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# The development of cerium oxide coatings from cryolite melts. A self-forming anode for aluminum electrowinning

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The anodic deposition of cerium oxide from cryolite melts onto tin oxide substrates was investigated. Such a coated structure offers promise as an oxygen-evolving anode in Hall–Heroult cells. The development and dimensional stability of the coating is established by the equilibrium between the bath components and the cerium oxide. The coating thickness and morphology is shown to be dependent on the initial cerium oxide bath concentration and, to a lesser extent, on current density. The presence of the cerium oxide coating greatly diminishes dissolution of the anode substrate and increases the purity of the electrowon aluminum. The protection afforded by the coating is achieved by reducing the exposed substrate surface area.

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## 1. Introduction

The use of dimensionally stable anodes for aluminum electrowinning has been proposed since the time of Hall's original invention, and has been the subject of considerable research [1, 2]. Inert anodes offer the promise of savings in operating cost by elimination of the consumable carbon anode. Despite the fact that the reversible potential for an oxygen-evolving anode is approximately 1 V higher than that of a carbon anode, this can be partially offset by a lower overvoltage and lower ohmic losses by reduction of the interelectrode gap [3, 4]. In the long term, further savings from a dimensionally stable anode are expected through a more compact cell design.

Early work on inert anodes concentrated on metals and ceramic oxides. Metals generally have high electrical conductivity but, with the exception of some of the precious metals, are subject to massive oxidative corrosion when polarized anodically in cryolite melts [5, 6].

Of the oxide ceramics considered, $SnO_2$ has received the most attention because of its low solubility in molten cryolite and its high electrical conductivity, achieved by doping. Unfortunately, unacceptably high levels of tin in the aluminum product have been observed repeatedly [7, 8]. It has been proposed that the corrosion of the $SnO_2$ is by chemical attack of dissolved Al, which is present in the cryolite melt at a level of several tenths of a per cent [9]. Various engineering approaches have been attempted to reduce $SnO_2$ corrosion [10, 11], including $O_2$ protection. However, none of these approaches have been adopted commercially. It is generally acknowledged that a more chemically inert anode needs to be developed.

In 1982, researchers at ELTECH Electrosearch discovered cerium oxide coatings could be anodically deposited from a molten cryolite bath onto a variety of substrates [12]. This discovery led to the concept of a cerium oxide self-forming anode technology, for which patents have recently been issued [13]. The self-forming anode technology is based upon the hypothesis that addition of $CeO_2$ to the cryolite bath under controlled conditions permits the spontaneous formation of an electrocatalytically active and protective coating onto an appropriate conducting substrate. The dimensional stability of this coating is maintained by maintaining a suitable concentration of the elements which form the coating in the molten electrolyte thereby establishing a dynamic equilibrium between the deposited and dissolved material.

In this work, the deposition of cerium oxide onto $SnO_2$ substrates using a commercial cryolite melt is described. The presence of a $CeO_2$ layer is shown to greatly decrease wear of the $SnO_2$ substrate and increase the aluminum product purity. The protection afforded by the coating is directly related to the coating thickness, which is influenced by the amount of cerium in the melt and the current density. A model, which takes into account the per cent surface coverage, is proposed to explain the protection afforded by the cerium oxide coatings.

## 2. Experimental details

All anode tests were performed in a bench-scale Hall cell shown in Fig. 1. Alumina crucibles were used to contain the electrolyte. Alumina was fed from a hopper at the top of the cell. Molten aluminum in an alumina cup served as the cathode, with an

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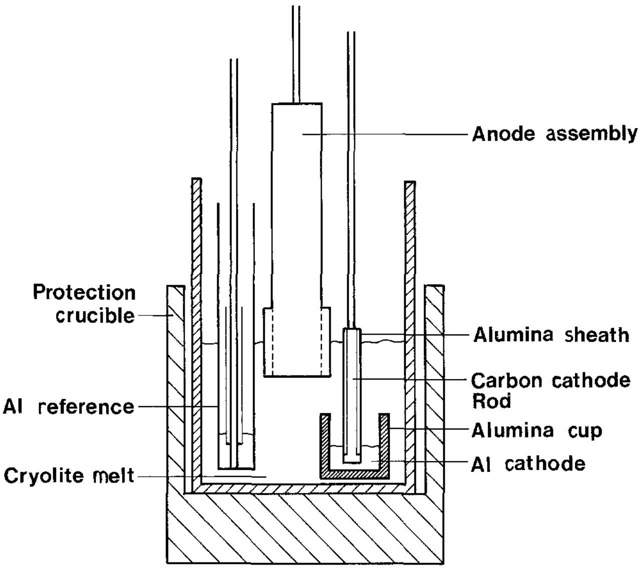

Fig. 1. Schematic diagram of the laboratory Hall cell used in all of the tests.

alumina-sheathed graphite rod used to make the connection.

In all tests, the electrolyte consisted of cryolite, adjusted with anhydrous aluminum fluoride to a ratio of 1.35, with nominal additions of 8% alumina and 5% calcium fluoride. Anhydrous aluminum oxide, calcium fluoride and cerium oxide were all obtained from Fisher Scientific. Anhydrous aluminum fluoride was purchased from CERAC Inc. and the synthetic cryolite was obtained from American Fluoride Co.

The tin oxide anode material was provided by Corning Glass Works. This is a commercially available material developed for use as electrodes for glass-melting furnaces. The material had the following composition: $Sb_2O_5$ 0.96%; CuO 0.53%; $SnO_2$ 98.5%. The CuO is found primarily as discrete phases in pores and between $SnO_2$ grains.

The anode substrates used in this work were 1.9 cm in diameter and were sheathed in alumina. The sheathing of the anodes was to mask off the anode sides, thereby limiting the active area to the bottom face.

The reference electrode used in these studies was basically that recommended by Piontelli *et al.* [14] and recently discussed by Burgman *et al.* [15]. An aluminum pool, covered with cryolite, was contained in a sintered alumina tube, with an alumina-sheathed molybdenum rod used to connect to the pool. A small hole was drilled in the tube to provide for a liquid junction, although it has been reported that this is unnecessary [15]. The stability of this type of reference electrode has been reported to be 3–5 mV [15].

The increase in cell resistance, attributable to the development of the cerium oxide coating was assessed by measuring the increase in the *iR* component of the anode potential. The total *iR* component was measured using a current interrupt technique, as described by McLeod *et al.* [16]. The current interrupter was manufactured by MS Industries. Potential decay transients following current interruption were measured with a Nicolet Model 3091 digital oscilloscope. The *iR*-free anode potentials were also obtained by subtracting the measured *iR* component from the measured anode potential.

Upon completion of a 10 h test, the anode was withdrawn from the bath and the cell was allowed to cool. Cryolite and aluminum samples were obtained, and elemental analysis performed by ICP. The anode specimen was sectioned and examined by both optical and scanning electron microscopy. Semi-quantitative information concerning the composition of the phases was gathered by use of both energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS).

## 3. Results

A series of 13 experiments were performed in a laboratory Hall cell varying the initial $CeO_2$ bath concentration (the true Ce bath concentration decreases as the coating develops) and anodic current density. Four $CeO_2$ bath concentrations were considered: 0%, 0.5%, 1.0% and 1.5%. Three current densities were employed: 0.8, 1.4 and 2.0 A $cm^{-2}$. Although conventional Hall cells operate at 1 A $cm^{-2}$, higher current densities were examined because operation at high currents is a potential advantage of inert anodes. This could reduce the capital cost or increase productivity of an aluminum smelter. The experiments performed constituted a full-factorial experimental design.

In all experiments in which the cryolite bath was doped with $CeO_2$, the $SnO_2$ anode was found to be coated with a blue-gray surface layer. In general, it was observed that the coating thickness and the average size of the pores increased with increasing $CeO_2$ concentration. The micrographs shown in Fig. 2 demonstrate the effect of $CeO_2$ bath concentration on the thickness and structure of the coatings. The samples shown in Fig. 2 were obtained at 0.8 A $cm^{-2}$. The composition of the deposited coatings was also examined by EDX and WDX. The results confirm that the major elements in the coating are Ce and O. However, low levels of F are also found without detec-

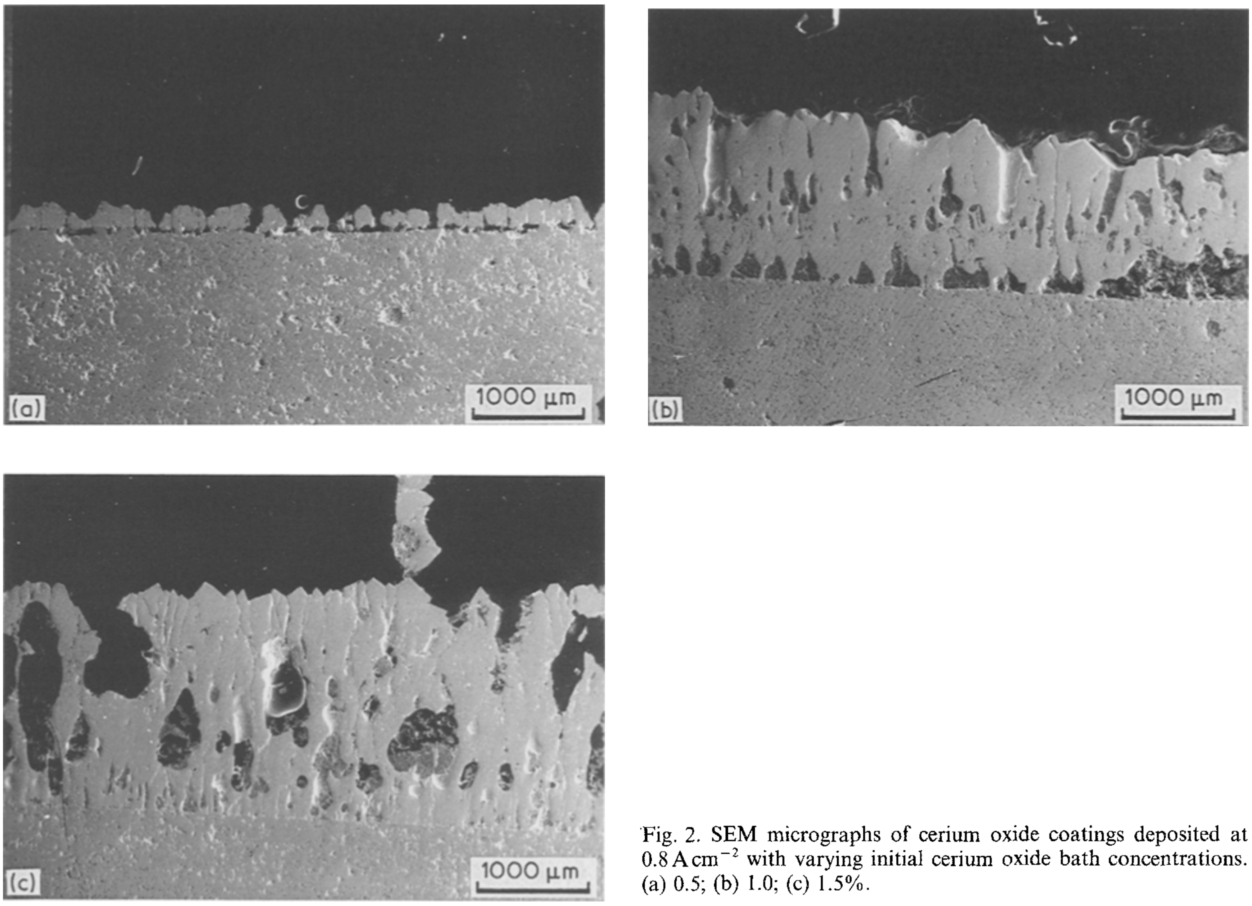

Fig. 2. SEM micrographs of cerium oxide coatings deposited at 0.8 A cm$^{-2}$ with varying initial cerium oxide bath concentrations. (a) 0.5; (b) 1.0; (c) 1.5%.

tion of Na or Al. It must be concluded that the coating is probably a fluoride-doped cerium oxide.

Figure 3 shows the dependence of coating thickness on both the $CeO_2$ bath concentration and current density. It can be seen that at any current density, the coating thickness increases dramatically with increasing $CeO_2$ concentration up to 1.0% $CeO_2$, but only slightly when increased from 1.0 to 1.5%. In fact, the coating thickness appears to be approaching an upper limit. The coating thickness does decrease with increasing current density, however the effect is much less pronounced. In general, the most uniform, dense coatings were obtained at the low end of the range of current densities examined.

As an indirect measure of the corrosive attack on the $SnO_2$ anode, the cryolite bath and Al pool were analyzed for Sn. In all cases, the impurity levels in the cryolite were quite low, usually below the detection limit. The low levels of Sn in the cryolite are due to the strong electrochemical driving force for cathodic deposition in the Al pool.

The Sn levels in the Al product are shown graphically in Fig. 4. In general, the Sn levels are reduced by the presence of cerium in the bath. The protection offered by the $CeO_2$ coating is most apparent at the lowest current density. At 0.8 A cm$^{-2}$ and no cerium in the bath, the recovered Al contained 0.52% Sn, whereas with 1.5% $CeO_2$ added to the bath, the levels

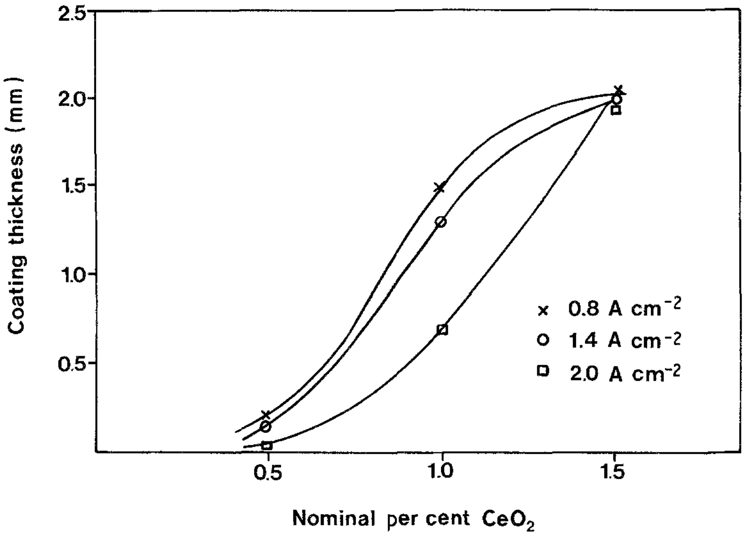

Fig. 3. Dependence of cerium oxide coating thickness on both the initial bath concentration and the anodic current density.

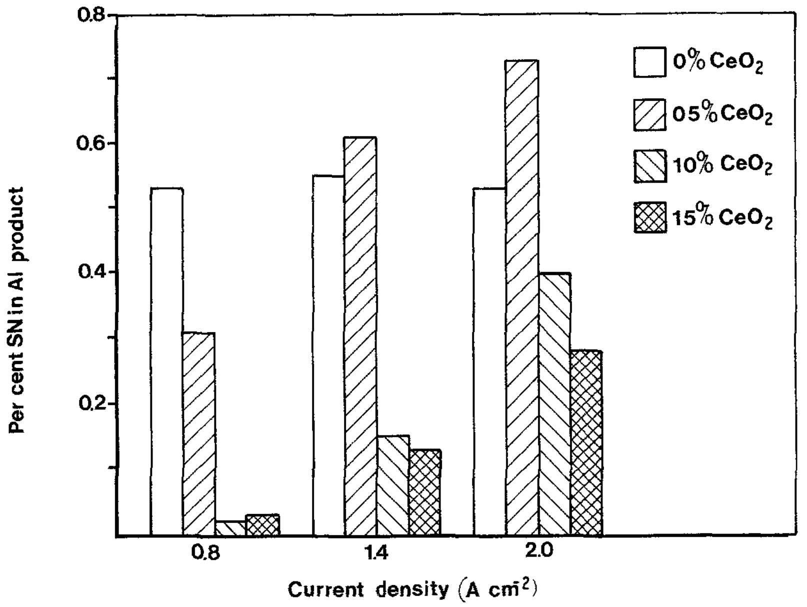

Fig. 4. Per cent tin in the recovered Al cathode as a function of both the initial cerium oxide bath concentration and anodic current density.

were reduced to 0.03%. This represents a 20-fold decrease in anode wear. This decrease in anode wear is by far the most significant feature of the $CeO_2$ coating technology.

It is interesting to note that in experiments performed at the higher current densities with bath containing 0.5% $CeO_2$, the Sn levels in the electrowon Al were actually higher than those obtained in the control, cerium-free experiments. However, higher cerium levels, i.e. 1.0% and 1.5%, did substantially decrease attack on the $SnO_2$ substrate. It is possible that with low levels of cerium in the bath, the $CeO_2$ may preferentially precipitate in the pores of the substrate, inducing stress and enhancing corrosion. The presence of $CeO_2$ in the substrate pores was verified by SEM. At higher cerium levels, however, a sufficiently thick protective coating is achieved, and attack is diminished, as assessed by Al metal purity.

Although addition of cerium to the cryolite melt decreases the amount of substrate impurities in the electrowon Al, appreciable Ce levels in the Al product were observed. In our experiments, the Ce levels in the Al ranged from 2.0 to 3.5%. As shown in Table 1, the final cerium concentrations in both the bath and the aluminum increased with increasing initial $CeO_2$ concentration. However, the levels are relatively insensitive to current density.

The contamination of the Al product with Ce is the result of the equilibrium between the soluble cerium species in the cryolite melt and the aluminum product. At constant bath ratio and alumina concentration the weight ratio of Ce in the Al and the Ce in the melt should be constant. Therefore a partition coefficient can be defined as

$$PC = \text{wt\% Ce(Al)}/\text{wt\% Ce (melt)} \quad (1)$$

The partition coefficients obtained in our experiments are also shown in Table 1. An average value of 8.1 was calculated. It should be noted that a reduction in bath ratio, i.e. an increase in $AlF_3$ activity, should reduce the partition coefficient. Thus, it would be expected that lower Ce levels in the Al would be obtained with the use of a low-ratio cryolite bath.

In addition to the codeposition of Ce with the Al, the development of a $CeO_2$ coating also increases the total cell resistance, because of the intrinsic resistance of the coating. The electrical resistances of the $CeO_2$ coatings were estimated from the change in the *iR* component of the anode potentials, measured throughout each experimental run. These results are summarized in Table 2. The maximum resistance measured was $0.44\,\Omega\,cm^2$, obtained at $0.8\,A\,cm^{-2}$ and an initial $CeO_2$ bath concentration of 1.5%. At the other extreme, there was no measurable resistance at 1.4 and $2.0\,A\,cm^{-2}$ with a $CeO_2$ bath concentration of 0.5%. Although the increase in resistance could be due to a change in bubble distribution or entrapped bubbles at the anode surface, it is believed that the increase is due to the resistivity of the $CeO_2$ layer.

The data shown in Table 2 indicate that increasing the $CeO_2$ concentration in the bath increases the resistance attributed to the development of the coating. This is consistent with the observation that the $CeO_2$ level is the major factor affecting the coating thickness. Increasing current density decreases the resistance of the coating. This is probably due to increased coating porosity obtained at high current.

*Table 1. Cerium partition coefficient*

| *Nominal $CeO_2$ level (w/o)* | *Current density ($A\,cm^{-2}$)* | *Ce (Al) (w/o)* | *Ce (melt) (w/o)* | *Partition coefficient* |
|---|---|---|---|---|
| 0.5 | 0.8 | 2.20 | 0.26 | 8.5 |
| 0.5 | 1.4 | 2.40 | 0.29 | 8.3 |
| 0.5 | 2.0 | 1.60 | 0.27 | 5.9 |
| 1.0 | 0.8 | 2.10 | 0.26 | 8.1 |
| 1.0 | 1.4 | 3.00 | 0.31 | 9.9 |
| 1.0 | 2.0 | 2.70 | 0.32 | 8.4 |
| 1.5 | 0.8 | 3.40 | 0.44 | 7.7 |
| 1.5 | 1.4 | 3.40 | 0.36 | 9.4 |
| 1.5 | 2.0 | 3.20 | 0.53 | 6.0 |

Average partition coefficient = 8.1.

*Table 2. Calculated coating resistance from change in anode potential*

| *Nominal $CeO_2$ concentration (w/o)* | *Current density ($A\,cm^{-2}$)* | *Calculated resistance ($\Omega\,cm^2$)* |
|---|---|---|
| 0.5 | 0.8 | 0.175 |
| 0.5 | 1.4 | * |
| 0.5 | 2.0 | * |
| 1.0 | 0.8 | 0.304 |
| 1.0 | 1.4 | 0.290 |
| 1.0 | 2.0 | 0.120 |
| 1.5 | 0.8 | 0.440 |
| 1.5 | 1.4 | 0.339 |
| 1.5 | 2.0 | 0.135 |

It should be noted that the factors which decrease the coating resistance also decrease the degree of protection afforded the substrate by the coating. It appears that the most protective coating will also be the most resistive.

## 4. Discussion

Although $CeO_2$ is added to the cryolite melt, the dissolved cerium species should be trivalent. This is due to the equilibrium between the dissolved cerium and aluminum species in the melt. Assuming a simple solution without ionization, the following equation represents the equilibrium between aluminum and cerium species. This reaction is favored thermodynamically at conditions and bath compositions typical of Hall cell operation.

$$CeO_2 + AlF_3 = CeF_3 + 1/2Al_2O_3 + 1/4O_2 \quad (2)$$

The predominant soluble aluminum species in a cryolite melt is undoubtably an oxyfluoride [3] and it is likely that the soluble cerium species is also present as an oxyfluoride. However the assumption of a simple solution is of utility in establishing chemical relationships [17].

Again assuming a simple solution, the anodic deposition of $CeO_2$ can be described as the following two half reactions.

$$\text{Anode: } 2CeF_3 + 4/3Al_2O_3$$
$$= 2AlF_3 + 2CeO_2 + 2/3\,Al^{3+} + 2e^-$$
$$\text{Cathode: } 2/3Al^{3+} + 2e^- = 2/3Al.$$

The net reaction would then be

$$2CeF_3 + 4/3Al_2O_3 = 2CeO_2 + 2AlF_3 + 2/3Al \quad (3)$$

The standard Gibb's free energy for this reaction at 1300 K is 590 kJ, which corresponds to an EMF of 3.06 V.

The anodic deposition of $CeO_2$ is of course in competition with the oxygen evolution reaction.

$$Al_2O_3 = Al + 3/2O_2 \quad (4)$$

Equation 4 has a free energy change of 1264 kcal, corresponding to an EMF of 2.18 V.

Based only on standard free energy change, it appears that $CeO_2$ deposition would not occur. However, it must be noted that the $\Delta G$ for Equation 3 is influenced by the $AlF_3$ activity, which in pure cryolite has been estimated to be between $10^{-3}$ and $10^{-5}$ [3]. In a cryolite bath with ratio 1.35, Dewing and Yoshida estimated the $AlF_3$ activity to be approximately $5 \times 10^{-3}$ [18].

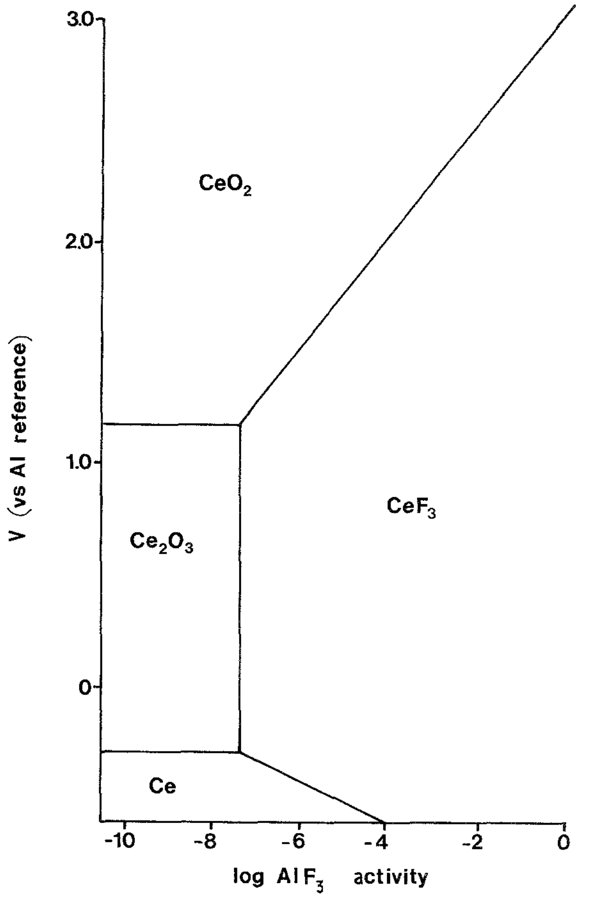

Fig. 5. Predominance diagram showing the potential for cerium oxide deposition as a function of $AlF_3$ activity in the bath.

In order to visualize the dependence of $CeO_2$ deposition of $AlF_3$ activity and applied potential, a predominance diagram (Fig. 5) was constructed from thermodynamic data presented in Barin *et al.* [19]. All species other than $AlF_3$ were assumed to have unit activity.

As can be seen in the figure, at $AlF_3$ activities less than $10^{-2}$, the deposition of $CeO_2$ becomes thermodynamically possible at normal $O_2$-evolving potentials in pure cryolite. Therefore, it appears that $CeO_2$ deposition is observed only because of the low $AlF_3$ activity in cryolite melts. Under extremely acidic conditions, where the $AlF_3$ activity is higher, $CeO_2$ deposition would not be expected.

As shown in the results, the presence of a $CeO_2$ layer significantly reduces the wear of the anode substrate. The degree of protection also appears to be directly related to the amount of $CeO_2$ deposited. As the coating thickness increases, the per cent surface coverage also appears to increase. This suggests that the protection afforded by the coating is a result of limiting surface exposure to the cryolite bath.

It has been proposed that the wear of ceramic oxide anodes is a chemical dissolution process, described by a psuedo-first order rate expression [20].

$$\text{Rate} = k(C_s - C)A \qquad (5)$$

where $k$ is a rate constant, $C_s$ is the solubility limit of the dissolving species, $C$ is the concentration of the dissolving species in the bath and $A$ is the exposed anode surface area. This rate expression makes no assumption concerning the mechanism of dissolution. A dissolution mechanism has been proposed which involves an exchange reaction with $AlF_3$ [21]

$$MeO_x + 2x/3AlF_3 = MeF_{2x} + x/3Al_2O_3 \qquad (6)$$

Dissolution could also proceed by reaction with dissolved Al [10]

$$MeO_x + 2x/3Al = Me + x/3Al_2O_3 \qquad (7)$$

This could be followed by an exchange reaction

$$Me + 2x/3AlF_3 = MeF_{2x} + 2x/3Al \qquad (8)$$

Of course, the net reaction for the two processes is the same.

Assuming that the rate of reaction of the dissolved species with the Al product is fast compared to the rate of dissolution, $C$ would be much less than $C_s$, and the rate of anode dissolution would reduce to

$$\text{Rate} = K \times C_s \times A \qquad (9)$$

This predicts that anode dissolution is proportional to the exposed anode surface area. As mentioned previously, the protection provided by the $CeO_2$ coatings does appear to be related to surface coverage.

The benefit of a self-forming cerium oxide anode is clearly in reducing the wear rate of the anode substrate. This should not only increase the service life of the substrate material, but also improve the purity of the electrowon Al. The codeposition of Ce, to a level of approximately 2%, dictates that the Al product must be refined and that the recovered Ce be recycled back into the cryolite melt. Such a technology presently exists. In addition, the coating resistivity imposes an additional energy penalty, with the most protective coatings having the highest resistance. Clearly, for commercial applications, there may be a trade-off between anode wear rate and voltage. Further testing is required to quantify the dependence of anode lifetime and the voltage penalty on coating thickness.

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