THE STRUCTURE OF ALUMINA DISSOLVED IN CRYOLITE MELTS

Halvor Kvande
Årdal og Sunndal Verk a.s.
P.O. Box 5177, Majorstua
N - 0302 Oslo 3
Norway

A structural model with three oxygen-containing species: $Al_2OF_6^{2-}$, $Al_2OF_8^{4-}$ and $Al_2O_2F_4^{2-}$, is used to calculate their mol fractions in cryolite-alumina melts. For low alumina contents in cryolite all three species are found to be of about equal importance, while $Al_2O_2F_4^{2-}$ ions are dominating at high alumina contents. Increasing bath acidity will favour the relative amount of $Al_2OF_6^{2-}$ ions. Chemical equations for the formation of these species are suggested, as well as possible anode reactions during electrolysis. The occurrence of the anode effect is discussed in terms of the present results.

Introduction

Because of its industrial interest, the structure of dissolved alumina in molten cryolite is probably one of the most investigated subjects in molten salt chemistry (1). In spite of the large number of investigations, however, the problem is not yet resolved. This year, at the hundredth anniversary of the Hall-Héroult process, is a good opportunity for reviewing the situation and looking at the present status of our knowledge on the ionic species formed when alumina dissolves in cryolite melts.

For the last forty to fifty years there have been numerous suggestions of possible oxygen-containing ionic species in cryolite-alumina melts (2). Most of these species are now of historical interest, and it is generally agreed that aluminium-oxygen-fluorine complexes are formed. In the 1960-ies and the first half of the 1970-ies there seemed to be little doubt that alumina dissolved predominantly as oxyfluoride complexes of the type $AlOF_x^{1-x}$ (3). However, cryoscopic measurements of Ratkje and Förland (4,5) indicated that $Al_2OF_x^{4-x}$ complexes were dominating for low alumina contents in basic melts (high NaF/AlF_3 molar ratio). These complexes were not the only ones formed, however, and the authors (5) proposed the following equilibrium reaction in these melts at low alumina contents:

$$Al_2OF_x^{4-x} = AlOF_y^{1-y} + AlF_{x-y}^{(3-x+y)} \quad (1)$$

Probable values for x are 6 or 8 in this equation, while y may be 2. The species $AlF_{x-y}^{(3-x+y)}$ is then AlF_6^{3-} or AlF_4^-, the most important complexes in oxide-free cryolite melts.

A major breakthrough came in 1976 when Gilbert, Mamantov, and Begun (1) succeeded in detecting alumina concentrations as low as 2 mol% (1 wt%) in cryolite melts by Raman spectroscopy. The exact nature of the alumina species could not be determined, but only those which have bridging Al-O-Al bonds, corresponding to $Al_2OF_x^{4-x}$ complexes, were considered. This was done because species

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involving non-bridging Al-O bonds, i.e., the previously accepted species $AlOF_x^{1-x}$, were not consistent with the bands observed by the Raman spectroscopic measurements. These species were then eliminated from consideration in cryolite melts containing more than 3 to 5 mol% Al_2O_3.

Sterten (6) used experimental activity data for NaF and AlF_3 in melts saturated with alumina to develop an ionic model for these melts, based on the assumption of an ideal ionic mixture. He found that the oxygen atoms in the complexes most probably are involved in bridging bonds, which imply the species $Al_2OF_x^{4-x}$ and $Al_2O_2F_x^{2-x}$. Again, the species $AlOF_x^{1-x}$ were found to be of minor importance. In very basic melts (molar ratio of NaF/AlF_3 higher than 5) the species $Al_2O_2F_4^{2-}$ and $Al_2O_2F_6^{4-}$ were dominating, while in acidic melts (molar ratio less than 3) the complexes $Al_2OF_6^{2-}$ and $Al_2O_2F_4^{2-}$ were the most important.

Julsrud (7) used both cryoscopic and calorimetric measurements to develop a thermodynamic model for cryolite-alumina melts. His oxygen-containing species were $Al_2OF_6^{2-}$, $Al_2OF_8^{4-}$, $Al_2OF_{10}^{6-}$, $Al_2O_2F_4^{2-}$, and $Al_2O_2F_6^{4-}$. From the interpretation of vapour pressure measurements the present author (8,9) found that $Al_2OF_8^{4-}$ was probably the most important species formed at low alumina contents in molten cryolite.

Objective of the present work

The purpose of the present work is to attempt to reach a step further towards a solution to the problem of the structure of dissolved alumina in cryolite melts. The major source of information from the literature will be the model of Sterten (6) and the thermodynamic data of Julsrud (7). This leads to some important changes in Sterten's data for the anion fractions of the Al-O-F species for various NaF/AlF_3 molar ratios in melts saturated with alumina.

Furthermore, calculated data for cryolite-alumina melts not saturated with alumina will be presented. From the literature it is unknown how the mol fractions of the oxygen-containing species vary with increasing alumina content in molten cryolite.

The effects of the bath acidity, the temperature and the common additives will be discussed, and some of the physico-chemical properties of the melt may be explained by the structural species present. Chemical equations for the dissolution of alumina are presented, as well as equations for the anode reactions during electrolysis. Finally, the occurrence of the anode effect is discussed in terms of the mol fractions of the Al-O-F complex species present in these melts at low alumina contents.

Dissolution of alumina in cryolite melts

The solubility of alumina has its maximum value at, or very close to, the cryolite composition (2). It is therefore reasonable to assume that alumina reacts with the aluminium hexafluoride ion (AlF_6^{3-}) when it dissolves:

$$Al_2O_3 + 4\ AlF_6^{3-} = 3\ Al_2OF_6^{2-} + 6\ F^- \quad (2)$$

$$Al_2O_3 + 4\ AlF_6^{3-} = 3\ Al_2OF_8^{4-} \quad (3)$$

$$Al_2O_3 + AlF_6^{3-} = \frac{3}{2}\ Al_2O_2F_4^{2-} \quad (4)$$

As will be shown later, these species are the most important ones in melts of industrial interest (NaF/AlF_3 molar ratios between 2 and 3). The stoichiometry of eqns. (3) and (4) indicates that both $Al_2OF_8^{4-}$ and $Al_2O_2F_4^{2-}$ have their maximum concentrations at the cryolite composition, while $Al_2OF_6^{2-}$ has its maximum on the acidic side of the system, at a molar ratio of 1.5.

These reactions involving Al_2O_3 are fairly straightforward, but they may be viewed more as total reactions. An alternative reaction sequence would be that Al_2O_3 first dissociates and then the dissociation products react with ions in the cryolite melt. If we then try to write step equations for the dissolution of alumina, we first consider the dissociation reaction. Since Al^{3+} ions are very unlikely to be present in cryolite melts, the following two dissociation reactions may be possible:

$$Al_2O_3 \rightarrow 2\ AlO^+ + O^{2-} \quad (5)$$

$$Al_2O_3 \rightarrow Al_2O^{4+} + 2\ O^{2-} \quad (6)$$

The arrow indicates that the reactions are shifted completely to the right. Furthermore, these dissociation products are not stable and react immediately in cryolite melts.

Reactions with F^- ions are less likely, since the solubility of alumina in pure molten NaF is extremely low. We therefore expect that the dissociation products will react with $AlF_6{}^{3-}$ ions in the cryolite melt. Reaction (6) is then considered less important, since it is not expected that Al_2O^{4+} ions would react with $AlF_6{}^{3-}$ ions to form a species with three aluminium atoms.

Thus, eqn. (5) is probably much more important, and we will then write formal equations for the formation of the three main oxygen-containing species in molten cryolite. Again, it is emphasized that the AlO^+ and O^{2-} ions are not stable in these melts, as indicated by the arrows in the reactions that follow. First, for $Al_2OF_6{}^{2-}$:

$$AlO^+ + AlF_6{}^{3-} \rightarrow Al_2OF_6{}^{2-} \quad (7)$$

$$O^{2-} + 2\ AlF_6{}^{3-} \rightarrow Al_2OF_6{}^{2-} + 6\ F^- \quad (8)$$

If eqn. (7) is multiplied by 2 and eqn. (8) is added, we get the following reaction:

$$2\ AlO^+ + O^{2-} + 4\ AlF_6{}^{3-} \rightarrow 3\ Al_2OF_6{}^{2-} + 6\ F^- \quad (9)$$

Then we have for $Al_2OF_8{}^{4-}$:

$$AlO^+ + AlF_6{}^{3-} + 2\ F^- \rightarrow Al_2OF_8{}^{4-} \quad (10)$$

$$O^{2-} + 2\ AlF_6{}^{3-} \rightarrow Al_2OF_8{}^{4-} + 4\ F^- \quad (11)$$

and combining eqns. (10) and (11) gives:

$$2\ AlO^+ + O^{2-} + 4\ AlF_6{}^{3-} \rightarrow 3\ Al_2OF_8{}^{4-} \quad (12)$$

Finally, for $Al_2O_2F_4{}^{2-}$:

$$AlO^+ + 2\ F^- \rightarrow \frac{1}{2}\ Al_2O_2F_4{}^{2-} \quad (13)$$

$$O^{2-} + AlF_6{}^{3-} \rightarrow \frac{1}{2}\ Al_2O_2F_4{}^{2-} + 4\ F^- \quad (14)$$

and combining eqns. (13) and (14) gives:

$$2\ AlO^+ + O^{2-} + AlF_6{}^{3-} \rightarrow \frac{3}{2}\ Al_2O_2F_4{}^{2-} \quad (15)$$

It has been shown that three new species are formed when a small amount of alumina is added to pure molten cryolite (2), while this number is gradually reduced at higher alumina contents. Eqns. (9),(12), and (15) then indicate that the species $Al_2OF_6{}^{2-}$ and $Al_2OF_8{}^{4-}$ will be more important for low alumina additions, and that $Al_2O_2F_4{}^{2-}$ may dominate at high alumina contents.

Species present in cryolite melts saturated with alumina

Julsrud (7) has determined the value of the equilibrium constant for the reaction:

$$Al_2OF_6{}^{2-} + 2\ F^- = Al_2OF_8{}^{4-},\ K_{(16)} = 13.0, \quad (16)$$

By setting the activities of the complex ions equal to their mol fractions, we may write:

$$K_{(16)} = \frac{a_{Al_2OF_8{}^{4-}}}{a_{Al_2OF_6{}^{2-}} \cdot a^2{}_{F^-}} =$$

$$= \frac{N_{Al_2OF_8{}^{4-}}}{N_{Al_2OF_6{}^{2-}} \cdot a^2{}_{F^-}} = 13.0 \qquad (17$$

Here, a_{F^-} means the activity of NaF in the melt, and is thus not a single ion activity.

Rearrangement of eqn. (17) then gives:

$$\frac{N_{Al_2OF_8{}^{4-}}}{N_{Al_2OF_6{}^{2-}}} = 13.0 \cdot a^2{}_{F^-} \qquad (18$$

The present author (8) calculated the activity of NaF (a_{F^-}) to be 0.38 in pure cryolite and 0.30 in cryolite saturated with alumina at 1300 K. These data give the ratio of the oxygen-containing ions in eqn. (18) to be 1.9 and 1.2 at these compositions. Sterten's (10) activity data give ratios of 1.6 and 1.5, respectively. Thus, in any case the mol fraction of $Al_2OF_8{}^{4-}$ is higher than that of $Al_2OF_6{}^{2-}$ in cryolite-alumina melts, based on these activity data and the value of the equilibrium constant of eqn. (16) given by Julsrud (7).

Sterten (6) did not discuss specifically the presence of $Al_2OF_8{}^{4-}$ species in these melts even if it is included in his model, and he did not give any value for the equilibrium constant of eqn. (16). An indirect comparison of his and Julsrud's data may be made for the reaction:

$$Al_2OF_6{}^{2-} + 4\ F^- = Al_2OF_{10}{}^{6-} \qquad (19)$$

The equilibrium constant of eqn. (19) is 12.6 according to Julsrud (7), while the value of 7.9 may be calculated from the data of Sterten (6). For 1250 K (977 °C) these data give Gibbs energy values of -26.3 kJ/mol and -21.5 kJ/mol, respectively, for reaction (19), and the agreement may be considered as satisfactory. It is noted here that the activities of NaF show that $N_{Al_2OF_{10}{}^{6-}}$ is only 10 to 20 % of $N_{Al_2OF_6{}^{2-}}$ in cryolite-alumina melts, and it may thus be neglected.

For the reaction:

$$Al_2O_2F_4{}^{2-} + 2\ F^- = Al_2O_2F_6{}^{4-} \qquad (20)$$

the equilibrium constant given by Julsrud is 1.1 and by Sterten 0.5. The activity data then show that $N_{Al_2O_2F_6{}^{4-}}$ is only about 10 % of $N_{Al_2O_2F_4{}^{2-}}$ in cryolite-alumina melts.

Of much more interest is the reaction:

$$2\ Al_2OF_8{}^{4-} = Al_2O_2F_4{}^{2-} + 2\ AlF_6{}^{3-} \qquad (21)$$

$$K_{(21)} = 13.2$$

where the equilibrium constant is given by Julsrud (7). The ratio of the mol fractions is expressed as:

$$\frac{N_{Al_2O_2F_4{}^{2-}}}{N^2{}_{Al_2OF_8{}^{4-}}} = \frac{13.2}{a^2{}_{AlF_6{}^{3-}}} \qquad (22)$$

Activity data for Na_3AlF_6 in cryolite melts (10) then show that $N_{Al_2OF_8{}^{4-}}$ is 3 to 4 times higher at very low alumina contents, but that $N_{Al_2O_2F_4{}^{2-}}$ is 3 to 6 times higher than $N_{Al_2OF_8{}^{4-}}$ in molten cryolite saturated with alumina.

Now we consider the results of Sterten (6) given in Fig. 1. This figure shows correctly that the two dominating species are $Al_2O_2F_4{}^{2-}$ and $Al_2O_2F_6{}^{4-}$ in very basic melts (molar ratio of NaF/AlF_3 higher than 5), and $Al_2OF_6{}^{2-}$ and $Al_2O_2F_4{}^{2-}$ in very acidic melts (molar ratio less than 2). Possibly, the $Al_2OF_6{}^{2-}$ peak may be too high, since Sterten did not find the maximum alumina solubility close to the cryolite composition, but for a more acidic melt.

In the NaF/AlF_3 molar ratio range of 2 to 3, which is of major industrial interest, the species $Al_2OF_8{}^{4-}$, which was negligible according to Sterten's calculations, is

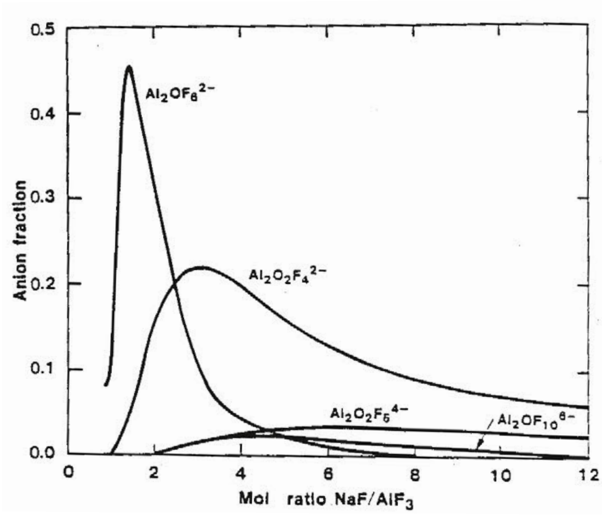

Fig. 1.
Calculated anion fractions of Al-O-F complexes as a function of NaF/AlF$_3$ mol ratio, for melts saturated with alumina at 1012 °C, from Sterten (6).

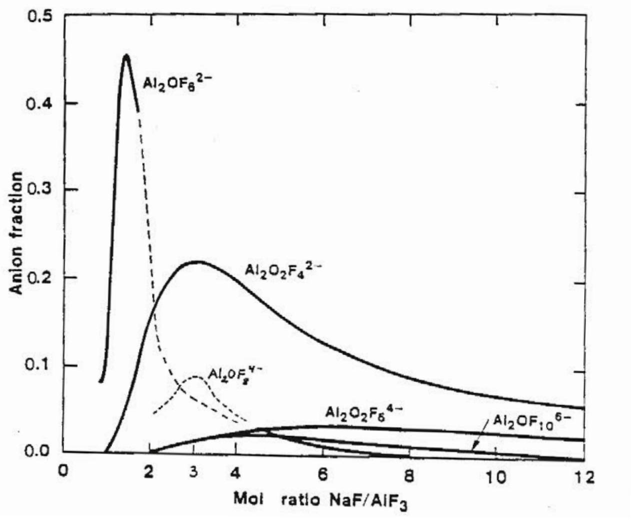

Fig. 2.
Calculated anion fractions of Al-O-F complexes as a function of NaF/AlF$_3$ mol ratio, for melts saturated with alumina at 1012 °C, from Sterten (6). The changes from Fig. 1 are shown as dashed lines for $Al_2OF_6^{2-}$ and $Al_2OF_8^{4-}$, calculated from the present work.

present with about the same mol fraction as $Al_2OF_6^{2-}$. Fig. 2 is an improved version of Sterten's figure. The changes that have been made, are indicated by the dashed lines for $Al_2OF_8^{4-}$ and $Al_2OF_6^{2-}$ in the molar ratio range between 2 and 3. These dashed lines then illustrate the principal changes required in Sterten's figure when $Al_2OF_8^{4-}$ species are included.

Species present in cryolite melts not saturated with alumina

As mentioned previously, it is unknown from the literature how the mol fractions of the oxygen-containing species vary with increasing alumina content in cryolite melts. On the basis of the literature data (6,7,10) and the assumption of ideal ionic mixture, calculations have been performed to illustrate this. The three dominating species were assumed to be $Al_2OF_8^{4-}$, $Al_2OF_6^{2-}$, and $Al_2O_2F_4^{2-}$.

The results for cryolite are shown in Fig. 3. It is interesting to note the shift from $Al_2OF_8^{4-}$ and $Al_2OF_6^{2-}$ as dominating at low alumina contents (less than about 5 mol%, or 2.5 wt%), to the complete dominance of $Al_2O_2F_4^{2-}$ for alumina contents approaching saturation. It is also seen that $Al_2OF_8^{4-}$ is more important than $Al_2OF_6^{2-}$ in molten cryolite in the whole alumina concentration range.

Similar curves may be drawn for baths with different NaF/AlF$_3$ molar ratios. In the following a brief discussion is given of the effects of increasing bath acidity, lower bath temperature, and also addition of the common fluorides used industrially.

Increasing bath acidity

Increasing bath acidity implies reduced activity of NaF. This increases the relative importance of $Al_2OF_6^{2-}$, while the mol fractions of $Al_2OF_8^{4-}$ and $Al_2O_2F_4^{2-}$ decrease. Common bath compositions used in industrial cells are mainly in the range of molar ratios of 2.6 to 2.2, corresponding to 6 to 13 wt% AlF$_3$ in excess of the cryolite composition. For these concentrations the general trend is the same as illustrated in Fig. 3. For more traditional compositions with ratios close to 2.6, the amounts of $Al_2OF_8^{4-}$ and $Al_2OF_6^{2-}$ are about equal. At a

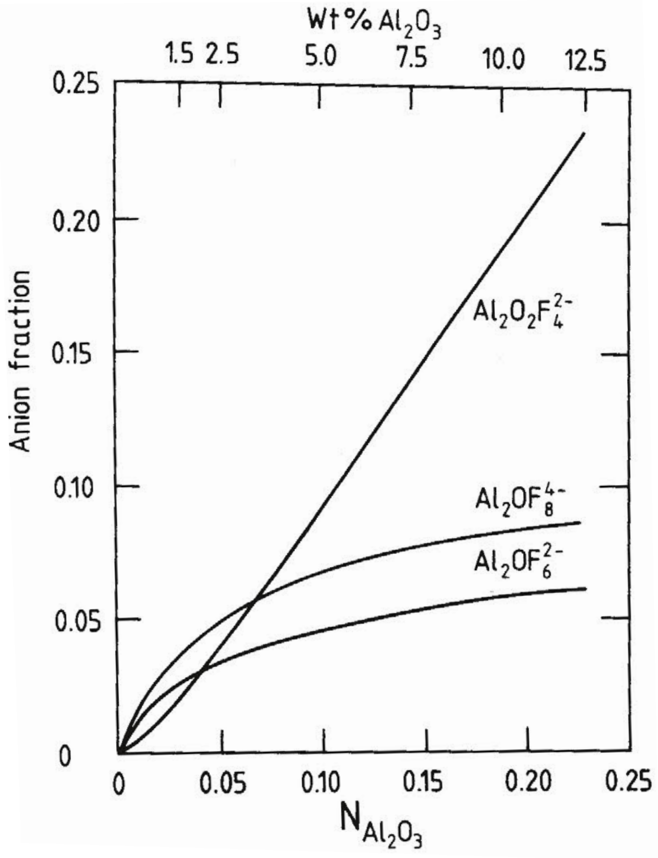

Fig. 3.
Calculated anion fractions of Al-O-F complexes in molten cryolite as a function of the mol fraction of alumina added at 1012 °C.

NaF/AlF_3 molar ratio of 2.2, the species $Al_2OF_6^{2-}$ is more important than $Al_2OF_8^{4-}$ for all alumina additions (by a factor of about 2), but still $Al_2O_2F_4^{2-}$ is completely dominating close to saturation of alumina.

Lower bath temperature

The values of the equilibrium constants of the two main reactions, eqns. (16) and (21), are dependent on the bath temperature and so are the activities of Na_3AlF_6 and NaF. Julsrud (7) considered the values of these equilibrium constants to be unchanged by a temperature reduction of 20 °C, while the activities then will decrease very little (10). The importance of $Al_2OF_6^{2-}$ will increase relative to $Al_2OF_8^{4-}$ and $Al_2O_2F_4^{2-}$ when the bath temperature is lowered, but the changes are small.

Additives: CaF_2, LiF, and MgF_2

These additives all reduce the alumina solubility and the activity of Na_3AlF_6 in the melt. LiF is an F^- donor (2), and increases the relative importance of $Al_2OF_8^{4-}$ in acidic baths. CaF_2 and MgF_2 are F^- acceptors (2,11) and thus favour $Al_2OF_6^{2-}$. The combined effect of fluoride additives to the bath and lower bath temperature is expected to be determined mainly by the influence of the additives, but the changes are not very drastic in most cases.

Physico-chemical properties of cryolite-alumina melts

Here some of the physico-chemical properties of cryolite-alumina melts will be briefly discussed in view of the complex Al-O-F species present.

Alumina solubility

The alumina solubility has its maximum value at, or very close to the cryolite composition (2,12), and thus it decreases in both acidic and basic melts. As mentioned previously it is reasonable to assume that the solubility is directly influenced by the availability of AlF_6^{3-} ions in the melt. The phase diagram of the system NaF-AlF_3-Na_2O-Al_2O_3 given by Foster (12) shows that the solubility is extremely low in pure NaF, and about 3 wt% Al_2O_3 is soluble in very acidic melts, saturated with AlF_3. In the latter concentration range the species $Al_2OF_6^{2-}$ will be completely dominating. Since the activity of Na_3AlF_6 then will be very low, AlF_4^- ions are probably involved in the formation of $Al_2OF_6^{2-}$.

Density

The density of cryolite melts decreases with increasing alumina addition, in spite of the high density of alumina itself (2). This has been interpreted as due to the formation of voluminous Al-O-F complexes, but presently it is very difficult to discuss the density data in terms of which complex species that may dominate for different bath compositions.

Electrical conductivity

The electrical conductivity decreases strongly with increasing alumina addition to cryolite melts (2). This is assumed to be caused by a relative decrease in the concentration of Na^+ ions, which contribute considerably to the conductivity of cryolite melts. Thus, it is not very probable that the aluminium oxyfluoride species are of direct influence here.

Viscosity

Törklep and coworkers (13,14) have published some very accurate viscosity measurements in the system $NaF-AlF_3-Al_2O_3$, see Fig. 4. The viscosity increases with increasing content of alumina, and particularly for basic melts the influence of the alumina is very drastic. In attempting to interpret the shape of their viscosity curves, the authors (14) used the following pairs of oxygen-containing species in their model for the melt:

$Al_2O_2F_4^{2-}$ - $Al_2OF_6^{2-}$

$AlOF_3^{2-}$ - $Al_2OF_8^{4-}$

$Al_2O_2F_6^{4-}$ - $Al_2OF_6^{2-}$

However, none of these models were found to describe the experimental data in even a qualitative way. If we look at the selected pairs from the point of view of Figs. 2 and 3, it is realized that a two-species model cannot be expected to be sufficient to cover the whole range of NaF/AlF_3 molar ratios. A three-species model is required, and even then the concentration range should be limited, for example to baths of industrial interest.

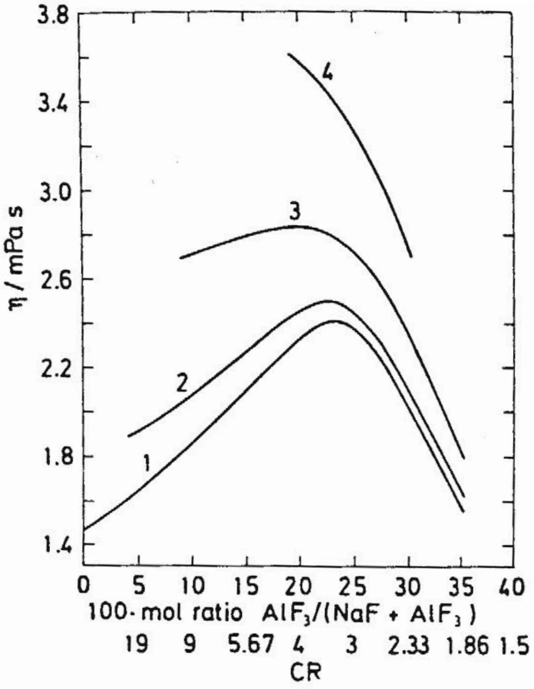

Fig. 4.
Isothermal viscosity-composition curves for $NaF-AlF_3-Al_2O_3$ melts at 1000 °C, from Törklep and Øye (13). The numbers have the following meaning:
1. 0 % Al_2O_3.
2. 4 wt.% Al_2O_3.
3. 8 wt.% Al_2O_3.
4. 12 wt.% Al_2O_3.

According to Figs. 1 and 2 the species $Al_2O_2F_4^{2-}$ is completely dominating in the basic melts where the alumina content gave rise to a very high increase in the viscosity values. Possibly this species will give a high intrinsic viscosity compared to $Al_2OF_8^{4-}$ and $Al_2OF_6^{2-}$. It has also been suggested to describe the melt structure at high alumina concentrations by large undefined clusters (network formation), (13, 14).

Anode reaction

It is generally accepted that the oxygen for formation of $CO_2(g)$ is transported to the anode in the form of Al-O-F complexes. The equations for possible anode reactions involving the three main species are written:

$$4\ F^- + 2\ Al_2OF_6^{2-} + C = CO_2 + 4\ e^- + 4\ AlF_4^- \qquad (23)$$

$$2\ Al_2OF_8^{4-} + C = CO_2 + 4\ e^- + 4\ AlF_4^- \qquad (24)$$

$$4\ F^- + Al_2O_2F_4^{2-} + C = CO_2 + 4\ e^- + 2\ AlF_4^- \quad (25)$$

All these equations involve the formation of AlF_4^- ions, and they thus explain why the bath becomes more acidic close to the anode during electrolysis. It it seen that the reactions are complex, especially eqns. (23) and (25) that involve six and five reacting anions, respectively. Thus, from the point of view of simplicity reaction (24) involving $Al_2OF_8^{4-}$ may seem to be favoured. However, reactions (23) and (25) may occur in several steps, giving AlF_3 as an intermediate reaction product, which subsequently reacts with F^- to form AlF_4^- ions.

The dependence of anodic overvoltage on the alumina content has been discussed by Grjotheim et al. (2). However, it is doubtful whether the anodic overvoltage will depend on which oxygen-containing ions that dominate in the melt.

Recent information from Haupin (15) suggests that the anode reaction may be:

$$2\ Al_2O_2F_4^{2-} + C = CO_2 + 4\ e^- + 2\ Al_2OF_4 \quad (26)$$

and then the equilibrium between $Al_2O_2F_4^{2-}$ and $Al_2OF_6^{2-}$ is restored by the reaction:

$$Al_2OF_4 + Al_2OF_6^{2-} = Al_2O_2F_4^{2-} + 2\ AlF_3 \quad (27)$$

However, if we add eqns. (26) and (27):

$$2\ Al_2OF_6^{2-} + C = CO_2 + 4\ e^- + 4\ AlF_3 \quad (28)$$

which is closely identical to eqn. (23), with AlF_3 reacting subsequently with F^- to form AlF_4^- ions in the melt.

It has been suggested (15) that it requires much less energy to remove the first oxygen from $Al_2O_2F_4^{2-}$ than the second oxygen, or the oxygen from $Al_2OF_6^{2-}$. However, the presence of neutral molecules like Al_2OF_4 is not very probable in these ionic melts, where we know that AlF_3 is highly complexed. This neutral molecule may be formed by the reaction:

$$Al_2O_3 + 4\ AlF_3 = 3\ Al_2OF_4 \quad (29)$$

If it exists in these melts, it will have its maximum concentration at very low NaF/AlF_3 molar ratios, where solid AlF_3 is present. At the cryolite composition it is probably less abundant than $Al_2OF_6^{2-}$. Thus, in any case it is not very likely to exist in any appreciable amounts in baths of industrial interest.

The anode effect

Ratkje and Förland (5) have attempted to explain the onset of the anode effect in aluminium electrolysis cells as due to a shift in the melt equilibria concerning the Al-O-F complexes at low alumina contents. The authors explained the main oxygen discharge reaction at the anode by the equation:

$$AlOF_x^{1-x} + (6-x)\ F^- = AlF_6^{3-} + O_{ad} + 2\ e^- \quad (30)$$

Again, it should be reminded that more recent Raman spectroscopic data (1) have shown that this species is probably not very important in these melts. For alumina contents around 1.5 wt% Al_2O_3, at which the anode effect usually occurs, the only oxygen-containing species may be $Al_2OF_x^{4-x}$ in the melt. Ratkje and Förland (5) imagined that the discharge reaction:

$$Al_2OF_x^{4-x} + (12-x)\ F^- = 2\ AlF_6^{3-} + O_{ad} + 2\ e^- \quad (31)$$

required more energy than eqn. (30). Thus, they explained the occurrence of the anode effect by the dominance of the species $Al_2OF_x^{4-x}$ in the melt.

The results in Fig. 2 show that this is probably not an adequate explanation. For acidic melts with molar ratios less than two, the electrolysis proceeds very well, even if

$Al_2OF_6{}^{2-}$ is the completely dominating species. Fig. 3 shows that $Al_2OF_8{}^{4-}$ and $Al_2OF_6{}^{2-}$ dominate at very low alumina contents, but the ratio of their mol fractions to that of $Al_2O_2F_4{}^{2-}$ is only about 2 or less at 1.5 wt% Al_2O_3.

Thus, another explanation is required. The three main species $Al_2OF_8{}^{4-}$, $Al_2OF_6{}^{2-}$, and $Al_2O_2F_4{}^{2-}$ are in chemical equilibrium, given by eqns. (16) and (21). If only one of these species was consumed by the anode reaction, the chemical equilibria will be shifted in order to counteract the changes. Therefore, it seems more probable that it is the total sum of the concentrations of these species that is important. This means that the anode effect occurs because there is a lack of availability of Al-O-F species in the melt. The total amount of these species becomes too small for normal electrolysis. A tentative estimate from Fig. 3 shows that the minimum total mol fraction at equilibrium may be about 0.08 at the onset of the anode effect.

However, it is quite possible that equilibrium conditions do not exist during electrolysis, and that slow mass-transfer will cause a concentration gradient of the oxygen-containing species in the bath. Thus, the anode effect may occur because the concentration of these species actually becomes zero in the bath close to the surface of the anode.

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