4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

EXISTENCE OF LIQUID LATTICE IN MO - MF_2 MELTS

Hiromichi Takebe*, Yoshio Ohta** and Kenji Morinaga*

*Dept. of Materials Science and Technology
Graduate School of Engineering Sciences
Kyushu University, Japan

**Dept. of Electronic Materials Engineering
Fukuoka Institute of Technology, Japan

Synopsis: The crystal structure of fluorite has the high Madelung constant; the relative long range order is maintained even in liquid state. We call this state "liquid lattice". The electrical conductivities of MO-MF_2 melts (MO<17mass%; M: Ca, Sr and Ba) have varied with oxygen partial pressure in argon and oxygen mixed atmosphere. The formation of positive holes in "liquid lattice" caused the dependence.

Key words: electrical conductivity, melt, fluoride, oxygen partial pressure, positive hole

1. Introduction

CaF_2 is one of main constituents of fluxes in steel-refining. Since physical properties of molten flux containing fluorides have become so important in practical fields, the measurement of density, surface tension, viscosity and electrical conductivity have been attempted on various fluxes [1]. We have not, however, had established data for fluoride-containing fluxes because of changeful composition [2], two liquids [2] and "liquid lattice" [3].

In this study the dependence of oxygen partial pressure (OPP) on electrical conductivity (EC) have been studied for MO-MF_2(M: Ca,Sr and Ba) melts and discussed the newly-observed phenomenon caused by the liquid lattice of fluorite-like structure.

2. Experimental procedure

All samples were prepared from special-grade reagents. Mixed samples were preheated for about several hours at 723K to make the samples free from moisture, the cause of fluorine volatilization. Dried argon and oxygen gasses were used as atmosphere.

The so-called hot-thermocouple method [2] was used for observing the transparent / opaque appearance of melts. In this technique the sample is heated by a Pt-Rh (30%) / Pt-Rh (10%) filament which is simultaneously used as a measuring thermocouple. This method makes it possible to measure the exact temperature of a melt and to observe it directly through the microscope. The modified four-electrodes method [4] for electrical conductivity was employed.

Measured samples were melted with Na_2CO_3 at 1273K, and then fluorine was completely extracted by hot water. Fluorine content in the hot water was determined by ion-chromatography.

3. Results and discussion

3.1 Observation of melts under various oxygen partial pressure

Through direct observation of MO-MF_2 melts, two liquids, which was observed in CaF_2-Al_2O_3, CaF_2-Al_2O_3-CaO systems [2], was not occurred. We observed, however, the new phenomenon in these melts, that is, the change from transparent melts to opaque melts in dependence on oxygen partial pressure (OPP). The pictures of some typical changes are shown in Fig.1, where as seen in (a), a melt is transparent under a relative low OPP

(10Pa), as seen in (b) and (c) melts look partly and perfectly opaque at 10^3 and 10^4Pa. These changes should be reversible with OPP in argon and oxygen mixed atmosphere.

As shown in Fig.2, a sample quenched from (a) state in Fig.1 is pure white; a sample quenched from (c) state looks grey. The color of quenched samples indicates the existence of positive holes in (c) state in Fig.1, in which light is absorbed by positive holes and the melt looks opaque.

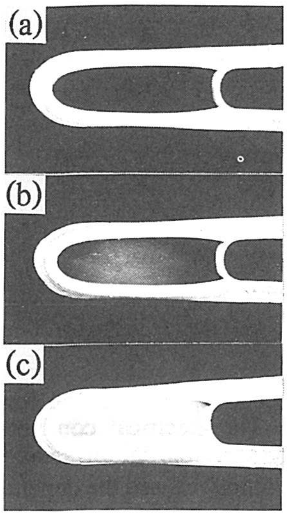


Figure1 Appearance of the 15mass%CaO-85mass% CaF_2 melt: (a)transparent, (b)partly-opaque and (c)opaque.

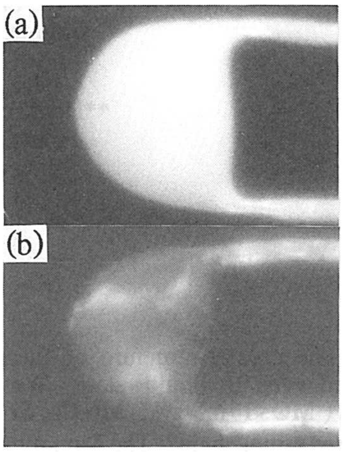


Figure2 Appearance of (a)a sample quenched from (a) state in Fig.1 and (b)a sample quenched from (c)state in Fig.1.

Fluorine content was determined for mixed and measured samples by chemical analysis. The difference in fluorine content for both samples was not apprecible, and therefore it was considered that the composition of the melts was almost constant within experimental error when the dehydration of the atmosphere and samples was done completely.

The lines in Fig.3 show the boundaries between the domains of OPP and MO content combinations that are transparent or opaque state for melts. In $CaO-CaF_2$ system, melts become to be opaque at relative higher OPP than that in $SrO-SrF_2$ and $BaO-BaF_2$ systems. In pure MF_2 and within 2 mass% MO systems, we have not observed the opaque state at the experimental OPP range. The opaque region become to be extended with increasing MO content.

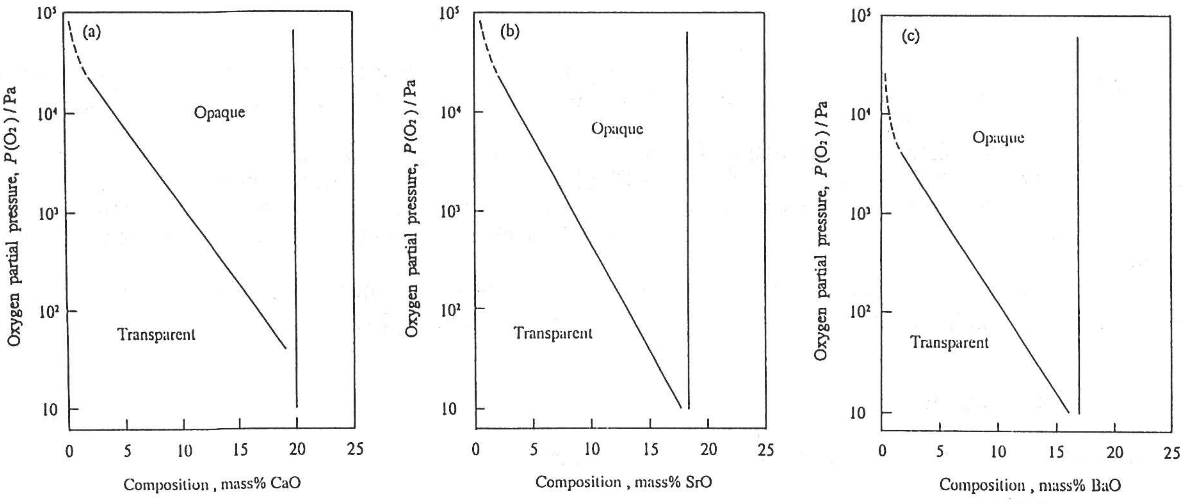


Figure3 Effects of oxygen partial pressure and composition on appearance of $MO-MF_2$ (M: Ca, Sr and Ba) melts.

3.2 Formation mechanism of positive holes in melts

We have observed the reversible change from transparent to opaque state of melts with OPP. Samples quenched from opaque melts were grey. From these facts, we have concluded that positive holes in the melts were formed by gaseous oxygen in the atmosphere.

The structure of CaF_2, SrF_2 and BaF_2 are fluorite-type. The Madelung constant of this structure is relatively high compared with other crystal structures, therefore, MF_2 has a relative long range order even in melt state, that is, the liquid lattice [5],[6]. In MO-MF_2 melts, MO may be incorporated into these lattices. M^{2+} and O^{2-} ions of MO are located on M^{2+}-sites and F^--sites in MF_2 liquid lattices. Such substitution makes anion vacancies even in liquid state. The vacancies and oxygen gas in the atomsphere form positive holes P as following equation:

$$1/4\ O_2\,(g) + 1/2\ V_{anion} = 1/2\ O^{2-}\ (\text{ on lattice }) + P \qquad (1)$$

These positive holes make the melt opaque and the quenched sample grey by absorption of light. The strength of Ba-F bond is more weak than that of Ca-F; in BaO-BaF_2 system, so that BaO is likely to be incorporated into the BaF_2 liquid lattice, then a lot of anion vacancy are formed. A little amount of oxygen ionize and dissolve into the anion vacancy and form the positive hole.

3.3 Change of electrical conductivity related to positive holes

Through direct observation of the melts, the reversible change from transparent to opaque state with OPP could be caused by the positive hole formed in terms of equation (1). This assumption leads to the change of conduction carrier from ions to positive holes.

It was found that the electrical conductivity (EC) of MO-MF_2 melts varies with OPP in the atomsphere. Figure 4 shows, for example, a reversible change in electrical conductivity at 1773K for the 10 mass%CaO-90 mass% CaF_2 melt. The value of EC is about 700 S/m in dried argon (OPP≈10Pa) and when OPP is changed to 10^4Pa the value increases to 2200 S/m after 800 seconds. Then when OPP is changed back to that in dried argon the value returns to 700 S/m. Since the composition of the sample is not changed by the presence of oxygen, this newly-observed behavior is attributed to the effect of oxygen on the conduction mechanism in MO-MF_2 melts. This result agrees with the state change of melts shown in Fig.1.

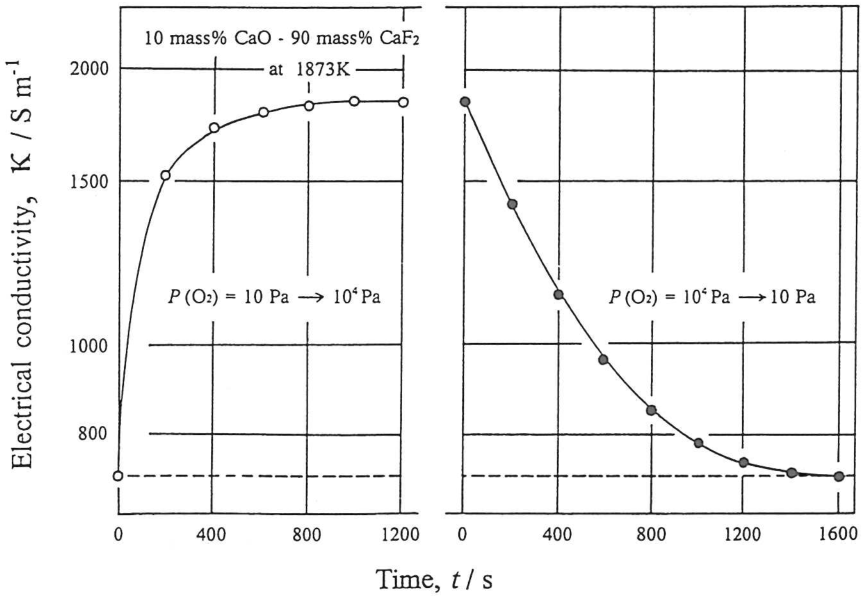


Figure4 A reversible change in electrical conductivity of the 10mass%CaO-90mass%CaF_2 melt.

Figure 5 shows the relationships between the electrical conductivity (EC) and oxygen partial pressure (OPP) for 5 mass% MO - 95 mass% MF_2 melts. There is a critical value in OPP for each system. Under the critical value of OPP, EC is not varied with OPP, therefore, the conduction carrier is mainly ion. Above the critical OPP, EC is varied with OPP. In this area the main carrier contributing to conduction is probably positive hole, enough the positive hole can be formed easily at higher OPP, resulting in higher conductivity with increasing OPP according to equation (1). These critical values of OPP are in good agreement with the boundary from transparent to opaque state shown in Fig.1. These two newly-observed results, the change to opaque state and the increase of electrical conductivity with increasing OPP, are caused by positive hole formation in MO-MF_2 melts.

We support the existence of positive holes in MO-MF_2 melts to explain the new observations. The dependence of oxygen partial pressure $P(O_2)$ on electrical conductivity κ can be qualitatively expressed by the following equation:

$$\kappa_{total} = \kappa^0_{ion} \exp(-E/RT) + \kappa^0_p P(O_2)^{1/4} \exp(-E'/RT) \qquad (2)$$

where κ^0_{ion} exp (-E/RT) and $\kappa^0_p P(O_2)^{1/4}$ exp (-E'/RT) are partial conductivity for ions and positive holes. In the area of the positive hole conduction, the electrical conductivity κ is in direct proporion to OPP ($P(O_2)$) to the one-quater power. The relationships between log κ and log $P(O_2)$ in Fig.5 are straight lines with a slope equal to ca. 0.25 as expected from equation (2).

Figure 6 shows the relationships between log κ and log $P(O_2)$ in CaO-CaF_2 melts. Pure CaF_2 and 20 mass% CaO-80 mass% CaF_2 have no changes in electrical conductivity with OPP, then the conduction is mainly contributed by Ca^{2+}, F^- ions in the experimental OPP range. At the composition range from 2.5 to 17 mass% CaO, the electrical conductivities are varied with OPP. The results also indicate that the effect of oxygen on electrical conductivity is noteworthy at the composition of 15 mass% CaO-85 mass% CaF_2. The concentration of anion vacancy increases with increasing CaO content and have a maximum value at 15 mass% CaO, so that the critical value of OPP is the lowest in CaO-CaF_2 melts. At the higher OPP, the electrical conductivity of the 15 mass% CaO-85 mass% CaF_2 melt has a tendency to reach to the constant value, because of the saturation of oxygen ions into melts.

The unequal charge of O^{2-} and F^- causes the formation of anion vacancy in MO - MF_2 melts; pure CaF_2 has no vacancies in the melt, resulting in no change of electrical conductivity(EC) with OPP. When EC is measured for samples containing more than 20 mass% CaO, the OPP dependence on EC is not observed because of the decay of fluorite-like liquid lattice.

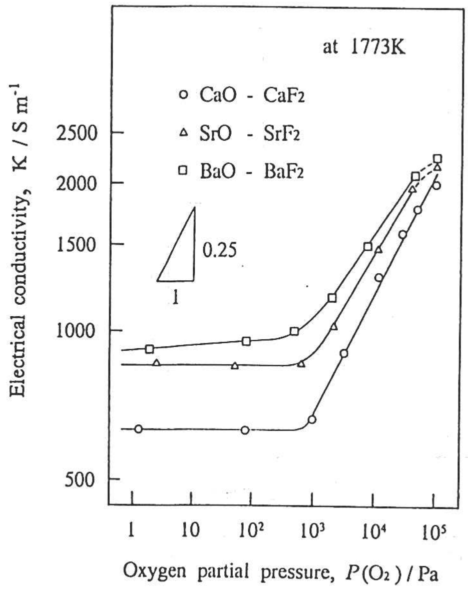


Figure5 The relationships between electrical conducitivity and oxygen partial pressure in 5mass%MO-95mass%MF_2 melts.

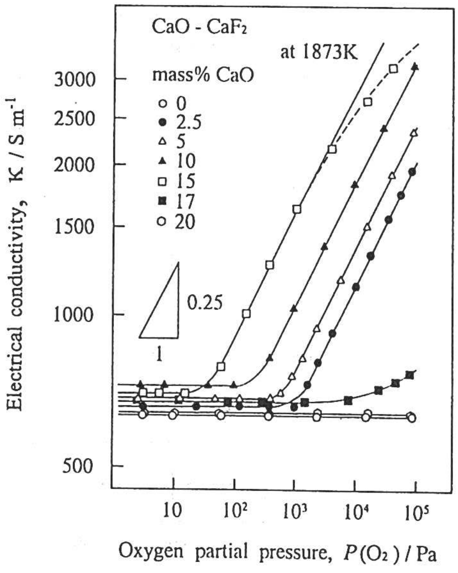


Figure6 The relationships between logκ and log $P(O_2)$ in CaO-CaF_2 melts.

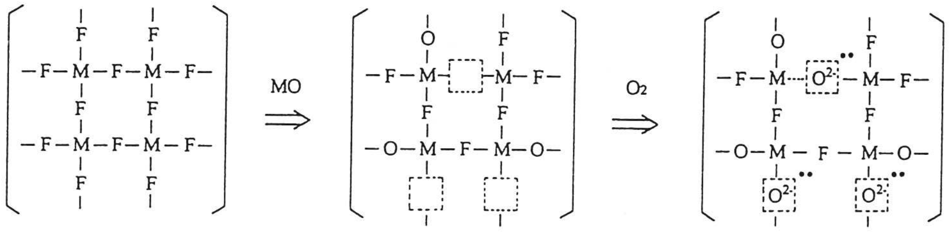
4. Conclusions

The electrical conductivities of MO-MF_2 melts (MO < 17 mass%; M: Ca, Sr and Ba) have varied with oxygen partial pressure in argon and oxygen mixed atmosphere. The newly-observed phenomenon have caused by the formation of positive holes in the melts.

Figure 7 shows the structural model to interpret the phenomenon. The crystal structure of fluorite such as CaF_2, SrF_2 and BaF_2 has the high Madelung constant, therefore, the relative long range order is maintained even in liquid state. We call this state " liquid lattice". When MO is added, MO is incorporated into the liquid lattice. M^{2+} of MO is located on the M^{2+} -site and O^{2-} of MO on the F^- -site in the liquid lattice formed by MF_2. The unequal charges of O^{2-} and F^- causes the anion vacancy in the melts.

The gaseous oxygen are ionized and dissolved into the melts above a critical OPP in the atmosphere and reacted with the anion vacancy, resulting in the formation of positive hole. These positive holes make the melt to be opaque by absoption of light and contribute to the conduction.

In results, we conclude that the newly-observed phenoma are caused by the existence of liquid lattice in MO-MF_2 melts.



Relative long range order in melts < liquid lattice >

V_{anion} formation (⬚)

Reactions between O_2 and V_{anion} make positive hole (•).

Figure7 Structural model to be formed positive holes.

References

[1] K.C.Mills and B. J Keene: International Metals Reviews, No.1(1981),21.
[2] K.Morinaga, T.Yanagase, Y.Ohta and Y.Ueda: The Metallurgical Soc. of AIME, (1979), Paper Selection A-79-18.
[3] K.Morinaga, Y.Ohta and T.Yanagase: J.Japan Inst.Metals,50(1986),907.
[4] Y.Ohta, A.Miyanaga, K.Morinaga and T.Yamagase: J. Japan Inst. Metals, 45(1981),1036.
[5] T.Baak: Acta Chem. Scand.,9(1955),1406.
[6] R.Kammel and H.Winterhager: Erzmetall,9(1968),399.