WEAR AND SODIUM EXPANSION BY ALUMINIUM ELECTROLYSIS IN ALUMINA SLURRIES

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ABSTRACT

The physical abrasion, electrochemical corrosion and sodium expansion of carbon cathode materials were studied in cryolitic melt-alumina slurries. The physical abrasion of graphite is about 5 times the physical abrasion of anthracitic carbon, this is similar to the room temperature result. The electrochemical corrosion is a much stronger wear process than the physical abrasion, but it is suppressed by excess alumina addition. Different carbon cathode materials have approximately the same resistance to the electrochemical corrosion. In the acidic, cryolitic melt-alumina slurry, a 25% to 65% increase in expansion was observed compared to the expansion in the corresponding slurry-free melt. The larger expansion is attributed to diffusion hindrance by the slurry resulting in an increased sodium concentration on the interface. The expansion increased radically in the basic cryolitic melt-alumina slurry compared to the expansion in the corresponding slurry-free melt: 180-560%. This large expansion increase is considered due to diffusion hindrance combined with precipitation of β-alumina on the interface. The present findings constitute a strong argument against basic start-up and muck-up of the cell bottom during this period.

INTRODUCTION

One of the most important properties of carbon cathode materials for aluminium electrolysis is their resistance to wear and to sodium expansion which can be dominant factors affecting the cell life of industrial aluminium electrolysis cells. As modern cells become more sophisticated, the cell life is becoming more important affecting the profitability of the aluminium industry. It is then of importance to develop good test methods to understand the wear and expansion mechanisms and be able to rank the materials used, towards the goal to obtain better wear and expansion resistant materials and designs.

It is generally believed that carbon cathode wear is caused by a combined process of physical wear (detachment of particles) and chemical wear (Al₄C₃ formation and...
removal). The physical wear is referred to as physical abrasion or abrasion in the present paper since it is mainly caused by friction between carbon cathode and solid alumina particles. The chemical wear is referred to as electrochemical corrosion or corrosion in the present paper since it is electrochemical (galvanic or electrolytic) in nature.

### Room Temperature Abrasion

As the first step a room temperature test (Figure 1) was developed [1]. The following main results were reached. Relative abrasion resistance of different carbon cathode materials is shown in Table I. The resistance increases with decreasing value.

**Table I. Ranking of abrasion resistance of cathode materials relative to CS graphite**

| Cathode Material | Density g/cm³ | Hardness HV* | Abrasion Value** | Standard Deviation |
|------------------|---------------|--------------|------------------|-------------------|
| G (CS), Ref.     | 1.75          | 8.5, 9.2, 9.7, 10.6, 11.5, 12.2 | 100              | 2.8 |
| G A (CS)         | 1.60          | 7.4, 8.0, 9.8, 10.3, 10.6, 11.6 | 132.7            | 4.1 |
| G B              | 1.63          | 8.2, 9.1, 10.5, 12.6, 13.2, 14.1 | 112.7            | 4.2 |
| SGZ A            | 1.65          | 9.5, 9.7, 10.5, 12.6, 14.2, 15.1 | 87.4             | 2.7 |
| SGZ B            | 1.64          | 8.6, 9.7, 10.1, 11.3, 14.9, 20.3 | 102.0            | 4.2 |
| SG A             | 1.62          | 11.6, 13.4, 14.7, 16.5, 18.1, 19.2 | 68.0             | 3.5 |
| SG B             | 1.60          | 10.8, 12.8, 13.5, 14.7, 15.6, 16.1 | 77.4             | 4.7 |
| An. A            | 1.54          | 13.4, 15.9, 17.5, 202, 235, 248 | 17.8             | 3.1 |
| An. B***         | 1.53          | 14.2, 14.9, 15.5, 225, 238, 259 | 17.4             | 2.3 |
| An. C***         | 1.40          | 33.2, 52.7, 80.9, 95.8, 190, 222 | 11.4             | 1.8 |
| TiB₂-SGZ B       | -             | 9.1          | 3.2              |

G: Graphite; SGZ: Semigraphitized carbon; SG: Semigraphitic carbon; An.: Anthracitic carbon; TiB₂-SGZ B: The material SGZ B was coated with a non-carbon bonded TiB₂. The composite material was heat-treated to 950°C.

The diameter of CS graphite is about 10.14 mm. The diameter of TiB₂-SGZ B is about 12 mm. The diameter of other samples is 9.95-10.00 mm. No corrections were used for the diameter differences.

* Digital micro hardness tester (model MXT70 (B)) was used. All values are estimated since the images of the diamond indentation were not well defined.

** Average of four measurements; *** Side wall materials.

Parameter study shows the wear increases with alumina content, velocity and pressure. Their effects can be described with a power equation:
\[ W_r = kX^n \]  

where \( W_r \) is the wear rate (mm\(^3\)/h or cm/year), and \( k \) and \( n \) are constants, \( X \) represents alumina content (g/ml), velocity (m/s) or pressure (Pa). Alumina content has the largest effect with \( n \geq 7 \), velocity intermediate \( n = 2-4 \) and pressure lowest \( n = 0.5-1.4 \).

Sodium expansion of carbon cathode materials is a well-known phenomenon in aluminium electrolysis. It is caused by penetration of metallic sodium into carbon micropores [2]. The dependence of the sodium expansion on the factors like the type of material, melt composition and current density etc. in an alumina saturated or undersaturated cryolitic melt is well established. The sodium expansion in a cryolitic melt-alumina slurry, however, has not been received much study before, but the importance is highly significant from an industrial point of view as such a slurry is present underneath the aluminium pool in contact with the top of the cathode carbon.

**EXPERIMENTAL**

**Apparatus.**

The apparatuses for wear study and sodium expansion study are shown in Figure 2 and Figure 3, respectively.

**Samples.**

Most samples for wear study were core drilled parallel to the extrusion direction and had a diameter of 9.95-10.00 mm and a length of about 60 mm. The graphite samples used in ranking experiments were as-received rods with a diameter of about 10.14 mm. The part of the sample extending from the sample holder was 45 mm, with an immersed length of 40-45 mm for experiments without electrolysis, and 25-35 mm for experiments with electrolysis to avoid short circuiting by contact between the sample holder and the cryolitic melt. Samples for sodium expansion study were core drilled perpendicular to the extrusion direction and had a diameter of about 30 mm and a length about 100 mm.

**Melts.**

Some estimated properties of cryolitic melts employed are given in Table II.
Table II. Properties of cryolite-based melts with 5 wt% CaF$_2$ at 980 °C [3]

|       | CR  | $S_A$ | $d_{m}$ | $d_{m}'$ | $t_{liq.}$ | $\sigma$ |
|-------|-----|-------|---------|----------|------------|---------|
| Melt A| 2.2 | 9.05  | 2.050   | 2.079    | 932        | 100     |
| Melt B| 3.0 | 9.89  | 2.086   | 2.136    | 951        | 127     |
| Melt C| 4.0 | 9.00  | 2.090   | 2.136    | 941        | 142     |

CR: cryolite ratio: mole NaF/mole AlF$_3$

$S_A$: solubility of alumina in the melt, wt%

$d_{m}$: density of melt saturated with alumina, g/cm$^3$

$d_{m}'$: density of melt without alumina, g/cm$^3$

$t_{liq.}$: liquidus temperature of melt saturated with alumina, °C

$\sigma$: surface tension of melt saturated with alumina, mN/m

The concentration of undissolved alumina in the melt was expressed as $A_{c}^{E}$ (g undissolved alumina)/(cm$^3$ alumina-saturated melt) [4].

For the experiment with a slurry melt (the amount of alumina is in excess of the solubility limit), the temperature was first held 30-50 °C higher than the test temperature for one to several hours. This procedure was found necessary to homogenize the slurry. After the temperature was reduced to the test temperature, the samples were lowered into the slurry. The experiment was started by rotating or polarizing the samples.

WEAR STUDIES

Physical Abrasion

In a cryolitic melt-alumina slurry without aluminium and without an externally applied current, the carbon samples undergo no corrosion, the wear process is a pure abrasion caused by solid alumina particles which is similar to the room temperature test.

The velocity effect on the wear rate in a dense, cryolite-alumina slurry is shown in Figure 4. The wear increases rapidly with velocity, similarly to the room temperature test. The wear equation is the following:

$$W_{R} \text{ (cm/year)} = 2.22 \ [V \ (m/s)]^{1.77} \quad (2)$$

The wear rate in the cryolitic melt-alumina slurry is smaller than that in the sodium poly-tungstate solution (SPT)-alumina slurry. The possible reasons for this are

a). Alumina particles become less abrasive since their edges and corners preferentially dissolve in the cryolitic melts (the sharpness is reduced).

b). The surface tension of cryolitic melts is higher than that of SPT; the moving alumina particles are hence less compact in the cryolitic melt than in the SPT. With a less compact alumina particle packing the shear stress required to rotate the samples, and hence the wear, is reduced.
c). The cryolitic melt-alumina slurry does not wet the carbon material, the contact between the slurry and the sample is poor, and the friction is hence probably less intensive than that in the room temperature test.

d). The material is stronger at the electrolysis temperature than at the room temperature.

A more rapid increase in apparent viscosity with alumina content in the cryolitic melt than in SPT was observed. The cryolitic melt-alumina slurry with excess alumina content larger than $1.20 \, \text{g/cm}^3$ was found to lose fluidity at $\text{CR}=3.0$ and $t=1015 ^\circ\text{C}$, then the moving path of the sample was found empty after the slurry was cold. In the case of SPT-alumina slurry, the alumina content can go up to about $1.50 \, \text{g/cm}^3$ before it loses fluidity at room temperature.

The main difference between the present study and the abrasion in aluminium cells is the pressure acting on the sample surface due to gravity. In the present study the pressure acting on the carbon cathode is much smaller than in aluminium cells. If the total height of electrolyte and aluminium metal in an aluminium cell is taken as 45 cm, and the average density of the electrolyte and the metal is taken as $2.15 \, \text{g/cm}^3$, then the pressure ratio between the aluminium cell and the present study is about 17. In the room temperature study, the wear rate was found to be proportional to the pressure [5, 6]. Assuming that the proportionality holds also in cryolite-alumina slurries, the wear rate in aluminium cells is expected to be approximately 17 times that in the present study.

The wear rates in cm per year of CS graphite under industrial smelting conditions in the velocity range 0.1–0.5 m/s were calculated in Table III. In order to compensate for the higher pressure effect in an industrial aluminium cell on the wear rate, a pressure conversion factor of 17 was used when converting the laboratory wear depths to the industrial wear depths.

Table III illustrates that the wear rate increases rapidly with increasing velocity, since the exponent in Equation (2) is 1.77.

Table III. Calculated wear rates in cm/year of CS graphite under industrial smelting conditions by extrapolation of Equation (2)

| Velocity, m/s | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 | 0.40 | 0.50 |
|---------------|------|------|------|------|------|------|------|
| Wear rate, cm/year | 0.6  | 1.3  | 2.2  | 3.2  | 4.5  | 7.5  | 11.1 |

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Electrochemical Corrosion without Electrolysis

When aluminium is added to a slurry melt, the galvanic corrosion mechanism is active. The corrosion is stimulated by the potential difference between carbon and aluminium, the more noble carbon acting as a cathode undergoing reduction, the more active aluminium acting as the anode undergoing oxidation. The cathodic, anodic and cell reactions responsible for the corrosion are the following:

Cathodic: \[ 3C \text{ (cathode)} + 4\text{Al}^{3+} \text{ (bound in AlF}_6^{-} \text{ or AlF}_6^{2-}) + 12e^- = \text{Al}_4C_3 \text{ (s)} \] (3)

Anodic: \[ 4\text{Al} \text{ (l)} = 4\text{Al}^{3+} \text{ (l)} + 12e^- \] (4)

Cell: \[ 3C \text{ (s)} + 4\text{Al} \text{ (l)} = \text{Al}_4C_3 \text{ (s)} \] (5)

The standard cell voltage for Reaction (5) is calculated to 0.126 V at 980 °C [7], which means that the reaction is thermodynamically favoured.

The corrosion process is complicated due to alumina layer formation on the sample surface. The layer was found to have very large influence on the wear process. A dense, cohesive alumina layer strongly suppresses both physical and electrochemical wear. A dilute, noncohesive layer has a limited effect. It has been found that the density and cohesiveness of the alumina layer increase with the density, viscosity and cleanness of the slurry, the wetting between the sample and the slurry, the rotating speed, current density and roughness of the sample.

It is seen from Figure 5 that the wear rate decreased rapidly with excess alumina content, showing that addition of alumina to the cryolitic melt-aluminium mixture strongly suppresses the corrosion due to carbide formation. It is also seen that the wear in the slurry increases significantly with temperature. This is probably due to reaction kinetics and a rapid decrease of the viscosity when the temperature was increased. The slurry was found to lose fluidity when excess alumina content reached about 1.25 g/cm³ at 990 °C, and the moving path of the sample was found empty after the slurry was cold. The viscosity was greatly reduced when temperature was increased from 990 °C to 1015 °C. The mechanism for the wear reduction due to excess alumina addition seems to be the greatly increased ohmic resistance through alumina layer formation on the sample surface.

The density and cohesiveness of the alumina layer were found to decrease with the number of time the slurry was used, and the wear increases, as shown in Figure 6. The slurry becomes more and more dirty with the number of time used, probably due to contamination of carbon dust and aluminium carbide. On the other hand, the viscosity of the slurry is found to decrease with the number of time used, this is probably because the porosity of alumina particles decreased with the number of time used through solution and reprecipitation of alumina. Each time corresponds to one cycle of melting and freezing of the melt, and hence one cycle of solution and precipitation of alumina.
particles. The porosity of new alumina (Industrial primary alumina) is very large, typically 75%, giving a very large BET surface area. The precipitated alumina crystals are probably $\alpha$-\( \text{Al}_2\text{O}_3 \) with less defaults, higher densities, and larger particle size. All these factors should contribute to the viscosity reduction since the porosity, surface area and effective volume fraction of alumina are decreased.

When the rotating disc with one 50 mm holder and one 20 mm holder was used, the wear rate of the sample connected in the 50 mm holder was smaller than that of the sample connected in the 20 mm holder in a viscous slurry. A denser alumina layer was observed on the outer sample than the inner sample. This was probably why the faster sample had a smaller wear rate than the slower sample.

Electrochemical Corrosion with Electrolysis

When an external current is applied, the electrolytic corrosion mechanism is active. The cathodic reaction is the same as the galvanic corrosion (Reaction 3), but the anodic and corrosion reactions are different. The anodic and cell reactions responsible for cathode corrosion are the following:

Anodic: \[ \text{Al}_4\text{C}_3 = 4\text{Al}^{3+} + 3\text{C} \text{ (anode)} + 12e^- \] (6)

Cell: \[ \text{C (cathode)} = \text{C (anode)} \] (7)

Reaction (7) is usually one of the parallel cell reactions.

The wear rate of CS graphite as a function of excess alumina content in the cryolitic melts is shown in Figure 7. It is seen that the wear rate decreases more rapidly with excess alumina content than that in the cryolitic melt-aluminium system without electrolysis. In the alumina-saturated electrolyte the wear is about 52 cm/year or 9.9 mm/week which is in fair agreement with measurements made by Taylor et al.[8] of 9.1 mm/week in industrial cells and Gudbrandsen et al.[9] of 12 mm/week in a laboratory cell.

The alumina layer has been found to be more cohesive on the anthracitic carbon material than on the CS graphite, this is probably because the anthracitic carbon has a much rougher surface than CS graphite. Since anthracitic carbon dissolves in concentrated sulphuric acid solution, the removal of the alumina layer is difficult.
The wear rates of CS graphite and anthracitic carbon in cryolitic melt with electrolysis or with aluminium added are given in Table IV.

Table IV. Wear comparison of CS graphite (G) and anthracitic carbon (A) in cryolitic melts at 980 °C, Melt A, $V=0.55 \text{ m/s}$

| Experiment | Sample | 1 | 2 | 3 | 4 |
|------------|--------|---|---|---|---|
|            | CC0, A/cm² | G | A | G | A |
|            | 0.15    | 0.21 | 0 | 0 | 0 |
|            | $A_c$, g/cm³ | 0 | 0 | 0 | 0.60 |
| Time, hour | 3 | 3 | 3 | 5 | |
| $W_{R}$, cm/year | 43.4 | 41.7 | 53.3 | 55.6 | 19.5 | 23.2 | 14.5 | 14.1 |

* 5-6 wt% aluminium was added.

Table IV shows that the wear rates for both materials are essentially the same, indicating that graphite and anthracitic carbon have approximately the same resistance to the chemical corrosion due to carbide formation, although graphite is more resistant to air oxidation and sodium attack. This is in agreement with earlier studies [10].

When no aluminium is added or electrolysis performed, the electrochemical corrosion disappears. The ranking of results between CS graphite and anthracitic carbon in such systems are given in Table V. The results show that in a cryolitic melt-alumina slurry without aluminium and without polarization, the wear rate of anthracitic carbon is about one fourth to one fifth of CS graphite. This is similar to the results for the room temperature test [1].

Table V. Ranking of CS graphite (G) and anthracitic carbon (A) in cryolitic melt-alumina slurries without aluminium and without electrolysis, $V=1.58-1.75 \text{ m/s}$

| Experiment | Sample | 1 | 2 | 3 | 4 |
|------------|--------|---|---|---|---|
|            | $A_c$, g/cm³ | G | A | G | A |
|            | 0.90 | 1.15 | 0.85 | 1.10 |
|            | A | A | B | B |
|            | Temperature, °C | 960 | 990 | 980 | 1015 |
|            | Weight loss, mg | 29.3 | 6.3 | 49.3 | 7.9 | 47.8 | 8.5 | 73.6 | 14.8 |
|            | $W_{R}$, mm³/h | 2.09 | 0.51 | 3.52 | 0.64 | 3.41 | 0.69 | 5.26 | 1.20 |
|            | $W_{R}$, cm/year | 1.99 | 0.48 | 3.35 | 0.61 | 3.24 | 0.66 | 4.99 | 1.14 |
|            | Relative $W_{R}$* | 0.241 | 0.182 | 0.213 | 0.228 |

* The relative wear rate is calculated by dividing the wear rate of anthracitic carbon by the corresponding wear rate of graphite.

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Expansion Results.

The expansion curves for the three cathode materials in acidic and basic melts are given in Figures 8-12. The initial cryolite ratio and the electrolysis regime were varied. The expansion data are listed in Table VI. The reproducibility is comparable to earlier studies [11]. The somewhat lower sodium expansion for one sample with $A_c = 0.80$ g/cm$^3$ in Figure 8 may be due to the cracking of the sample.

Table VI. Sodium expansion in % and expansion ratios

| CD  | $A_c$ | CR  | CR=2.2 | CR=4.0 |
|-----|-------|-----|--------|--------|
|     | A/cm$^2$ | g/cm$^3$ | 2.2    | 4.0    | $A_c=0.80$ | $A_c=0.80$ |
| AN  | 0.14/0.70 | 0.00   | 0.93   | 1.31   | 1.2 | 2.8 |
|     | 0.70     | 0.80   | 2.65   | 0.59   |        |        |
| SG  | 0.14/0.70 | 0.00   | 0.31   | 0.93   | 1.5 | 3.9 |
|     | 0.70     | 0.80   | 1.73   | 0.34   |        |        |
| SGZ | 0.14/0.70 | 0.00   | 0.39   | 2.12   | 6.2 | 2.3 |
|     | 0.70     | 0.80   | 0.78   | 1.6    |        |        |

An increase in the cell voltage was also observed with increased alumina content. For slurries with $A_c = 0.80$ g/cm$^3$ the voltage was approximately 0.5 V higher than in the corresponding melt without slurry. The voltage increase is probably partly due to cathodic concentration overvoltage increase and partly due to an increase in ohmic resistance.

Table VII gives some melt analysis before and after electrolysis. The composition is for the bulk melt with one exception.

Some of the anthracitic samples were analyzed for concentration of metallic sodium after the experiments (Figure 13). A linear dependence between expansion and sodium content is found.
Table VII. Melt Analysis: Before and After Electrolysis

| Carbon sample | Before electrolysis | After electrolysis |
|--------------|---------------------|--------------------|
|              | CR | Excess NaF wt% | Al₂O₃ content wt% | CR | Excess NaF wt% |
| Anthracitic  | 4.0 | 16.7 | 34.3 | 4.15* | 18.7* |
| SGZ**        | 4.0 | 16.7 | 34.3 | 3.52  | 9.4   |
| SGZ          | 8.0 | 50.0 | 7.7 | 5.78  | 35.7  |
| SGZ          | 8.0 | 50.0 | 33.8 | 4.07  | 17.7  |
| CS graphite  | 4.0 | 16.7 | 34.3 | 3.41  | 7.5   |

* Melt samples taken very close to the cathode surface.
** Semigraphitized

**Fundamental Issues.** The experimental results show a strongly enhanced sodium expansion in Al₂O₃-slurry melts with CR > 3. The expansion is proportional to the sodium metal content in the material (i.e., for anthracite carbon). In order to understand the present observations some fundamental facts have to be pointed out.

Figure 14 gives the activity of Na (I) due to the reaction

\[ \text{NaF (I)} + \frac{1}{3}\text{Al (I)} \rightarrow \text{Na (I)} + \frac{1}{3}\text{AlF}_3 (I) \]  

(8)

using the activity data of Dewing [12]. The vapour pressure of Na (I) at 980°C is 2.24 atm [13]. By extrapolation of the data in Figure 14 the pressure of sodium is 1 atm for CR=10.3 and vaporization may occur.

Figure 15 gives the absorption of Na in similar materials as function of the sodium vapour pressure. The absorption is not proportional to the vapour pressure. Instead, it varies according to a BET model [14].

The electrical transport number of Na⁺ is equal to unity in cryolite [15], while it is 0.64 in pure NaF [16]. Al³⁺ is complexed as AlF₆³⁻, AlF₅²⁻ and AlF₄⁻, and will not electromigrate to the cathode. The electromigration of Na⁺ to and deposition of Al³⁺ on the cathode will give a concentration gradient in the boundary layer with an increased NaF concentration on the cathode surface. A stationary state is obtained by the diffusion of NaF away from the cathode and aluminium compounds to the cathode. From the data and model of Thonstad and Rolseth [17], the following CRs were calculated for a current density of 0.75 A/cm² [18]:

**Bulk Melt → Surface:** 2.25 → 3.5, 3.0 → 8.0, 5.0 → 9.4.
Mechanism of Enhanced Sodium Expansion.

The sodium expansion in slurry melts is surprisingly reproducible considering the expected difficulties to keep reproducible conditions in the slurry during electrolysis (Figs. 8-12). The sodium expansion correlates well with the content of sodium metal in the carbon material (Figure 13). It is hence concluded that the observed phenomena are fundamental.

The increased sodium expansion of Al₂O₃-saturated melts with CR=4.0 compared to melts with CR=2.2 is expected due to a shift to the right of Eq. (8). The expansion ratios are 1.4, 1.9 and 1.4 for anthracitic, semigraphitic and semigraphitized carbon, respectively.

A moderately increased expansion is also observed for CR=2.2 when a slurry melt is compared with a saturated melt. The expansion ratios are 1.2, 1.5 and 1.6 (Table VI).

However, when a slurry melt with CR=4.0 is compared with a saturated melt, a dramatic increase is found with ratios 2.8, 3.9 and 6.2. As expected the largest total expansion of 3.5% is found for anthracitic carbon, but the semigraphitized carbon has the largest ratio, 6.2. By increase of the CR ratio to 8.0 the expansion of the semigraphitized in a slurry melt is as high as 3.5% (Figure 12).

The effect of the slurry is expected to be a hindrance of the diffusion due to a reduction of the cross sectional area and a more tortuous path. The electromigration of Na⁺ remains unchanged as the current density is kept constant but the diffusion, of NaF away from and AlF₃ to the surface, is hindered. The consequence is a much larger NaF gradient in the boundary layer. The gradient \( C_{NaF}(surface) - C_{NaF}(bulk) \) is expected to make the cryolite ratio at the surface higher than 8.5 which is estimated for non-slurry melts [17]. An additional effect in basic melt is the reduced solubility of Al₂O₃ as the cryolite ratio increases [19]. This will enhance surface precipitation of Na₂O·11 Al₂O₃. This phenomenon is not necessarily present in the melts with CR=2.2 as the solubility increases up to CR=3 and becomes equal to the solubility for CR=2.2 at about CR=4.0 [19].

Both aluminium and sodium are observed on the surface of the cathode showing codeposition of the two metals. The aluminium globules, found in the bulk melt, may be aluminium separated from the surface or formed by back reaction of sodium in the less basic bulk melts according to Eq. (8). As the solubility of Na in liquid aluminium is very low (0.022 wt% at 1019°C and CR 2.9 [20]) only negligible amounts of sodium will enter the liquid aluminium.

A quantitative model for the present observations cannot be developed due to lack of detailed data for the boundary layer, but some numerical facts can be pointed out. In the basic melts the sodium metal pressure equals 1 atm for CR=10.3. The formation of gaseous sodium with partly evaporation is confirmed by melt analysis before and after
electrolysis (Table VIII). All bulk samples show lower excess NaF after electrolysis than the initial amount. Approximate calculations show that the diminished amount of NaF cannot be explained by absorption of sodium in the carbon samples. Even the small change from 16.7 to 9.4 wt% excess sodium fluoride (Table VIII) leaves 75% of the NaF unaccounted for, i.e., it has evaporated. The one sample taken very close to the surface shows a higher excess NaF after electrolysis than the bulk confirming the presence of a concentration gradient.

The sodium absorption properties of the electrocalcined anthracitic material is expected to be between material A and B in Figure 15. The sodium absorption of the electrocalcined material is then estimated to be about 5 wt% for 1 atm sodium pressure (Figure 15). The measured absorption in the present experiments is, however, up to 10 wt% (Figure 14). This means that the overpotential sets up a sodium activity higher than unity. If, however, the BET model used in [14] is valid, only a slight overpressure is needed to accomplish the doubling of absorption. Although the absorption is not expected to be proportional to the activity, it can be mentioned that 53 mV will give a doubling of the sodium activity.

The diffusional resistance set up by the slurry can explain the present phenomena in general, but it cannot explain the fact that the current regime 0.14 A/cm\(^2\)/0.70 A/cm\(^2\) gives a larger expansion than using 0.70 A/cm\(^2\) throughout (Table VI). The effect is especially strong for the semigraphitized material where the sodium expansion is 2.12 and 0.78%, respectively. In a preliminary paper [4] deposition of \(\beta\)-alumina on the cathode surface was considered to be a dominant cause of the enhanced sodium expansion. \(\beta\)-alumina is the stable oxide in basic melts [19] and a pure Na\(^+\) ion conductor with a specific conductivity of about 0.5 \(\Omega^{-1}\) cm\(^{-1}\) at 980°C [21]. Precipitation at the surface of the cathode is expected due to the reduced solubility of alumina with the increased basicity. The effect of \(\beta\)-alumina was possibly overemphasized since a continuous coating was not found in later experiments. But it was also observed that the slurry electrolyzed at a low current density was much cleaner than the slurry electrolyzed at a high current density. This cleanness helps the formation of an alumina layer and probably a denser \(\beta\)-alumina coating. Hence, the most likely explanation of different sodium expansion for different carbon regimes is a set-up of a more stable solid or semi-solid \(\beta\)-alumina coating during the lower current density. This coating may be more important to the expansion enhancement of the semigraphitized material since the material is more resistant to the sodium absorption.

Technical Implications.

High sodium expansion acts destructively on carbon cathodes. Spalling and cracks may occur. The industrial electrolysis, however, is usually not carried out with the conditions for the high sodium expansion realized in the present set-up. Modern electrolysis uses electrolysis with CR: 2.2 - 2.3 [22], and slurry formation is tried
avoided. But the present experiments illustrate the dangers of a highly irregular operation. It is also a strong argument against basic start-up and simultaneous formation of muck. The paper also provides an explanation for some rather unusual results when cathodes are tested in sodium expansion equipment.

CONCLUSIONS

1. The electrochemical corrosion is a much stronger wear process than the physical abrasion. It is suppressed in alumina slurries. The density, viscosity and cleanliness of the slurry, the rotating speed and surface roughness of the sample, and the wetting between the slurry and the sample all have an influence on the suppression.

2. Graphite and anthracitic carbon have approximately the same resistance to the electrochemical corrosion due to carbide formation.

3. In a cryolitic melt-alumina slurry without aluminium and without polarization, the wear of anthracitic carbon is about one fourth to one fifth of CS graphite which is similar to the result at room temperature test.

4. The strong sodium expansion enhancement in a basic slurry is considered mainly to be due to diffusional hindrance. Formation of β-alumina may also play a part.

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Figure 1: Set-up for abrasion study at room temperature, dimensions in mm. The slurry consists of alumina powder (smelter grade) and sodium polytungstate aqueous solution (SPT). The rotating disc with two identical holders with a rotational radius of 62 mm is for ranking experiments, and the rotating disc with one holder with a rotational radius of 62 mm and one holder with a rotational radius of 40 mm is for parameter study.

Figure 2: Set-up for carbon cathode wear study at high temperatures, dimensions in mm. The slurry consists of a cryolitic melt and alumina powder (smelter grade). The rotating disc with two identical holders with a rotational radius of 50 mm is shown. HP6964A Power Supply was used for experiments with electrolysis.
Figure 3: Apparatus for sodium expansion measurement. The apparatus consists of a tubular furnace with a diameter of 160 mm and an active length of 400 mm, a graphite crucible and crucible support, a constant current DC power supply adjustable to 50 A/12.49 V, and an expansion measuring system. The crucible has an inner diameter of 90 mm and acts as the anode. A sintered alumina disk provides electrical insulation between the crucible and the cathode sample. The measuring system has a range of 10 mm and resolution 1 µm. The expansion signal is sent to a digital display and to a computer which is programmed to record the expansion at one minute intervals.
Figure 4. Wear rate of CS graphite as a function of velocity in cryolitic melt-alumina slurries. Melt B, $A_c = 1.10$ g/cm$^3$, $t=1015$ °C.

Figure 5: Wear rate of CS graphite as a function of alumina content in cryolitic melts with 5-6 wt% aluminium. Melt A, $t=990$ °C, $V=0.55-0.60$ m/s, test time=3 h.

Figure 6: Wear rate of CS graphite as a function of the number of time used. Melt A with 5.65 wt% aluminium, $A_c = 0.80$ g/cm$^3$, $t=990$ °C, each test time=3 hours.

Figure 7: Wear rate of CS graphite as a function of excess alumina content under polarisation. Melt A, $t=990$ °C, $V=0.55-0.60$ m/s, CCD=0.21 A/cm$^2$. 

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Figure 8: Sodium expansion of the anthracitic carbon material as a function of electrolysis time. The numbers on the curves denote cryolite ratio CR and excess Al₂O₃, $A_c^E$, respectively. *) The sample cracked.

Figure 9: Sodium expansion of the semigraphitic carbon material as a function of electrolysis time. The numbers on the curves denote cryolite ratio CR and excess Al₂O₃, $A_c^E$, respectively.
Figure 10. Sodium expansion of the semigraphitized carbon material as a function of electrolysis time. The numbers on the curves denote cryolite ratio CR and excess Al₂O₃, A_c, respectively.

Figure 11. Sodium expansion of three commercial cathode materials as a function of electrolysis time. CR=4.0, A_c=0.80 g/cm³. Current density=0.70 A/cm². An: Anthracitic carbon, SG: Semigraphitic carbon, SGZ: Semigraphitized carbon
Figure 12. Sodium expansion of the semigraphitized cathode materials with high cryolitic ratios. The numbers on the curves denote cryolite ratio CR and excess Al\textsubscript{2}O\textsubscript{3}, $A_c^E$, respectively.

Figure 13. Sodium expansion as a function of sodium metal content in the anthracitic carbon sample.

Figure 14: Activity of Na (l) from Eq. (8) by use of activity data from Dewing [12].

Figure 15: Sodium absorption isotherm at 1227 K for $\Delta W/W_0$; increase in weight relative to original weight of the carbon materials. Filled symbols: Increase in pressure; open symbols: decrease in pressure. A: Gas calcined anthracite with about 30% graphite added. Baked to about 1200. B: Semigraphitic carbon. C: Semigraphitization carbon [14].