ANODIC OxIDATION OF ALUMINIUM DISSOLVED IN CRYOLITE MELTS

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Abstract.
Aluminium dissolved in cryolite melts was oxidized anodically on platinum electrodes. A limiting current was observed which increased with increasing aluminium activity. The results are interpreted in terms of monovalent aluminium as the predominant oxidizable species together with sodium. The limiting cd increased with increasing NaF/AlF₃ ratio. Measurements made in industrial cells showed a constant limiting cd when the electrode was moved from 1 cm above the cathode to one cm below the anode, indicating that there was no appreciable concentration gradient in that range.

Introduction.
It is well known that metals dissolve in their respective molten halides. The solubility varies over a wide range, from complete miscibility for the alkali halides (1) to rather low values for aluminium, being about 0.1 wt% Al in cryolite (Na₃AlF₆) (2), and 0.02 wt% Al in Al₂Br₆ and Al₂I₆ (3).

In molten cryolite the dissolution of aluminium is accompanied by the formation of a so-called fog. Molten cryolite is a clear transparent liquid. Upon addition of aluminium streamers of fog spread from the piece of metal, and the melt rapidly becomes completely opaque. A dense fog was produced even when a Ag-Al alloy with aluminium activity as low as 0.07 was added. The same effect was observed by addition of sodium. The fog seems to have a higher density than the melt. In a quiescent melt the fog tended to sink towards the bottom of the crucible.

The dissolved metal can be oxidized by CO₂, CO or O₂. In the absence of excess aluminium the melt will gradually become clear again. The fog may be regarded as the visible part of the dissolved metal. The nature of the dissolved metal has not been established. Chemical analysis of
quenched samples indicate that it consists of aluminium as well as sodium (2, 4), either in the form of subvalent ions or as neutral species. The presence of a metal dispersion can also not be excluded.

For some molten salt-metal systems it has been shown that the dissolved metal can be oxidized anodically (5-7). In the cryolite-aluminium system Dewing and van der Kouwe (8) observed an anodic limiting current at potentials well below that of oxygen or CO₂ evolution, and this was later confirmed by Saget et al. (9) and by the present authors. Practically no current passes in this range when no metal is present.

In the present work the anodic oxidation of dissolved metal in cryolite-alumina melts was first studied in the laboratory. The method was subsequently used to assess the distribution of dissolved metal in the bath of industrial aluminium cells.

Laboratory Measurements.

In the laboratory experiments a sintered alumina crucible contained an aluminium cathode, a cryolite melt and a platinum wire serving as anode. The melt was saturated with alumina. The temperature was 1020°C.

As the imposed potential was increased stepwise the current would increase until a fairly distinct limiting current was reached. The potential at which it occurred depended on the condition of the platinum electrode. Newly immersed electrodes gave results as represented by Curve I in Fig. 1. If the Pt electrode was allowed to remain in the melt it would pick up aluminium and the potential would then be much lower, as shown by curve II. The alloy formation could be avoided by keeping the electrode anodically polarized, and this was done in the following. Current oscillations always occurred, but they are not shown on the curves.

Results obtained at various NaF/AlF₃ molar ratios (C.R.) are shown in Fig. 2. The curve acquired a more complicated shape at ratios above that of cryolite (>3). The limiting cd can be used as a measure of the concentration of electroactive species, although the absolute values are not known. The shape of plot of limiting cd versus composition can then be compared with corresponding plots of available data for metal solubility, as shown in Fig. 3. Although the data are somewhat conflicting, it appears that
the concentration of electroactive species is not proportional to the total concentration of dissolved metal.

The limiting cd in cryolite was measured in the presence of Ag-Al alloys, for which the aluminium activity is known (10). As expected the limiting cd increased with increasing aluminium activity. Fig. 4 shows a plot of the limiting cd versus the aluminium activity, obtained in the high potential range corresponding to curve I in Fig. 1. The log i versus log a plot shown in Fig. 5 exhibits a straight line relationship with a slope of $\frac{d \log i}{d \log a_{Al}} = 0.55 \pm 0.06$ within the 95% confidence limit. A corresponding plot for data from the low potential range represented by curve II in Fig. 1, gave a slope of $0.63 \pm 0.11$.

Two models can be suggested.

**Dissolution:** $2Al + Al^{3+} \rightarrow 3Al^{+}
\begin{align*}
\text{Oxidation:} & \quad Al^{+} \rightarrow Al^{3+} + 2e \\
\text{Dissolution:} & \quad Al + 3Na^{+} \rightarrow 3Na + Al^{3+} \\
\text{Oxidation:} & \quad Na \rightarrow Na^{+} + e
\end{align*}$

In the former case (A) the limiting cd will be proportional to the activity of monovalent aluminium ($a_{Al^+}$), which again is proportional to $a_{Al}^{2/3}$, i.e. the activity of aluminium to the power of 2/3.

In case B the limiting cd is proportional to the activity of dissolved sodium (Na) which in turn is proportional to $a_{Al}^{1/3}$. The same result is obtained if the dissolved species is written as Na$_2$.

Experimental data on aluminium solubility (2, 4) indicate that the dissolved metal consists of dissolved aluminium as well as sodium. The log i versus log $a_{Al}$ plot would then be expected to yield slopes between 1/3 and 2/3. The experimental slopes found in this work fall within this range, but rather close to the upper value.

In comparison Vetyukov and Dyblin (12) investigated the anodic oxidation of dissolved metal with a chronopotentiometric technique using a tantalum electrode. The results were fitted to a curve using the exponential $0.483$, i.e. $i \propto a_{Al}^{0.483}$. Chronopotentiometry was also tried as a part of the present work, but it was found that the chronopotentiograms were difficult to interpret due to the absence of distinct breaks in the curve.
Measurements in Industrial Aluminium Cells.

For analytical applications it is more convenient to use a continuously increasing potential instead of the very slow stepwise steady state method. The limiting current was not found to increase appreciably compared to the steady state method for low sweep rates in the range 0.008-0.016 V/s. The platinum electrode was permanently polarized in order to prevent uptake of aluminium.

The electrode used in industrial cells is shown in Fig. 6. It was protected by a thick-walled steel tube. The platinum wire electrode extended out of a boron nitride plug at the end of the tube. The electrode arrangement was mounted on a rig so it could be moved up and down as well as sidewise. The cell cathode was used as the counter electrode and the steel tube served as a reference electrode. The electrode was placed at various positions from the surface of the bath down to 0.5-1 cm above the metal. It could also be swung underneath the anode and could then reach up to 0.5-1 cm below the anode surface. When placed in the cathode-anode interspace the curves were somewhat distorted due to current oscillations.

An experimental curve is shown in Fig. 7. The current rose more gradually than in the laboratory measurement (Fig. 1). The potential was allowed to increase up to the beginning of oxygen evolution, which was identified as a sudden current increase. The limiting current was read at 400 mV below that point.

It is remarkable that no appreciable change in the limiting current was observed when the electrode was placed at different positions in the bath within the upper and lower limits mentioned above. This behavior was established by carrying out a number of measurements on cells with pre-baked anodes. The results indicate that there was no appreciable concentration gradient with respect to anodically oxidizable species in the bulk of the melt.

The limiting cd was of the order 60-90 mA/cm². Similar values were found in laboratory experiments for the same composition of the melt and in the same temperature range. It thus appears that the bulk of the melt is not far from saturation with respect to dissolved metal.

These findings are in conflict with results based on chemical analysis of bath samples, presented by Arthur (13). The bath was found to be practically saturated with dissolved metal up to a distance of 1 cm above the metal pad.
and then to fall off to practically zero at 1 cm below the anode. In spite of the fact that Arthur determined the total solubility and not the anodically oxidizable species, the two results are still not reconcilable.

The loss in current efficiency in industrial cells is caused by the continuous oxidation of dissolved metal by the anode gas. The mechanism of this reoxidation reaction is a matter of dispute. Information on the distribution of dissolved metal in the bath should help to solve this problem. Further work in this direction is obviously needed.

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Fig. 5. Plot of log $i$ (limiting cd) versus log $a_{Al}$.

Fig. 6. Electrode arrangement used in industrial cells.

Fig. 7. Current-voltage curves obtained in industrial cells.
Fig. 1. Current-voltage curve for anodic oxidation of dissolved metal on Pt electrodes in cryolite-alumina melts at 1020°C. I-new Pt electrode; II-electrode conditioned in melt (see text). Potentials are referred to aluminium.

Fig. 2. Current-voltage curves for anodic oxidation of dissolved metal at various CR's (mol NaF/mol AlF₃)

Fig. 3. Metal solubility (I-III) and limiting current density (IV) as a function of CR (mol NaF/mol AlF₃). Solubility (left axis), I- Vetyukov and Vinokurov (4); II-Haupin (11); III-Thonstad (3); Limiting current (right axis); IV-this work.

Fig. 4. Limiting current density in cryolite-alumina melts versus aluminium activity in Ag-Al alloy.