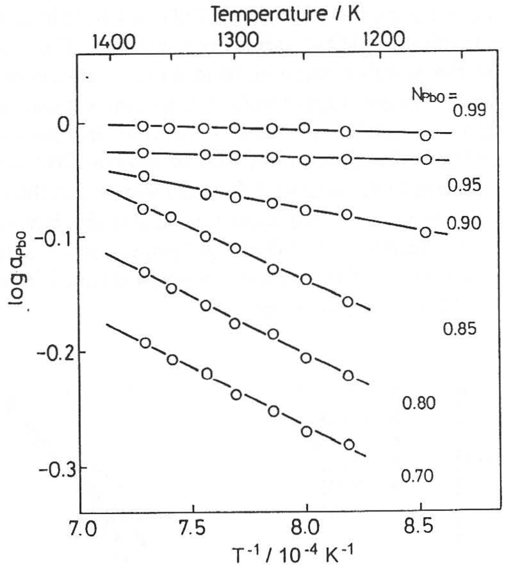

Fig.4 Activity of PbO in $PbO\text{-}Cr_2O_3\text{-}CrO$ slags equilibrated with liquid Pb.

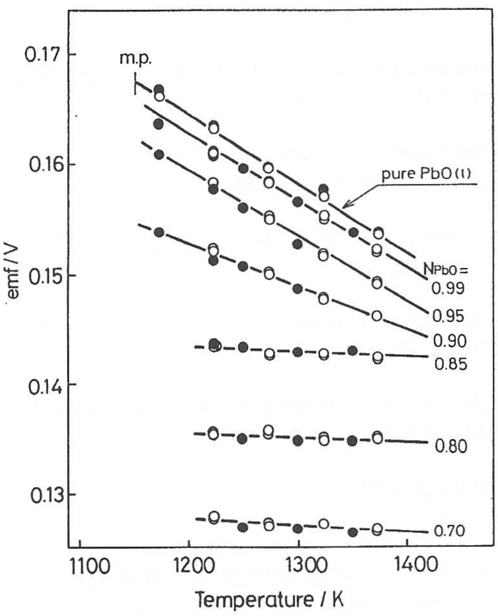

Fig.3 Emf of the Galvanic cells as a function of temperature.

Fig.4 shows the activity of PbO in slags which has been calculated using Eq.(3). It should be noted that there are good linear relations between log a_{PbO} and T^{-1} in each slag composition.

4. DISCUSSION

The liquidus line equilibrated with liquid Pb in the ternary Pb-Cr-O system at 1273 K is shown in Fig.5. The tie lines of oxygen activity between the slags and liquid Pb are also drawn in this figure. The oxygen activity is defined as $a_O = P_{O_2}^{1/2}$ in which the oxygen partial pressure, P_{O_2}, is measured by the Galvanic cell. The solubility of Cr in liquid Pb is 0.119 at% at 1275 K.[18] From Fig.2 it is also shown that at lower temperatures the liquidus line approaches the line connecting PbO and CrO and at higher temperatures to the line connecting PbO and Cr_2O_3.

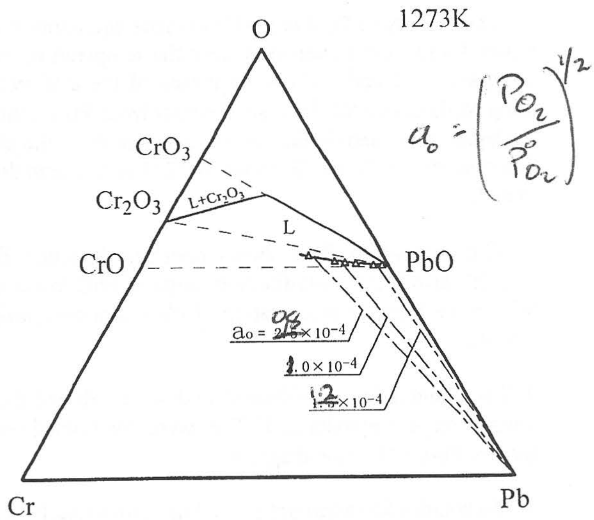

Fig.5 Liquidus line of the slag equilibrated with liquid Pb and tie lines of oxygen activity in Pb-Cr-O system at 1273 K.

Fig.6 shows the activities of PbO as a function of the mole fraction of PbO at various temperatures. The activity shows the negative deviation from Raoult's law except for the higher concentration of PbO. In the lower concentration of chromium oxides, the ratio of Cr^{2+}/Cr^{3+} increases with increasing PbO concentration. This means that CrO can act as a base and Cr_2O_3 as an acid. It is also shown that the large positive deviation of the activity from Raoult's law in the higher concentration of PbO at high temperature, in spite of small ratio of Cr^{2+}/Cr^{3+}. This is probably explained from the effect of Pb^{4+} in the mixtures.

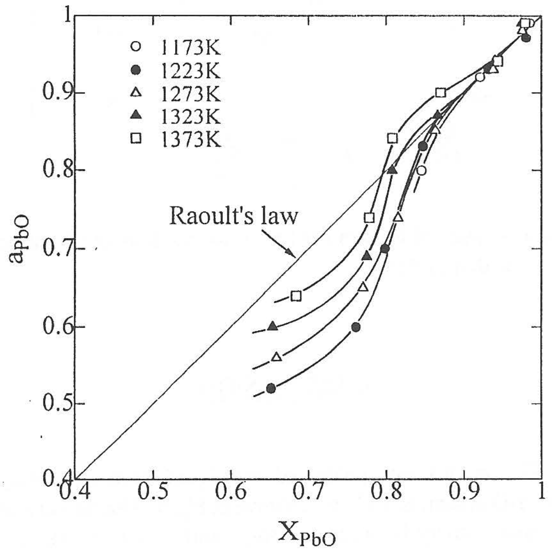

Fig.6 Activities of PbO in PbO-Cr_2O_3-CrO slags as a function of the mole fraction of PbO.

5. CONCLUSIONS

The activity of PbO in Pb-Cr-O melts equilibrated with liquid Pb has been measured over the temperature range between 1173 and 1373 K by means of the emf method using MgO-stabilized ZrO_2 solid electrolytes. Furthermore, the liquidus line and tie lines of oxygen activity in the phase diagram for the Pb-Cr-O system at 1273 K has been determined.

1. The activity of PbO shows negative deviation from Raoult's law in the mole fraction range of PbO lower than 0.8. In the higher concentration of PbO, it shows positive deviation.

2. The liquidus line equilibrated with liquid Pb and the tie lines of oxygen activity at 1273 K were determined on the ternary Pb-Cr-O phase diagram.

3. The liquidus line approaches the line connecting PbO and CrO at lower temperatures and to the line connecting PbO and Cr_2O_3 at higher temperatures. Then this slag system is the ternary system of PbO-Cr_2O_3-CrO.

4. The ratio of Cr^{2+}/Cr^{3+} in the slag increases with increasing the PbO concentration. This means that CrO acts as a base and Cr_2O_3 as an acid.

REFERENCES

1. T.Enokido, H.Katayama, M.Kuwahara, M.Fujita and T.Sasaki: J.ISIJ, Vol.70, 1984, p.S117.

2. K.Morita, T.Shibuya and N.Sano: J.ISIJ, Vol.74, 1988, pp.632-639.

3. D.C.Hilty: Metals Transactions, Feb., 1949, pp.91-95.

4. I.Takada, E.Katayama, M.Smito, T.Inatani, H.Hamada and N.Tsuchiya: J.ISIJ, Vol.70, 1984, pp.A25-28.

5. M.Kuwahara, H.Katayama, C.Saito and H.Ishikawa: J.ISIJ, Vol.70, 1984, p.S111.

6. M.Kuwahara, H.Katayama, H.Ishikawa, M.Fujita and T.Sasaki: J.ISIJ, Vol.70, 1984, p.S116.

7. K.Goto and Y.Matsushita: J.ISIJ, Vol.51,1965, pp.1240-1252.

8. H.Flood and W.J.Knapp: J.Am.Ceram.Soc., Vol.46, No.2, 1963, pp.61-65.

9. F.D.Richardson and L.E.Webb: Bull.Inst.Mining Met., 584, 1955, pp.529-64.

10. B.Björkman, G.Eriksson and E.Rosén: Metall.Trans. B, Vol.15B, 1984, pp.511-516.

11. M.Iwase, S.Miki and T.Mori: J.Chem.Thermodynamics, 11, 1979, pp.101-110.

12. T.K.Inoue, H.Fujiwara and M.Iwase: Trans.ISS, May, 1993, pp.77-86.

13. M.Iwase, Y.Kikuchi and Y.Kawai: Scandinavian Journal of Metallurgy, 22, 1993, pp.45-48.

14. F.M.Jaeger und H.C.Germs: Z.anorg.u.allg.Chem., 119, 1921, pp.153-157.

15. J.W.Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol.XI, 1931, pp.173, 296-297, 301-304.

16. T.Negas: J.Am.Ceram.Soc., Vol.51, No.12, 1968, pp.716-719.

17. V.T.Mal'tsev, G.A.Bukhalova and V.M.Manakov: Zh. Neorg.Khim., 17, No.2, 1972, p.532.

18. T.Alden, D.A.Stevenson and J.Wulff: Trans.AIME, 212, 1958, pp.15-17.