Role of Fluoride Ions in Molten Oxide-Fluoride Mixtures as Refining Fluxes for Molten Steel

Shigeta Hara and Toshihiro Tanaka
Department of Materials Science and Processing,
Faculty of Engineering, Osaka University
2-1 Yamadaoka, Suita , 565 , Japan
Phone : +81-6-879-7465

Abstract

We have measured the solubility of carbon dioxide in $BaO-CaO-BaF_2-CaF_2$ melts at 1673K. using the thermobalance method. The equilibrium constant for the reciprocal reaction, (BaO) + (CaF_2) = (CaO) + (BaF_2) determined by the solubility measurement, was used to be interpreted for dephosphorization of high carbon Fe-Cr liquid alloys by $BaO-CaO-CaF_2$ fluxes. It is shown that surface tensions in the systems $BaO-CaF_2$, $Na_2F_2-BaCl_2$ and $K_2F_2-BaCl_2$ can be also explained as the reciprocal salt systems.

1. Introduction

Oxide based melts had been used as slags and fluxed for conventional iron and steelmaking processes, but one of the exception was calcium fluoride which is used as an additive to decrease the viscosity of melts. Now, oxide-fluoride mixed melts are generally used as highly efficient fluxes for secondary refining of hot metals and electroslag remelting (ESR). In the melts, it is well known that fluoride ions added in oxide melts form oxy-fuoride complex ions, but it is not always recognized yet that physico-chemical properties of oxide-fluoride mixtures is also affected by the existence of reciprocal reaction as $AX+BY \rightleftarrows BX+AY$ (A,B:cation, and X,Y:anion). In this paper, the concept of the reciprocal reaction is applied not only to our experimental results on solubility of carbon dioxide in $(Ba,Ca)O-(Ba,Ca)F_2$ melts, but also to surface tensions of $MO-CaF_2$ (M:Mg,Ca,Ba) and MF_x-NCl_y(M:K,Na,Ba, N:Ba,Na) binary melts.

2. Solubility of Carbon dioxide in $(Ba,Ca)O-(Ba,Ca)F_2$ melts

Melts containing highly basic components such as Na_2O, Li_2O, BaO and so on, are expected to be efficient fluxes for refining of hot metals, but it is not always the true. As the example, we can point out the system in Li_2O-CaF_2 melts in which activity of Li_2O is very low1), because of reciprocal reaction, $Li_2O+CaF_2 \rightleftarrows CaO+2LiF$. Similar situations may occur in molten highly basic oxide-fluoride mixtures. We discuss here how to affect the reciprocal reaction, $BaO+CaF_2 \rightleftarrows CaO+BaF_2$ to the solubility of CO_2 in $(Ba,Ca)O-(Ba,Ca)F_2$ melts.

2. 1 Experimental

The thermo-balance method was applied to measure the solubility of CO_2 in oxide-fluoride mixtures at 1573-1673K. The solubility of CO_2 was determined by weight change of mixtures containing $BaCO_3$,$CaCO_3$,BaF_2 and CaF_2 during the heating under controlled $Ar+CO_2$ atmosphere. The experimental details were described elsewhere(3,4). Following two types of indexes were used for the solubility as,

$$X_{CO_2}=N_{CO_2}/(N_{BaO}+N_{CaO}+N_{BaF_2}+N_{CaF_2}+N_{CO_2}) \quad (1)$$

$$X_{BaCO_3}=N_{BaCO_3}/(N_{BaCO_3}+N_{BaO}+N_{CaO}+N_{BaF_2}+N_{CaF_2}) \quad (2)$$

where N_i is molar numbers of i-th component in a melt. The following relationship exists between X_{CO_2} and X_{BaCO_3}.

$$X_{BaCO_3}=X_{CO_2}/(1-X_{CO_2}) \quad (3)$$

2. 2 Results

Figure 1 shows the relationships between solubility of CO_2, X_{BaCO_3} and mole fraction of BaO, N_{BaO} in $BaO-BaF_2$ melts under various CO_2 partial pressures at 1673K.

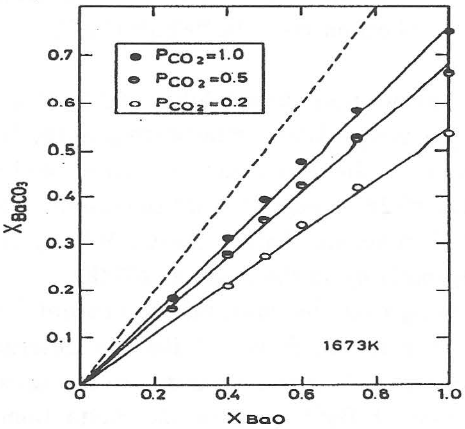

Figure 1 Solubility of CO_2 in $BaO-BaF_2$melts, X_{BaCO_3} melts at 1673K under various P_{CO_2}(atm).

In the figure, broken line indicates the maximum solubility that all of the BaO are used for formation of $BaCO_3$. In the BaO-BaF_2 system, the solubility of CO_2 linearly depends on BaO content in the melts. Figure 2 shows that the same relationship is also held for BaO-CaO system at 1673K.

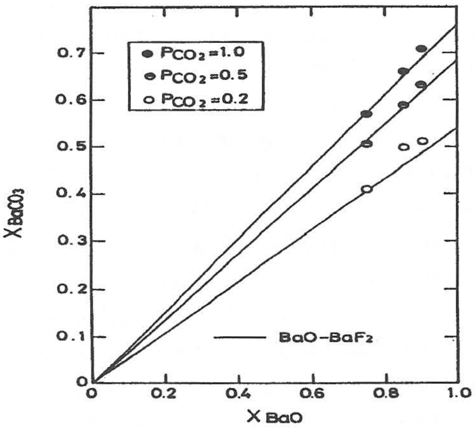

Figure 2 Solubility of CO_2 in BaO-CaO system at 1673K.

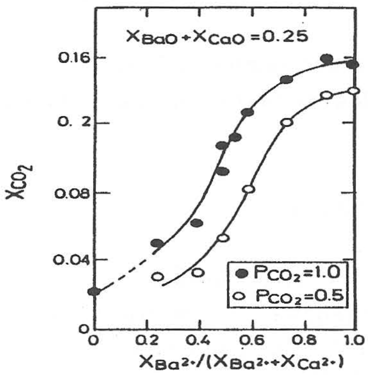

Figure 3 Solubility of CO_2, X_{CO2} in (Ba,Ca)O-(Ca,Ba)F_2 melts at 1673K as a function of cation ratio, $Ba^{2+}/(Ba^{2+}+Ca^{2+})$.

Figure 3 shows that the solubility of CO_2, X_{CO2} does not obey a simple linear relationship to the initial BaO content for BaO-CaO-BaF_2-CaF_2 melts at $X_{CaO}+X_{BaO}=0.25$. It suggests that the existence of the reciprocal reaction, BaO+CaF_2=CaO+BaF_2 affects the CO_2 solubility in the melts at 1673K.

Assuming that the equilibrium constant for the reciprocal reaction, K is 6.7 that is determined through trial and error procedure, we can calculate the content of BaO, X'_{BaO} in the melts from the initial compositions by the following equations.

$$K=[(c+X)x(d+X)]/[(a-X)x(b-X)] = 6.7 \qquad (4)$$

$$X'_{BaO}=a-X \qquad (5)$$

where a,b,c and d are molar fractions of BaO, CaF_2, BaF_2 and CaO in the initial mixtures, respectively. Figure 4 shows the relationship between X_{BaCO3} and calculated BaO content, X'_{BaO} for BaO-CaO-BaF_2-CaF_2 system under various P_{CO2}(atm) at 1673K.

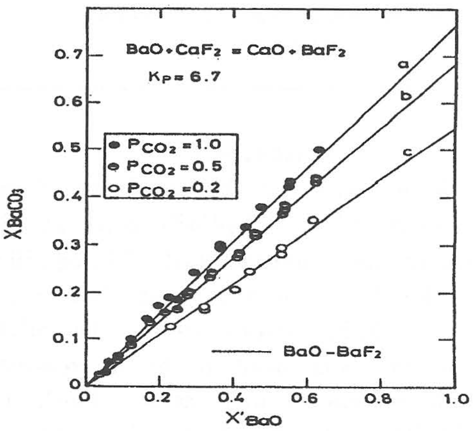

Figure 4 Relationship between X_{BaCO3} and calculated BaO content, X'_{BaO} by using K=6.7 for the reciprocal reaction, (BaO)+(CaF_2)=(CaO)+(BaF_2)in the (Ba,Ca)O-(Ba,Ca)F_2 quarterary melts at 1673K.

In the Figure, solid lines are those obtained for BaO-BaF_2 and BaO-CaO mixtures. These results suggests that the solubility of CO_2 can be explained by the reciprocal equilibrium in oxide-fluoride melts, and hence it was applied to the dephosphorization of liquid iron by fluxes containing oxides and fluorides.

3. Dephosphorization of Fe-2%C-5%Cr melt by CaO-BaO-CaF_2 and CaO-NaF Fluxes

Inoue et al(4) carried out dephosphorization tests of Fe-2%C-15%Cr liquid alloys(5 kg) by CaO-BaO-CaF_2 and CaO-NaF fluxes containing 5%Cr_2O_3 (500g) at 1693K . The results can be analyzed by using the equilibrium constant, K=6.7 for the reciprocal reaction (BaO)+(CaF_2)=(BaF_2)+(CaO), determined by the solubility of CO_2 in the melts. Figure 5 shows the dephosphorization ratio, Lp (%) as a function of calculated BaO content, X'_{BaO} in the melts on the assumption of K=6.7. As shown in Figure 5, there are a good correlation between them. Although some fluxes (denoted by a to f in the column) behave exceptionally, those fluxes may be accompanied with a solid phase at the temperature. From this consideration, we can predict the most suitable composition of CaO-BaF_2-5%Cr_2O_3 and BaO-CaF_2-5%Cr_2O_3 fluxes for the dephosphorization of the liquid alloy as shown in Figure 6.

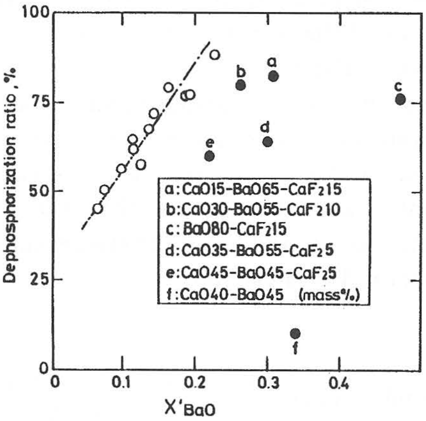

Figure 5 Relationship between dephosphorization ratio, *Lp*(%) of Fe-2%C-15%Cr liquid alloy (5kg) by (Ca,Ba)O-CaF_2 fluxes(500g) and calculated BaO content,X'_{BaO} in the melts by using *K*=6.7 at 1693K.

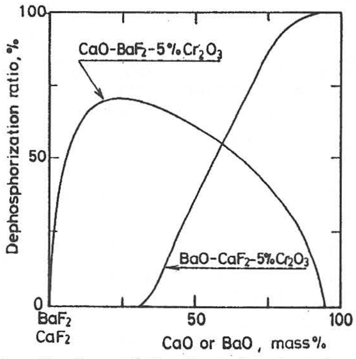

Figure 6 Prediction of dephosphorization ratio *Lp* when 5kg of Fe-2%C-15%Cr liquid alloy was equilibrated with 500g of BaO-CaF_2 or CaO-BaF_2 fluxes containing 5%Cr_2O_3 at 1693K.

Similar treatment may be possible in case of the CaO-NaF fluxes in which the reciprocal reaction, (CaO)+2(NaF)= (Na_2O) + (CaF_2) may be expected. Figure 7 shows the dephosphorization ratio, *Lp* (%) of the same liquid alloy(5kg) by CaO-NaF-5%Cr_2O_3 (500g) fluxes at 1693K as a function of calculated Na_2O content, X'_{Na_2O} on the assumption of *K*=7x10^{-4}. From the relation, most suitable composition of the CaO-NaF fluxes for the dephosphorization is estimated as shown in Figure 8. The result for pure NaF that woks for the dephosphorization, may be acceptable, if it contains 0.7%Na_2O by the reaction, $6(Na_2O)+(Cr_2O_3)\rightarrow 2CrF_3(gas)+3(Na_2O)$.

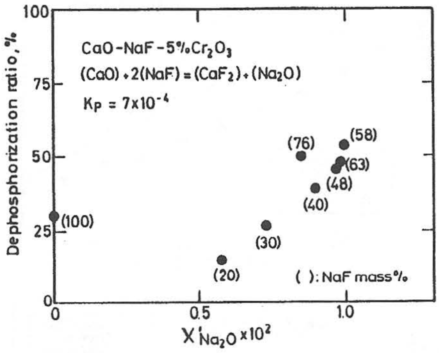

Figure 7 Dephosphorization ratio, *Lp* of Fe-2%C-15%Cr liquid alloy (5kg) by CaO-NaF-5% Cr_2O_3 fluxes at 1693K.

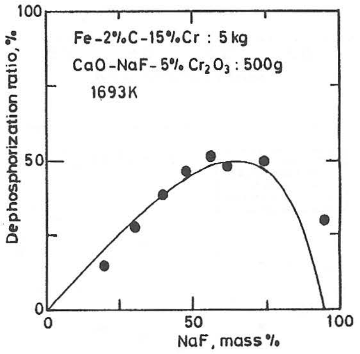

Figure 8 Prediction of dephosphorization ratio,*Lp* of Fe-2%C-15%Cr liquid alloy(5kg) by CaO-NaF-5%Cr_2O_3 fluxes(500g) at 1693K.

Those results clearly suggest that choice of melts as the solvent is of a great importance to use highly basic components such as Na_2O, K_2O, BaO for refining processes effectively.

4.Surface Tension of Some Reciprocal Salt Systems

We have applied the combination of the thermodynamic treatments by Butler, Speiser et al. and Monma & Sudo to evaluate surface tension of binary molten salt solutions(5,6). In general, surface tension of binary solution is higher than that of the terminal pure component having lower surface tension as shown in Figure 9(a) for BaF_2-Na_2Cl_2 binary melt(7). However, in some systems such as Na_2F_2-$BaCl_2$(7) and K_2F_2-$BaCl_2$(8)(Figure 9(b) and (c), the lowest value are observed at the intermediate composition range.

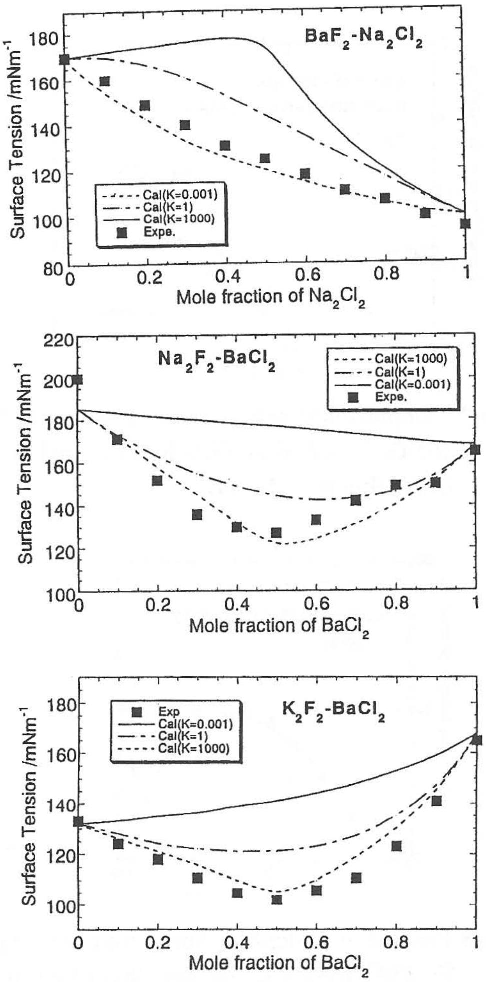

Figure 9 Surface tensions of BaF_2-Na_2Cl_2, Na_2F_2-$BaCl_2$ and K_2F_2-$BaCl_2$ melts at 1273K in comparison with those calculated, on the assumption of K=0.01, 1 or 1000.

These behavior could be explained by a reciprocal reaction, A + B ⇄ C + D. Assuming that every components denoted by A, B, C, and D behave ideally in quartenary A-B-C-D melts and the equilibrium constant $K(\equiv N_C N_D/N_A N_B)$ is known, surface tension, σ can be calculated by solving the following simultaneous equations.

$$\sigma S/RT = \sigma_A S/RT + \ln(N_A^S/N_A^B)$$
$$= \sigma_B S/RT + \ln(N_B^S/N_B^B)$$
$$= \sigma_C S/RT + \ln(N_C^S/N_C^B)$$
$$= \sigma_D S/RT + \ln(N_D^S/N_D^B) \qquad (6)$$

in which σ_i is the surface tension of pure component, i and N_i^S and N_i^B are mole fractions of component i on the surface phase and in the bulk phase. The average surface area is determined by the equation (7).

$$S=[(N_0)^{1/3}/4]\{(V_A)^{2/3}+(V_B)^{2/3}+(V_C)^{2/3}+(V_D)^{2/3}\} \qquad (7)$$

where the V_i is molar volume of pure component, i. The calculated results are also shown in Figure 9. For the BaF_2-Na_2Cl_2 system, best agreement between the measured and calculated values are obtained for K=0.001 which means practically no occurrence of the reciprocal reaction to form Na_2F_2 and $BaCl_2$. For the Na_2F_2-$BaCl_2$ and K_2F_2-$BaCl_2$ systems, however, the calculated values are in good accordance with the measured ones , when higher K-values as 1000 are given for the equilibrium constant , and it suggests that the reciprocal reaction proceeds and hence the minor component in the melts had disappeared.

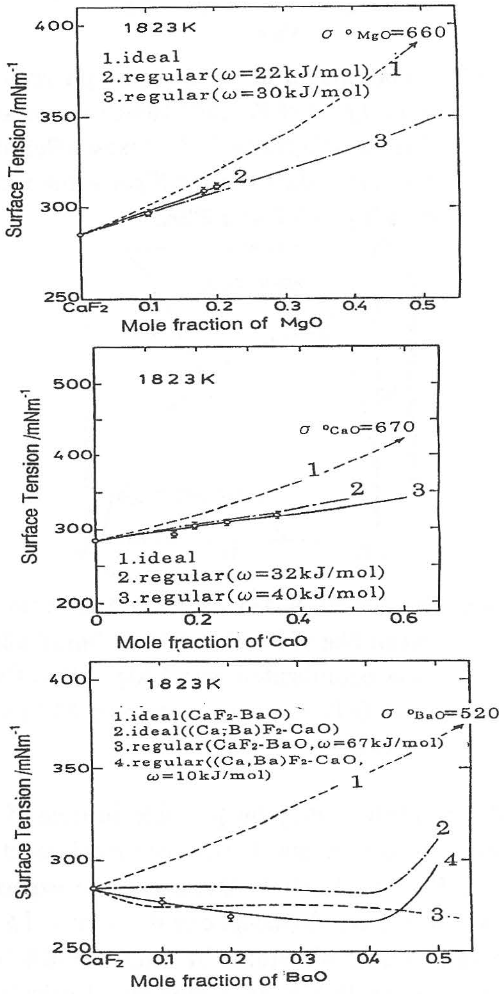

Figure 10 Surface tensions of MgO-CaF_2, CaO-CaF_2 and BaO-CaF_2 melts at 1823K.

Similar behavior is also observed for the systems in MO-CaF_2 (M:Mg,Ca,Ba)(9) as shown in Figure 10.

For the systems in $MgO-CaF_2$ and $CaO-CaF_2$, the measured values are in good accordance with the calculated ones, if regular solution model with a suitable interaction parameter, ω is assumed. For $BaO-CaF_2$ melts, it is very difficult to reproduce the measured values by calculation without the assumption of the reciprocal reaction, $(BaO)+(CaF_2) \rightleftarrows (CaO)+BaF_2$.

5. Concluding Remarks

After the ESR process has worked in practice, many types of oxide-fluoride mixture are used as fluxes in pyrometallurgical processes. In such oxide-fluoride melts, it is well known that formation of oxy-fluoride anions affects the physico-chemical properties. In this paper, we pointed out that for the flux design attention should be paid to the interaction between the solvent and the solute molecules, especially the reciprocal reaction as $A+B \rightleftarrows C+D$, plays important role if highly basic components were used as the additives

References

1)G.I.Ovcharenko,B.M.Lepinskii,V.M.Ryabov and A.V. Zaishev," On Activities of Components in Li_2O-CaF_2 Melts",Izvest,Akad,Nauch.SSSR, Metally,(1977),No.2,pp.74-77.

2)S.Hara,T.Araki, and K.Ogino,"Phase Equilibrium Studies in the $FeO-Fe_2O_3-CaO$ and $FeO-Fe_2O_3-2CaO$ SiO_2 Systems",Proc. 2nd Intern.Symp. on Met. Slags and Fluxes, edited by H.A.Fine and D.R.Gaskell, The Met.Soc of AIME,(1984),pp.441-451.

3)S.Hara,T.Ishida,H.Sugano,and K.Ogino, "Solubility of Carbon Dioxide in $BaO-BaF_2$ Melts",Tetsu-To-Hagane,78(1992),No.11, pp.1666-1673.

4)S.Inoue,T.Usui,K.Yamada,and K.Takahashi, Technol.Rept.NKK,(1989),Vol.125, pp.52-60.

5)T.Tanaka,K.Hack,T.Iida,and S.Hara "Application of Thermodynamic Databases of the Evaluation of Surface Tensions of Molten Alloys,Salt Mixture and Oxide Mixtures",Z.Metallkd.,87(1996),pp.380-389.

6)T.Tanaka and S.Hara,"Application of Thermodynamic Databases to Calculation of Molten Salt Mixtures", Proc. Molten Salts X. The Electrochemical Soc.,Los Angels,(1996)

7)M.V.Byshnova,B.V.Patorov,and A.G. Morachevskii, "Surface Tension of Melts in the System Na,Ba ‖ F,Cl" .Izvest.VUZov. Tsvetnaya Met., (1982),No.4,pp.73-75.

8)M.V.Byshonova,A.G.Marachevskii,and B.V.Patrov,"Surface Tension of Melts in the System K,Ba ‖ F,Cl",Izvest.VUZov. Tsvetnaya Met.,(1984),No.1,pp.117-118.

9)S.Hara, and K.Ogino,"Density and Surface Tension of Melts in the System CaF_2-MO (M:Mg,Ca,Ba)", J.Japan,Inst.Metals, 52(1988), No.11,pp.1098-1102.