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Electric Conductivities of Molten Salts of Some Binary Fluoride Systems*

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Synopsis

The specific electric conductivities of binary molten salts of $NaF-BaF_2$, $NaF-CaF_2$, $KF-BaF_2$ and $KF-CaF_2$ systems were measured at 1000°C.

1) In these binary molten salts, the specific electric conductivities decrease almost parabolically with the increase of barium fluoride or calcium fluoride contents.

2) The specific electric conductivities of these four binary molten salts were calculated by "Taniuchi's modified formula", which is a modification of "Markov's formula", and the calculated values agreed well with the measured values.

3) From above-mentioned results, we conclude that the ionic species of these molten salts which take part in the electric conduction are Na^+, K^+, Ba^{++}, Ca^{++} and F^- respectively.

4) We are of the opinion that sodium fluoride cannot be replaced by potassium fluoride in the aluminum refining electrolytes, because the latter is less electrically conductible and more hygroscopic.

I. Introduction

The high-grade aluminum above 99.99% Al is known by the name of "Raffinal", and its properties such as corrosion resistance and reflectivity for light are much better than those of the primary aluminum. Therefore, it is utilized for the foils of the electrolytic condenser, the reflecting mirrors, the vessels of the food industry, etc.

As the manufacturing process for the high-grade aluminum, the molten salts electrolysis, the so-called "three layer process" is solely operated on the industrial scale now.

In this process, the fluoride mixtures (Hoopes' bath, Hurter's bath, Sumitomo's bath et al.) or the fluoride-chloride mixtures (Gadeau's bath) have been used as molten electrolytes.

We have investigated such properties of these molten salt systems as melting temperature, density and electric conductivity. The electric conductivities of ternary molten salts of $NaF-BaF_2-AlF_3$ system (Hoopes' bath) and $NaF-BaCl_2-AlF_3$ system (Gadeau's bath) were measured. In our previous papers[(1),(2)] the measur-

* The **220th** report of the Research Institute of Mineral Dressing and Metallurgy, originally published in Japanese in the Bulletin of the Research Institute of Mineral Dressing and Metallurgy, Tohoku University, **27** (1971), 235.

ing method and the experimental results were reported. Moreover, the results were discussed and "Taniuchi's modified formula", which is a modification of "Markov's formula", was derived(3). According to this formula, the electric conductivities of the molten salt mixtures which contain the cations with different valencies can be calculated. This formula also gives one of the informations for making a decision of the existence of complex ions in a molten salt mixture. The calculated values of the above-mentioned molten salt systems agreed well with the measured values.

In this paper, the measuring results of the electric conductivities of four binary molten salt systems (i.e. NaF-BaF_2, NaF-CaF_2, KF-BaF_2 and KF-CaF_2) related to the electrolytes for aluminum refining are reported. And the experimental results were compared with the calculated values.

II. Materials and experimental methods

1. Materials

Sodium fluoride and potassium fluoride were the extra pure chemical reagents of Wako Pure Chemical Industries Ltd., and barium fluoride and calcium fluoride were the extra pure chemical reagents of Morita Chemical Industry Co. Ltd. These salts were dried before use for several hours at 110°C. Especially, potassium fluoride was dried at 130°C because of its hygroscopic property.

2. Experimental methods

As already stated in our previous reports(1),(2), the electric conductivity was measured by the use of the alternating current bridge method, Kohlrausch method and the electrical components were the same as those of Matsushima's(4). As a conductance cell of the molten fluoride salts, a platinum crucible ($50\sim60$ cm^3 in volume) combined with a platinized platinum wire (dia. 0.9 mm) was used. To prevent errors due to polarization,

(i) an electrode of a platinized platinum wire was used, and

(ii) resistances measured at a series of frequencies from 1 KC to 20 KC were plotted against $1/\sqrt{f}$ (where f is frequency) and linear extrapolations to infinite frequency were used.

Then the specific electric conductivities of the molten salts were calculated by the following equation:

$$R_\infty = R_0 + K/\kappa \quad (1)$$

where R_∞ is the resistance extrapolated to infinite frequency,

R_0 is the resistance of the lead wire,

(1) K. Taniuchi, Nippon Kogyokaishi, **84** (1968), 1533.
(2) K. Taniuchi, ibid., **85** (1969), 103.
(3) K. Taniuchi, Keikinzoku, **20** (1970), 157.
(4) T. Matsushima, Denkikagaku, **37** (1967), 778.

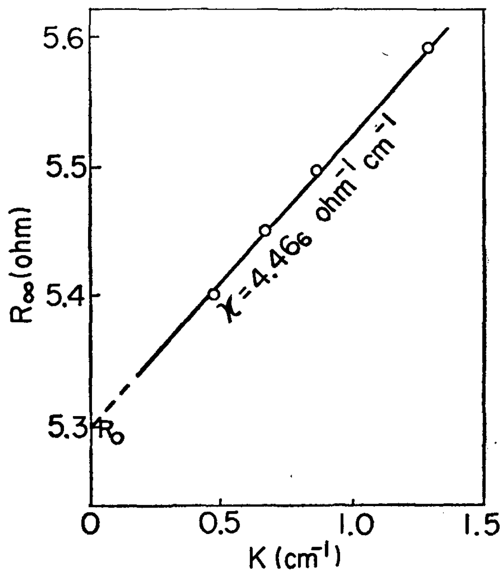

Fig. 1. Electric conductivity of KF-BaF_2 binary molten salts at 1000°C (BaF_2 60%).

κ is the specific conductivity of molten salts, and

K is a cell constant.

Fig. 1 shows this relation of R_∞ to K of KF-BaF_2 binary molten salts with 60%* BaF_2. As is seen from equation (1), a reciprocal of the slope of the straight line of Fig. 1 is κ.

The upper part of the stainless steel reactor was cooled with water. The melting temperatures of some compositions of each binary molten salt were measured by the thermal analysis, where the junction of Pt-Pt·Rh thermocouple was directly dipped in the molten salt, or by the differential thermal analysis with an electric potential recorder(4). All experiments were carried out under an argon atmosphere.

III. The empirical formula on the electric conductivity of the molten salt mixtures

We will outline some discussions about the electric conductivity of binary and ternary molten salt mixtures.

As the ionic species of the multi-component molten salt systems are complicated, there is not an established theory about their electric conduction yet and some empirical formulae to calculate the electric conductivity have been suggested(3).

According to Jaeger and Kapma(5), the following equation (2) is valid between the equivalent conductivity Λ and the specific conductivity κ.

$$\Lambda = \kappa V \, , \qquad V = \sum_i (X_i E_i)/d \tag{2}$$

(5) F.M. Jaeger und B. Kapma, Z. anorg. Chem., **113** (1920), 27.

* When there is no special designation, compositions are shown in mole percent hereafter.

where V is the equivalent volume of the molten salt,

X_i is the molar fraction of i component,

E_i is the equivalent weight of i component and

d is the density of the molten salt.

The equivalent volume V was provided for, and the measured values of both the density d and the specific electric conductivity κ being put into the equation (2), the equivalent conductivity Λ was calculated. Therefore, this equation expresses the additivity of the specific electric conductivity of each component but does not indicate the role of each cation and anion species which take part in the electric conduction.

According to many experimental results including the determination of the transference number, the greater part of the electric conduction in molten salts is carried out by their cation species.

Therefore the idea of the equation (2) may be reasonable.

Next, Grothe[(6)] has suggested the following equation (3) on the specific electric conductivity.

$$\kappa_{\text{total}} = \sum_i \kappa_i v_i \tag{3}$$

where κ_i is the specific electric conductivity of each component and v_i is the volume fraction of each component, that is,

$$v_i = \frac{N_i M_i / d_i}{\sum_i N_i M_i / d_i} \tag{4}$$

where N_i is the molar fraction, M_i is the molecular weight and d_i is the density of each component.

Namely, this equation (4) indicates the volume which is occupied by each component. Grothe's formula is based on the additivity of the electric conductance in which the electric conductivity of each of the components is allotted to the volume occupied by them.

Consequently this idea is not explicit in the case of the molten salts containing the ions of the various different charges.

As the third equation, Frank and Foster's formula has been proposed[(7)]. They distinguished the electric conductance which is carried by cation from that which is carried by anion.

$$\kappa = \sum C_i^+ \Lambda_i^+ + \sum C_j^- \Lambda_j^- \tag{5}$$

This equation (5) assumes the additivity of the specific conductivity of cation and anion. And total electric conductivity of the molten salt is computed as the arithmetic sum of its share of cation and anion. Namely, in equation (5) κ is the specific electric conductivity calculated by assuming the additivity of the specific

(6) H. Grothe, Aluminium, **5** (1962), 320.

(7) W.B. Frank and L.M. Foster, J. Phys. Chem., **64** (1960), 310.

conductivity of the mixed molten salts. Λ_i^+ and Λ_j^- are defined as the equivalent conductivity of cation and anion. C_i^+ and C_j^- are the equivalent ion concentration of cation and anion per one cm^3.

In general, the molten salts are known to be ionic melts. But it comes into question if we can assume the complete ionization of the molten salt even in the case of the simplest salt. Moreover, when complex ions are formed in a multi-component salt system, we must consider the ionization degree of one distinguishable component which takes part in the formation reaction of the complex ions. In such a case, it is considerably difficult to calculate the conductance of the molten salt by the equation (5).

Markov et al.[(8),(9)] have given the following discussion about the electric conductance of binary eutectic salt melts or melts giving a continuous series of solid solutions which are approximated to the ideal solution mixtures at high temperatures.

In the case of a binary molten salt mixture of uni-univalent salt system, M_1X-M_2X, the probability for the combination M_1X-M_1X is proportional to x_1^2, for the combination M_2X-M_2X is to x_2^2 and M_1X-M_2X (M_2X-M_1X) to $2x_1x_2$ respectively.

Here, M_1 and M_2 are univalent cations and X is a common anion of both salts. x_1 is the molar fraction of the component M_1X and x_2 is that of M_2X.

When the respective equivalent conductivities of this binary molten salt, component M_1X and M_2X are Λ, Λ_1 and Λ_2, the following equation (6) may be given.

$$\Lambda = x_1^2 \Lambda_1 + x_2^2 \Lambda_2 + 2x_1 x_2 \Lambda_1 \qquad (\text{where} \quad \Lambda_1 < \Lambda_2) \tag{6}$$

When this idea was applied to the specific conductivity, the specific conductivity κ being substituted for Λ, "Kuroda's approximated formula"[(10)] has been suggested as follows:

$$\kappa = x_1^2 \kappa_1 + x_2^2 \kappa_2 + 2x_1 x_2 \kappa_1 \tag{7}$$

where κ_1 and κ_2 are the respective specific conductivities of component M_1X and M_2X and $\kappa_1 < \kappa_2$.

Since the anion is contained as a common ion of both components, the equation (7) was derived by paying attention only to both kinds of cations and considering the number of cations which take part in the electric conduction from the standpoint of probability.

Then, "Kuroda's approximated formula" can be extended to the molten salt systems which contain cations of different charges.

"Taniuchi's modified formula"

(8) B.F. Markov and L.A. Shumina, DAN SSSR, **110** (1956), 411.
(9) Iu. K. Delimarskii and B.F. Markov, *Electrochemistry of Fused Salt,* (1961), 32, Sigma Press.
(10) J. Mochinaga, K. Cho and T. Kuroda, Denkikagaku, **36** (1968), 746.

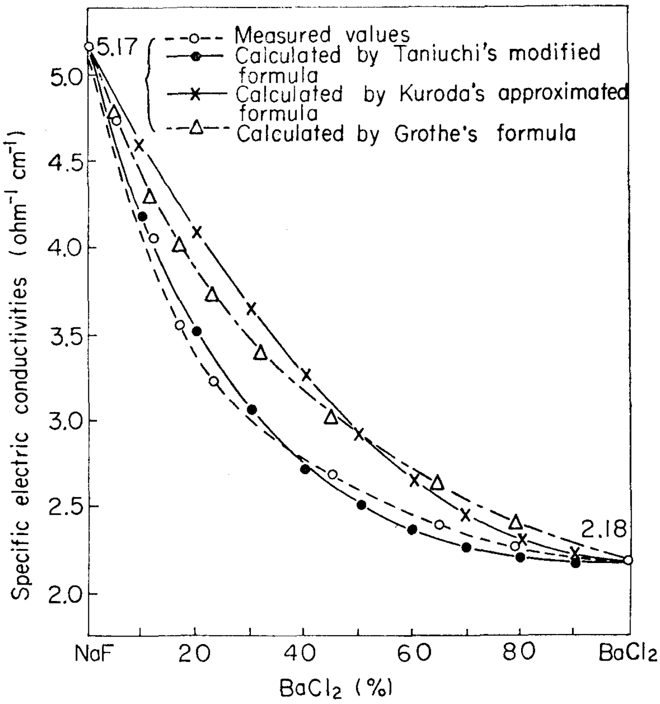

Fig. 2. Specific electric conductivities of binary NaF-$BaCl_2$ molten salts at 1000°C.

The above-mentioned "Kuroda's approximated formula", by which the additivity of the electric conductance is calculated, can be modified as follows when a molten salt system belonging to the univalent-polyvalent ionic system is dealt with. In this case, the idea of the Temkin's ionic fraction[11] is prescribed.

For example, as for the molten salt mixture which contains univalent and bivalent cations, Temkin's concentrations of univalent cation M_A^+ and bivalent cation M_B^{++} are defined as follows:

$$M_A X:\ \frac{x_1}{x_1+2x_2},\qquad M_B X_2:\ \frac{2x_2}{x_1+2x_2} \tag{8}$$

where the molar fraction of univalent cation M_A^+ is x_1 and that of bivalent cation M_B^{++} is x_2, and the next assumption is also adopted.

$$n_{F^-} + n_{Cl^-} = 1$$

The specific electric conductivity can be calculated by substituting the values of the equation (8) for x_1 and x_2 of the equation (7), and the following equation (9) can be derived.

$$\kappa = \left(\frac{x_1}{x_1+2x_2}\right)^2 \kappa_1 + \left(\frac{2x_2}{x_1+2x_2}\right)^2 \kappa_2 + 2\left(\frac{x_1}{x_1+2x_2}\right)\left(\frac{2x_2}{x_1+2x_2}\right)\kappa_2 \tag{9}$$

where $\kappa_2 < \kappa_1$ and the component of which the specific electric conductivity is κ_2 contains the bivalent cations.

(11) M. Temkin, Acta Physicochim., URSS, **20** (1945), 411.

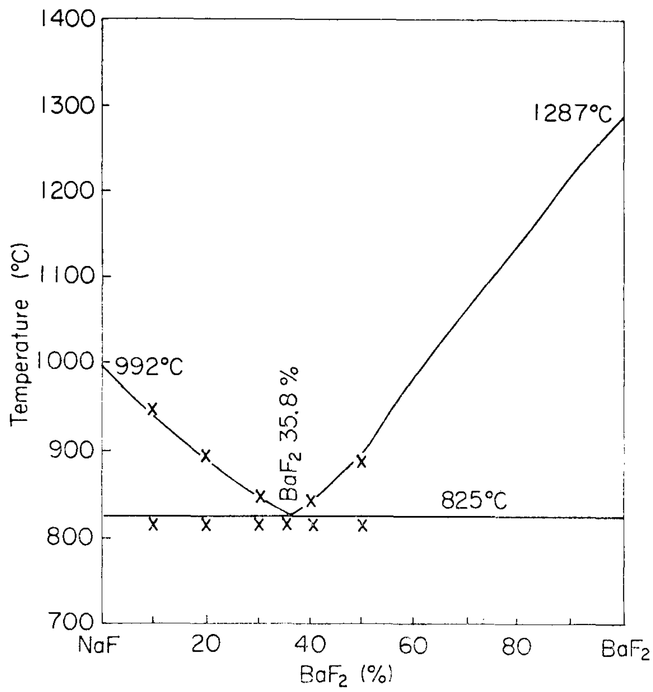

Fig. 3. Phase diagram of NaF-BaF_2 system (Weber).

The equation (9) is one of the modifications of "Markov's formula". We name it "Taniuchi's modified formula".

The specific electric conductivities of the binary NaF-$BaCl_2$ molten salts over the whole range of composition at 1000°C were calculated by Taniuchi's modified formula. The calculated values agreed well with the measured values as shown in Fig. 2(3), while the calculated values by "Grothe's formula" and "Kuroda's formula" deviated from the measured values as shown in this figure.

IV. The specific electric conductivities of the binary molten fluorides

As described above, the calculated values of the specific electric conductivities of binary NaF-$BaCl_2$ molten salts by Taniuchi's modified formula agreed with the measured values better than those by the other formulae. Therefore the specific electric conductivities of some binary molten salt systems with the combinations of univalent fluorides (KF, NaF) and bivalent fluorides (BaF_2, CaF_2) were measured and compared with their calculated values.

NaF-BaF_2 and NaF-CaF_2 binary molten salts are the salt mixtures which have relations to Hoopes' bath, Hurter's bath and Sumitomo's bath for the aluminum electrolytic refining. KF-BaF_2 and KF-CaF_2 binary molten salts are similar to the above-mentioned two binary molten salt systems.

The phase diagrams of the former three binary systems are of a simple eutectic type. In KF-CaF_2 binary system, however, a solid compound $KF \cdot CaF_2$ is formed and it forms the respective eutectics with KF and CaF_2.

Table 1. The specific electric conductivities of $NaF-BaF_2$ binary molten salts (at 1000°C).

Compositions (%)		Measured values of the specific electric conductivities ($ohm^{-1}\ cm^{-1}$)
NaF	BaF_2	
100.0	0	5.17
90.0	10.0	4.87_0
85.0	15.0	4.81_9
80.0	20.0	4.73_2
75.0	25.0	4.70_7
70.0	30.0	4.64_7
67.6	32.4	4.63
60.0	40.0	4.53_6
50.0	50.0	4.48_6

1. $NaF-BaF_2$ binary molten salt system

The phase diagram of this binary salts is reported by Weber(12),(13) as in Fig. 3. Pure barium fluoride melts at 1287°C, which is reported to be 1320°C in a recent study(14). This binary system is of a simple eutectic type and its eutectic temperature is 825°C with 35.8% BaF_2. The liquidus and eutectic temperatures of some compositions which melt below 1000°C were measured. These values of the present work are shown by cross points in Fig. 3 and they agreed well with the Weber's results.

The specific electric conductivities were measured at 1000°C with a few exceptions. In this binary molten salt system, the composition ranges which contain much barium fluoride have the freezing temperatures above 1000°C. Therefore the specific electric conductivities of the molten mixtures up to the composition range of 50% BaF_2 were measured.

Measured values are listed in Table 1.

In regard to the electric conductance of this binary molten salt, little work has been done except Thompson and Kaye's report on the mixture of NaF 25g and BaF_2 50g (equivalent to 67.6% NaF, M.P. 830°C)(15). Their results are shown in Fig. 4. The specific electric conductivity at 1000°C is given to be 4.603 ohm^{-1} cm^{-1}, while the corresponded value of the present work is 4.63 $ohm^{-1}\ cm^{-1}$(3).

The specific electric conductivities of barium fluoride at 1000°C are calculated by Taniuchi's modified formula by the use of the value of pure sodium fluoride (5.17 $ohm^{-1}\ cm^{-1}$) and that of the above-mentioned molten mixture (4.63 $ohm^{-1}cm^{-1}$). Though barium fluoride is not practically in a molten state at 1000°C, the calculated value was assumed to be the specific electric conductivity of the molten barium fluoride at 1000°C. And then, the specific electric conductivities of this

(12) K. Weber, Diplom-Arbeit Stuttgart (1925).
(13) V. Engelhardt, *Handbuch der technischen Elektrochemie*, III (1934), 29. Akademische Verlagsgesellschaft.
(14) G.J. Janz, *Molten Salts Handbook*, (1967), 3, Academic Press.
(15) M. deKay Thompson and A.L. Kaye, Trans. Am. Electrochem. Soc., **67** (1935), 169.

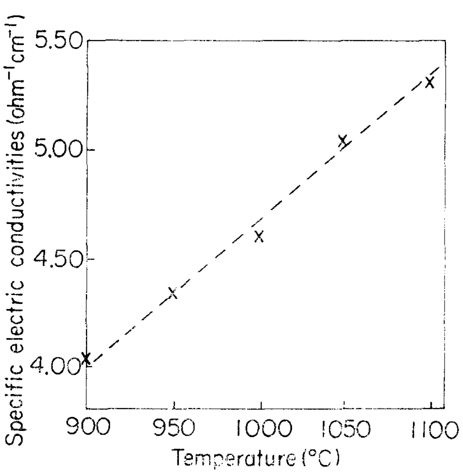

Fig. 4. Specific electric conductivities of NaF-BaF_2 binary molten salts (NaF 25g, BaF_2 50g) (Thompson and Kaye).

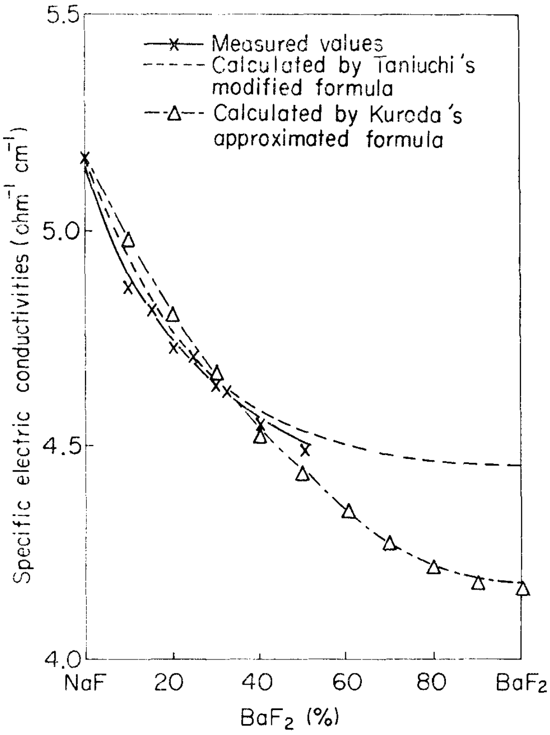

Fig. 5. Specific electric conductivities of NaF-BaF_2 binary molten salts at 1000°C.

binary molten salt system over the whole range of compositions at 1000°C were calculated by the use of both values of NaF and BaF_2. The dotted curve in Fig. 5 shows the calculated results, and the solid curve shows the measured values of the Table 1, which agreed with the calculated values very well. In addition, the calculated values by Kuroda's approximated formula are indicated in Fig. 5 as a dot-dash-curve in comparison with the former two results. They deviated much from the measured values.

The specific electric conductivities of NaF-BaF_2 binary molten salt

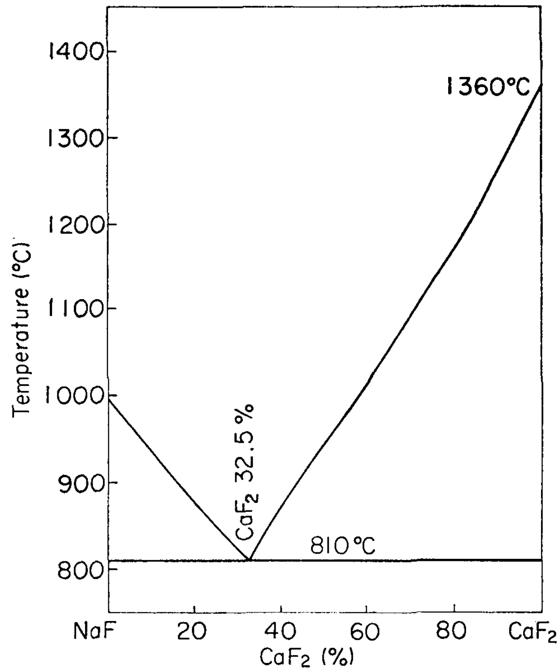

Fig. 6. Phase diagram of NaF-CaF_2 system (Fedotieff and Iljinsky).

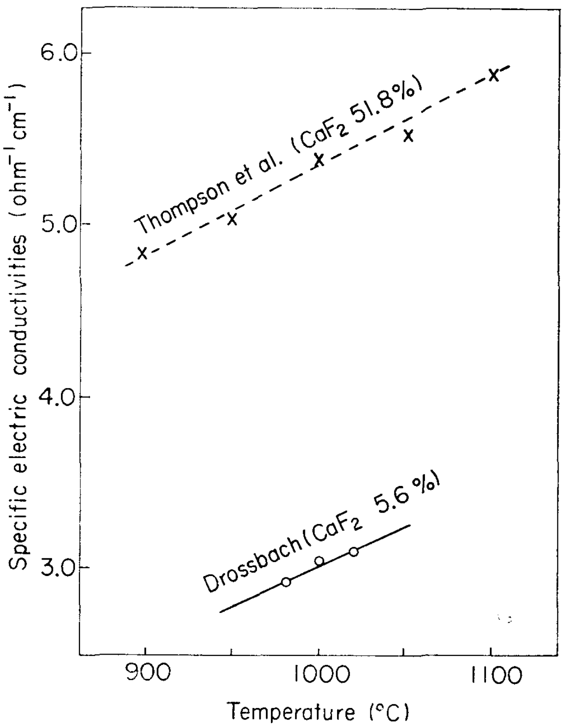

Fig. 7. Specific electric conductivities of NaF-CaF_2 binary molten salts.

decrease parabolically with the increase of the contents of barium fluoride and show the same tendency as in the case of NaF-$BaCl_2$ binary molten salt in the previous paper(3).

From above-mentioned results, the ionic species of this binary molten salt which take part in the electric conduction are assumed to be three kinds:

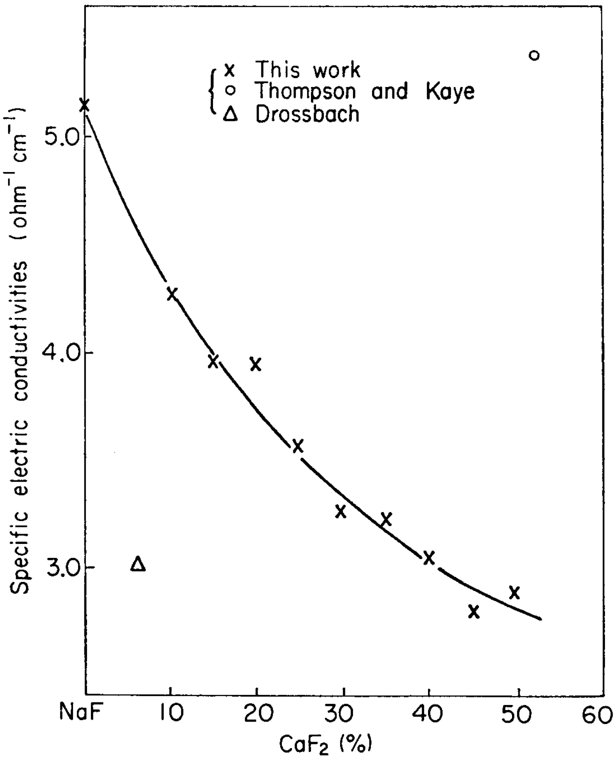

Fig. 8. Specific electric conductivities of NaF-CaF_2 binary molten salts at 1000°C.

Na^+, Ba^{++} and F^-.

2. NaF-CaF_2 binary molten salt system

The phase diagram of this binary system has been reported by Fedotieff and Iljinsky(16) as shown in Fig. 6. The melting temperature of pure calcium fluoride is 1360°C, which is reported to be 1418°C(14),(17) in a recent study. This binary system is of a simple eutectic type and the eutectic temperature is 810°C with 32.5% CaF_2.

As for the specific electric conductivity of molten calcium fluoride, Baak has reported that it is 3.56 ohm^{-1} cm^{-1} at its melting temperature, 1418°C(17),(18).

Few reports of the electric conductance of this binary molten salt seem to have been published except Thompson and Kaye's on the mixture of NaF 25 g and CaF_2 50 g which is equivalent to 51.8% CaF_2 and Drossbach's on the composition of 70 wt.% NaF which is equivalent to 5.6% CaF_2(19). These results are shown in Fig. 7.

The measured values of the specific electric conductivities in the present work at 1000°C are shown in Fig. 8 by cross points and a solid curve. The tendency of the conductance change of this binary system is similar to that of NaF-BaF_2

(16) P.P. Fedotieff und W.P. Iljinsky, Z. anorg. Chem., **129** (1923), 93.
(17) T. Baak, Acta Chemica Scand., **8** (1954), 1727.
(18) Yōyūen-Iinkai, *Tables for Properties of Molten Salts* (*Yōyūen-Busseihyō*) (1963), 131. Kagakudojin.
(19) P. Drossbach, *Elektrochemie geschmolzener Salze,* (1938), 73, Julius Springer.

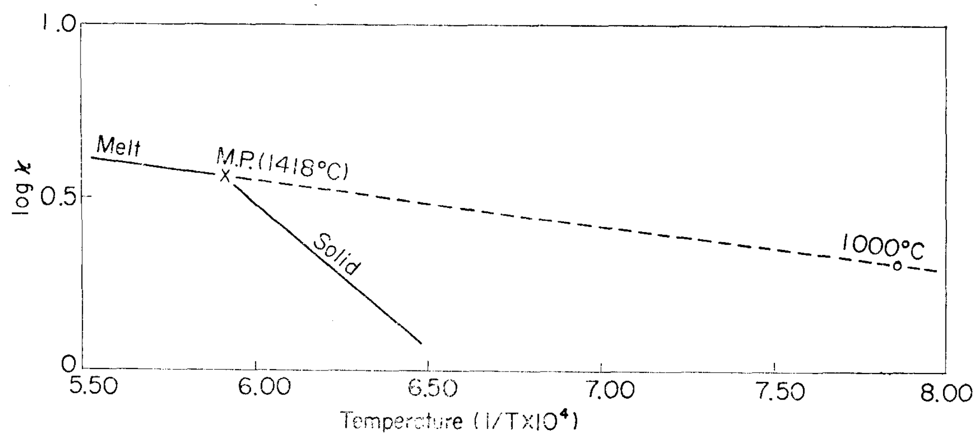

Fig. 9. Specific electric conductivities of CaF_2 (solid line: measured values of Baak).

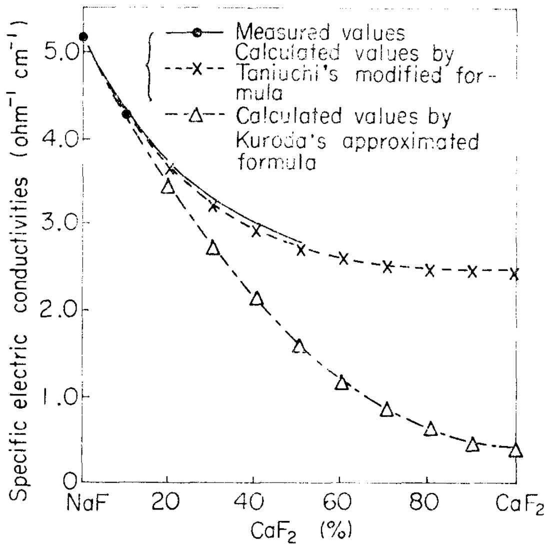

Fig. 10. Specific electric conductivities of NaF-CaF_2 binary molten salts at 1000°C.

system, that is, the specific electric conductivities of the binary molten salts decrease parabolically with the increase of the contents of calcium fluoride. When the content of calcium fluoride becomes higher, the melting temperatures of this binary molten salt system exceed 1000°C as shown in Fig. 6. Then, the specific electric conductivities of those compositions in a molten state cannot be measured at 1000°C. In comparison with the values of the present work, the results of Thompson and Kaye and of Drossbach are shown in Fig. 8 by an open circle point and a triangle point respectively. As the value of the former is larger than κ of pure sodium fluoride and the value of the latter is too small, we are of the opinion that both the values are unreasonable.

In the same way as stated above, the specific electric conductivity of pure calcium fluoride at 1000°C can be calculated by Taniuchi's modified formula. 2.45 $ohm^{-1}cm^{-1}$ was given from the measured values of pure sodium fluoride (5.17 ohm^{-1} cm^{-1}) and the binary molten mixture of 10% CaF_2 (4.27 $ohm^{-1}cm^{-1}$).

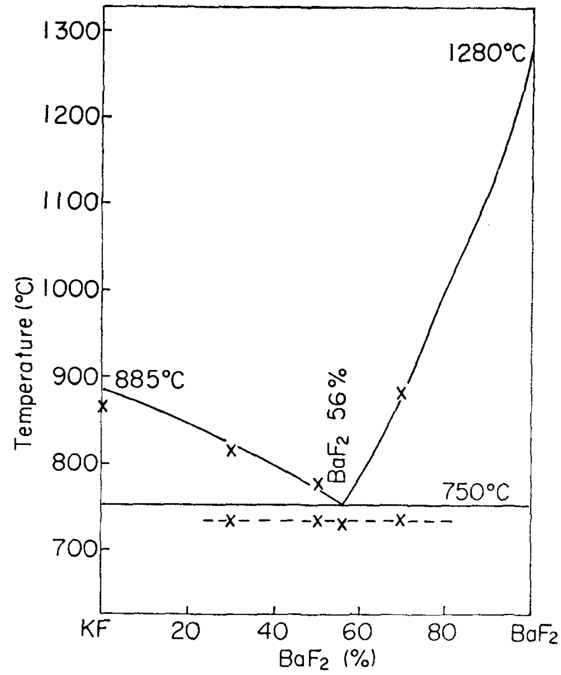

Fig. 11. Phase diagram of KF-BaF_2 system (Puschin and Baskow).

The results of the specific electric conductivity of calcium fluoride measured by Baak(17) in both liquid and solid states (i.e. above and below the melting temperatures) are shown in Fig. 9. Namely, the relation between the log κ and the reciprocal temperature, $1/T$ is rectilinear. When these measured values of κ in a liquid state is extrapolated to lower temperatures, it is estimated to be about 2 ohm^{-1} cm^{-1} at 1000°C which is indicated by an open circle point in Fig. 9. As the value calculated by Taniuchi's modified formula and Baak's extrapolated value are nearly equal to each other, the former is assumed to be reasonable.

The specific electric conductivities of this binary molten salt system over the whole range of compositions at 1000°C were calculated by the use of both values of NaF and CaF_2. These results are shown as a dotted curve in Fig. 10 and the solid curve indicates the measured values. These values agreed with the calculated values very well, while the values calculated by Kuroda's approximated formula deviated much from the measured values as shown in it as a dot-dash-curve.

Therefore, the ionic species of this binary molten salt which take part in the electric conduction are assumed to be three kinds: Na^+, Ca^{++} and F^-.

3. KF-BaF_2 binary molten salt system

As for the melting point of potassium fluoride, various values such as 846°C(20), 850°C(21), 856°C(14),(22) and 875°C(23), are reported. In the present work it was

(20) A.I. Beljajew, *Metallurgie des Aluminiums*, I, (1956), 48, Veb Verlag Technik.
(21) R.C. DeVries and R. Roy, J. Am. Chem. Soc., **75**, (1953), 2481.
(22) A.G. Bergmann and E.P. Dergunov, Compt. Rend. Acad. Sci., URSS, 31 (1941), 753.
(23) P.P. Fedotieff und R. Timofeeff, Z. anorg. Chem., **206** (1932), 265.

Table 2. The specific electric conductivities of KF-BaF_2 binary molten salts (at 1000°C).

Compositions (%)		Measured values of the specific electric conductivities (ohm^{-1} cm^{-1})
KF	BaF_2	
100	0	4.78
90	10	4.72_1
80	20	4.58_6
70	30	4.53_0
60	40	4.51_8
50	50	4.48_3
40	60	4.46_6
30	70	4.43_1

measured to be 867°C.

The phase diagram of KF-BaF_2 binary molten salt system is reported by Puschin and Baskow[(24)] as shown in Fig. 11. The melting temperature of potassium fluoride is 885°C. This binary system is also of a simple eutectic type and the eutectic temperature is 750°C with 56% BaF_2. In this figure, cross points indicate the measured values of the liquidus and the eutectic temperatures in the present work for some compositions which melt at comparatively low temperatures. As shown in Fig. 11, these measured liquidus temperatures are 730°~734°C and are lower than the values of Puschin and Baskow. According to the recent study by Bukhalova and Sementsova[(25)], the eutectic temperature of this binary molten salt is 728°C and this value closely approximates to our result.

As for the specific electric conductivity of potassium fluoride, various values are also reported and some values at 1000°C are listed as follows:

4.50 $ohm^{-1}cm^{-1}$[(26)], 4.70_1 $ohm^{-1}cm^{-1}$[(27)],

$4{\cdot}72_1$ $ohm^{-1}cm^{-1}$[(19)], 4.77 $ohm^{-1}cm^{-1}$[(18)].

The measured value in the present work was 4.78 $ohm^{-1}cm^{-1}$ and this value agreed well with those of the other authors except that of Yim and Feinleib[(26)].

No reports of the specific electric conductivities of this binary molten salts seem to have been published yet. The specific electric conductivities measured at 1000°C up to the composition range of 70% BaF_2 are listed in Table 2. According to the same idea as mentioned in Section 1, the values of this binary salts over the whole range of compositions at 1000°C were calculated by the use of the values of KF (4.78 $ohm^{-1}cm^{-1}$) and BaF_2 (4.44 $ohm^{-1}cm^{-1}$). They are shown as a dotted curve in Fig. 12. As the contents of barium fluoride increase, the specific electric conductivities of the binary salt system decrease almost parabolically as in the case of NaF-BaF_2 binary system.

The solid curve in Fig. 12 indicates the measured specific electric conductivities

(24) N.A. Puschin und A.W. Baskow, Z. anorg. Chem., **81** (1913), 360.
(25) G.A. Bukhalova and D.V. Sementsova, Zh. Neorg. Khim., **12** (1967), 795.
(26) E.W. Yim and M. Feinleib, J. Electrochem. Soc., **104** (1957), 626.
(27) G.J. Janz, *Molten Salts Handbook*, (1967), 290, Academic Press.

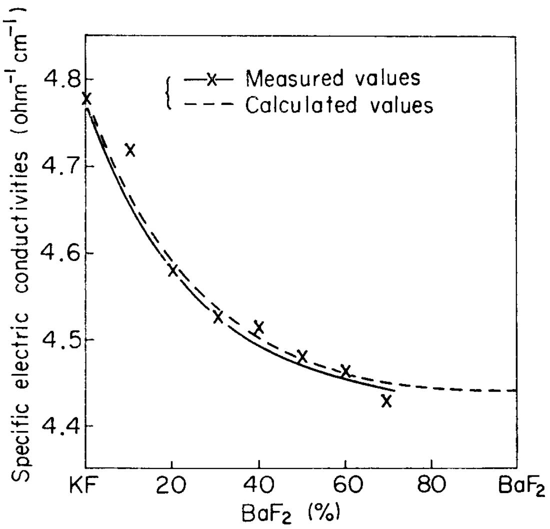

Fig. 12. Specific electric conductivities of KF-BaF_2 binary molten salts at 1000°C.

for the compositions which melt at comparatively low temperatures below 1000°C as shown in Table 2. These results agreed well with the calculated values.

Consequently, the ionic species which take part in the electric conduction in this binary molten salt system are assumed to be three kinds: K^+, Ba^{++} and F^-.

4. KF-CaF_2 binary molten salt system

The phase diagram of this binary system is reported by Krause and Bergmann[28]. As shown in Fig. 13, potassium fluoride and calcium fluoride form a compound KF·CaF_2 which melts at 1070°C, unlike the other three above-described binary salt systems. And this compound forms respective eutectics with KF and CaF_2. One of these two eutectics has the composition of 13.6% CaF_2 and melts at 782°C, and the other has the composition of 54.3% CaF_2 and melts at 1054°C. The cross points in this figure indicate the measured liquidus and the eutectic temperatures in the present work, which agree well with Krause and Bergmann's results.

Fig. 14 shows the results of the X-ray diffraction pattern for the solidified binary mixture with 40% CaF_2. The formation of the compound KF·CaF_2 may be confirmed by this figure. In this binary molten salts, the composition ranges which contain less than about 30% CaF_2 have the liquidus temperatures below 1000°C as shown in Fig. 13.

In regard to the electric conductivities of this binary molten salt system, few works seem to have been done also. The measured values of the specific electric conductivities at 1000°C are listed in Table 3.

According to the same idea as mentioned in Section 1, the specific electric conductivities of this binary molten salt system over the whole range of compositions at 1000°C were calculated from the values of KF and CaF_2. These values

(28) I.E. Krause and A.G. Bergmann, Compt. Rend. Acad. Sci., URSS, **35** (1942), 20.

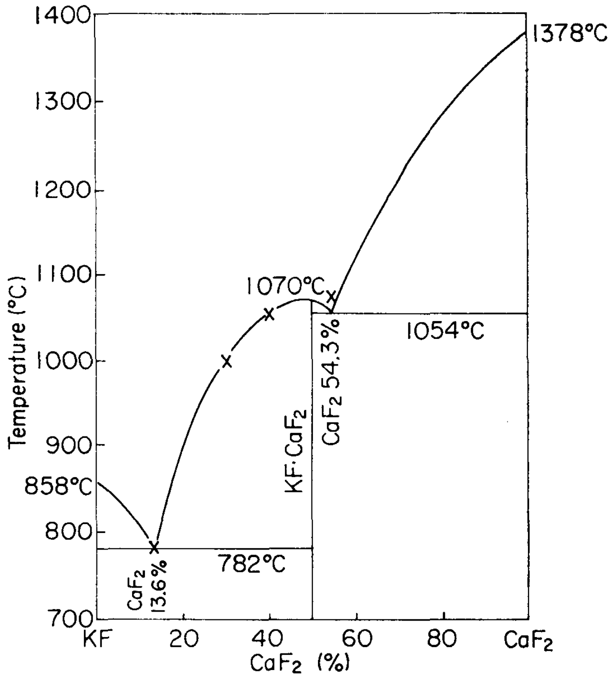

Fig. 13. Phase diagram of KF-CaF_2 system (Krause and Bergmann).

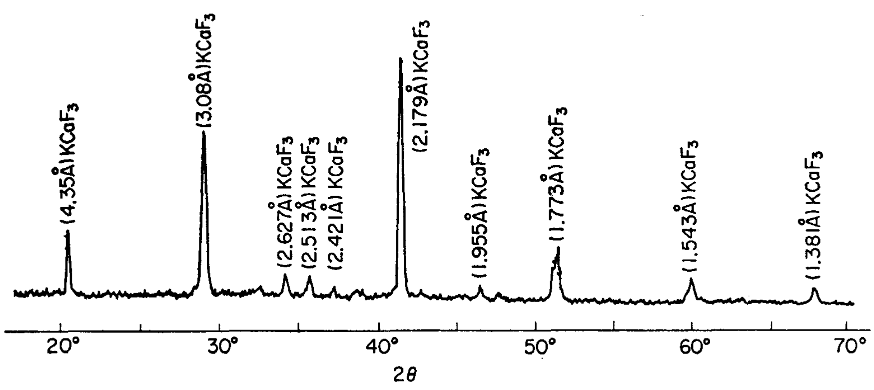

Fig. 14. X-ray diffraction pattern of KF-CaF_2 binary salts (CaF_2 40%).

Table 3. The specific electric conductivities of KF-CaF_2 binary molten salts (at 1000°C).

Compositions (%)		Measured values of the specific electric conductivities ($ohm^{-1}\ cm^{-1}$)
KF	CaF_2	
100	0	4.78
90	10	3.90
80	20	3.37
70	30	2.92
50	50	2.80*

* Measured value at 1070°C

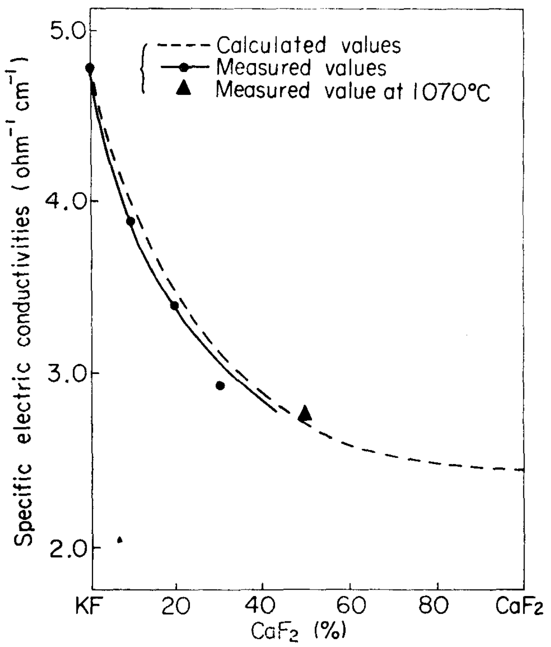

Fig. 15. Specific electric conductivities of KF-CaF_2 binary molten salts at 1000°C.

are shown as a dotted curve in Fig. 15, while the measured values in Table 3 are plotted and shown as a solid curve. The measured values agreed well with the calculated values in this case also.

As the contents of calcium fluoride increases, the specific electric conductivities of this binary molten salt system decrease parabolically. That is, Taniuchi's modified formula can be applied to the electric conductance of this binary molten salt system also. For this reason, we can assume that the molten salts of this binary system are in a mixing state of Temkin's type and it is not necessary to give special consideration to the existence of the compound KF·CaF_2 at such a high temperature as 1000°C. Then, the ionic species which take part in the electric conduction in this binary molten salt system are assumed to be three kinds: K^+, Ca^{++} and F^-.

From the above-mentioned results, we are of the opinion that sodium fluoride cannot be replaced by potassium fluoride in the aluminum refining electrolytes from the viewpoint of the electric conductivity at least, because the specific electric conductivity of the latter is smaller than that of the former. In addition, potassium fluoride is more hygroscopic than sodium fluoride, which is also its demerit.

5. Conclusion

The specific electric conductivities of four binary molten salt systems (NaF-BaF_2, NaF-CaF_2, KF-BaF_2 and KF-CaF_2) related to the electrolytes for aluminum refining were measured at 1000°C.

From the results we may reasonably conclude as follows:

1) In these binary molten salt systems, when barium fluoride or calcium fluoride are added to sodium fluoride or potassium fluoride, the specific electric conductivities decrease almost parabolically with the increase of the contents of the added fluorides.

2) We modified "Markov's formula" for the calculation of the specific electric conductivities of binary molten salts and named it "Taniuchi's modified formula".

The values calculated by our formula agreed well with the measured values.

3) The phase diagrams of NaF-BaF_2, NaF-CaF_2 and KF-BaF_2 binary systems are all of a simple eutectic type, while in KF-CaF_2 binary system a compound $KF \cdot CaF_2$ is formed.

According to the above-mentioned results of the specific electric conductivities of each binary system, the ionic species which take part in the electric conduction are assumed to be Na^+, K^+, Ba^{++}, Ca^{++} and F^-.

4) We are of the opinion that sodium fluoride cannot be replaced by potassium fluoride in the aluminum refining electrolytes, because the latter is less electrically conductible and more hygroscopic.

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