

PHYSICAL AND CHEMICAL WEAR OF CARBON CATHODE MATERIALS

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Abstract

The physical and chemical wear of carbon cathode materials for aluminium electrolysis was studied in mixtures of cryolitic melts, alumina and aluminium at 960-1015 °C. The very low wear in aluminium is attributed to poor contact between the metal and the carbon materials due to nonwetting and very low carbide solubility. The much larger wear in cryolitic melt-aluminium system is attributed to the improved wetting and the larger carbide solubility. Under cathodic polarization the samples show even larger wear. The wear mechanism is probably through solid carbide formation and removal with carbide dissolution as the slowest step. Addition of alumina suppresses the wear through physical barriers. Different carbon cathode materials have approximately the same resistance to the chemical corrosion due to Al_3C_4 formation. The physical wear in cryolitic melts is parallel to room temperature experiments using alumina slurries in polytungstate solution.

1. Introduction

The wear resistance is one of the most important properties of carbon cathode materials and is becoming an increasingly important factor as modern cathodes are becoming more sophisticated and expensive. Extending potlife may significantly impact a smelter's profitability. The purpose of the present work is to understand the wear mechanism and to develop a realistic evaluation for the cathode materials. It is generally believed that carbon cathode wear is caused by a combined process of physical abrasion and chemical corrosion. As the first step a room temperature test [1,2] has been developed for the study of the physical abrasion. The samples were rotated in a slurry of alumina dispersed in a sodium polytungstate solution (SPT). The relative abrasion resistance of different carbon materials is shown in Table I.

The resistance increases with decreasing value.

Table I Ranking of Abrasion Resistance of Carbon Cathode Materials Relative to CS Graphite at Room Temperature

Cathode material	Density g/cm^3	Abrasion value*	Standard deviation
G(CS), Ref.		100	
G A (CS)	1.74	99.6	2.8
G B	1.60	132.7	4.1
G C	1.63	112.7	4.2
SGZ A	1.65	87.4	2.7
SGZ B	1.64	102.0	4.2
SG A	1.62	68.0	3.5
SG B	1.60	77.4	4.7
An. A	1.54	17.8	3.1
An. B**	1.53	17.4	2.3
An. C**	1.40	11.4	1.8
TiB ₂ -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.

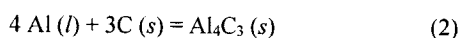
* Average of four measurements; ** Sidewall materials.

The wear increases with alumina content, velocity and pressure. Their effects can be described with a power equation:

$$W_R = k \cdot x^n \quad (1)$$

where W_R is wear rate (mm^3/h or cm^3/year), k and n are constants, x represents alumina content (g/cm^3), velocity (m/s) or pressure (Pa). Alumina content has the largest effect with $n \geq 7$, velocity intermediate $n=2-4$ and pressure lowest $n=0.5-1.4$. The room temperature test is simple, gives valuable insight into the abrasion process and is realistic in a quantitative ranking of commercial cathode materials. The experimental conditions are, however, far from that encountered in the industrial aluminium electrolysis. With the experience from the room temperature testing more realistic tests were set up by use of cryolitic melts, alumina slurries and aluminium with or without electrolysis.

In the industrial electrolysis physical as well as chemical wear were expected. The chemical corrosion is caused by aluminium carbide formation and removal. The reaction between carbon and aluminium



is thermodynamically favoured at all temperatures of concern in aluminium production by electrolysis. The standard Gibbs' energy change for Reaction (2) is -147 kJ at $970 \text{ }^\circ\text{C}$ [3]. Usually, contact between liquid aluminium and carbon does not give appreciable carbide formation below $1000 \text{ }^\circ\text{C}$. The reaction is enhanced by the presence of a cryolitic melt due to the much higher solubility of Al_4C_3 in cryolite relative to aluminium. The dissolved carbide may be transported to the anode where it is oxidized.

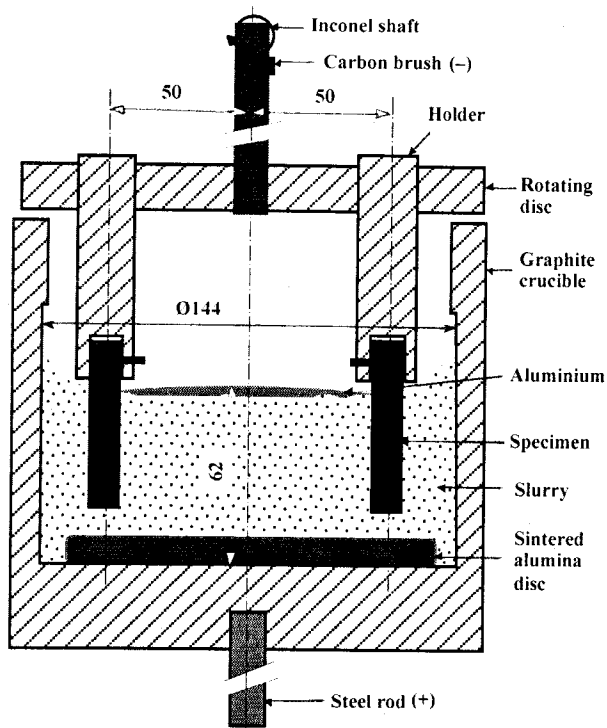


Figure 1: Set-up for carbon cathode wear study in molten cryolitic melts. The rotating disc with two 50 mm holders is shown.

2. Experimental

2.1 Set-up

The set-up (Figure 1) is similar to the room temperature one [1,2]

2.2 Samples

All samples were core drilled and had approximately the same diameter of about 9.98 mm and the length of about 60 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 equal to or less than 35 mm for experiments with electrolysis to avoid short circuiting by contact between the sample holder and the cryolitic melt.

2.3 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 $990 \text{ }^\circ\text{C}$ [4]

	CR	S_A	d_m^s	d_m	t_{liq}	σ
Melt A	2.2	9.46	2.04	2.079	930	109
Melt B	3.0	10.39	2.075	2.128	949	142

CR: cryolite ratio: mole $\text{NaF}/\text{mole AlF}_3$,
 S_A : solubility of alumina in the melt, wt%,
 d_m^s : density of melt saturated with alumina, g/cm^3 ,
 d_m : density of melt without alumina, g/cm^3 ,
 t_{liq} : liquidus temperature of the melt saturated with alumina, $^\circ\text{C}$,
 σ : surface tension of the 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) [5, 6].

In several experiments Al_4C_3 (-325 mesh, Aldrich Chemical Company, Inc., USA) was added in excess of the solubility limit (1.97 wt%) [8].

For the experiment with an alumina-oversaturated melt or slurry, the temperature was first held $30-50 \text{ }^\circ\text{C}$ higher than the test temperature for 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 and the experiment was started by rotating or polarizing the samples.

2.4 Sample Preparation

New samples were rinsed in acetone, washed in distilled water, cleaned in an ultrasonic bath for 20 minutes, and their volumes were measured in distilled water as their initial volumes. The standard deviation of volume measurements by the hydrostatic method is less than 3 mm^3 . The sample was dried in a drying

cabinet for 8 hours or more at 120 °C, and its weight was measured as the initial weight.

2.5 Wear Rate Measurements

For samples without chemical corrosion, such as samples from an experiment with an alumina-oversaturated slurry without aluminium or electrolysis, the following cleaning procedure was employed: The sample was boiled in distilled water for 6 hours, immersed in a water-30 vol% acetone mixture and cleaned ultrasonically in an ultrasonic bath for 30 minutes, dried for at least 8 hours and finally weighed. The above procedure was repeated until the weight change of the sample between two measurements was less than 1 mg. The weight loss was converted to volume loss by dividing by the apparent density of the sample.

Samples subjected to chemical corrosion were cleaned in a 3 M or more concentrated H₂SO₄ solution at 90-100 °C. The volume was measured in distilled water and the volume loss was calculated. In addition, mechanical cleaning with a knife may be involved.

3. Results and Discussions

3.1 Physical Abrasion

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

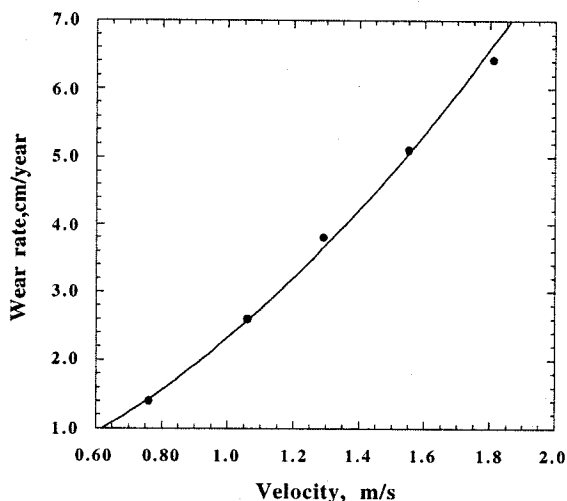


Figure 2: Wear rate of CS graphite as a function of velocity in cryolitic melt-alumina slurries. Melt B, $A_c^E=1.10 \text{ g/cm}^3$, $t=1015 \text{ }^\circ\text{C}$.

The velocity effect on the wear rate in a dense cryolite-alumina slurry is shown in Figure 2. The wear increases rapidly with velocity, similarly to the room temperature test. The wear equation is the following:

$$W_R (\text{cm/year}) = 2.22 [V (\text{m/s})]^{1.77} \quad (3)$$

The wear rate in the cryolitic melt-alumina slurry is smaller than that in the SPT-alumina slurry[1,2]. The possible reasons for this are

1. Alumina particles become less abrasive since their edges and corners preferentially dissolve in the cryolitic melts (the sharpness is reduced).
2. 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.
3. 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.
4. The temperature is very different.

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 g/cm^3 was found to lose fluidity at $\text{CR}=3.0$ and $t=1015 \text{ }^\circ\text{C}$, 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 g/cm^3 before it loses fluidity at room temperature.

3.2 Prediction of Physical Wear in Industrial Aluminium Electrolysis Cells

The main difference between the present study and the abrasion in aluminium cells is that the pressure acting on the sample surface due to gravity in the present study is much smaller than the pressure acting on the carbon cathode 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 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 [2, 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 an industrial aluminium cell in the velocity range 0.1–0.5 m/s were estimated 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.

It is seen from Table III that the wear rate increases rapidly with velocity as the exponent in Equation (3) is 1.77.

Table III Estimated Wear Rates in cm/year of CS Graphite under Industrial Smelting Conditions by Extrapolation of Equation (3)

Velocity m/s	0.10	0.15	0.20	0.25	0.30	0.40	0.50
Laboratory wear rate	0.04	0.08	0.13	0.19	0.26	0.44	0.65
Industrial wear rate	0.6	1.3	2.2	3.2	4.5	7.5	11.1

3.3 Chemical Corrosion without Electrolysis

When aluminium is added to a cryolitic melt with or without Al₄C₃, the wear mechanism of carbide formation (eq. 2) and dissolution will be active. Figure 3 shows that the wear in mm³ of CS graphite increases with time in cryolitic melt with 5-6 wt% aluminium without electrolysis, but the increase slowed down significantly after the test time was increased to 4 hours or longer. This was probably due to the formation of a carbide film which presented a diffusion barrier [8]. However, some wear was still observed in an oversaturated solution of Al₄C₃ (Figure 3). When the melt without carbide addition was used for the second time with new samples, wear rates similar to the first experiment were found. This also indicates that the contribution to the wear from carbide concentration is limited.

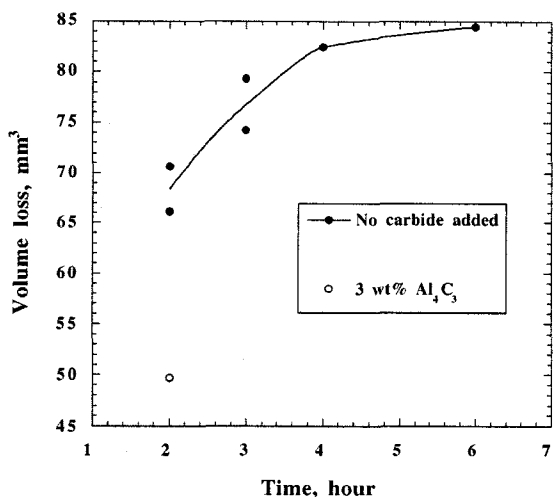


Figure 3: Volume loss of CS graphite as a function of test time in cryolitic melt with 5-6 wt% aluminium without electrolysis. Melt A, t=990 °C, V=0.55-0.60 m/s.

3.3.2 Effect of Velocity

Figure 4 shows the wear rate of CS graphite as function of velocity in liquid aluminium and in cryolitic melt with 5-6 wt% aluminium. Little wear occurred in aluminium. The data were fitted to the following equation:

$$W_R \text{ (cm/year)} = 0.22 + 2.58 V \text{ (m/s)} \quad (4)$$

The wear rate was greatly increased when a cryolitic melt was added. The wear rate again increases linearly with velocity. The data was fitted to the following equation:

$$W_R \text{ (cm/year)} = 18.14 + 25.38 V \text{ (m/s)} \quad (5)$$

The very low wear in aluminium is probably due to poor contact between the carbon material and the metal since the metal does not wet carbon materials. Another important factor is the very low solubility of aluminium carbide in molten aluminium, about 0.04 wt% under the present conditions[9]. On the other hand, aluminium can dissolve in a cryolitic melt and give sodium activity. This makes the melt wet carbon materials quite well, and the solubility of aluminium carbide in cryolitic melts is approximately 50 times of that in aluminium[9, 10]. The improved wetting and higher carbide solubility are considered responsible for the much larger wear when a cryolitic melt is added.

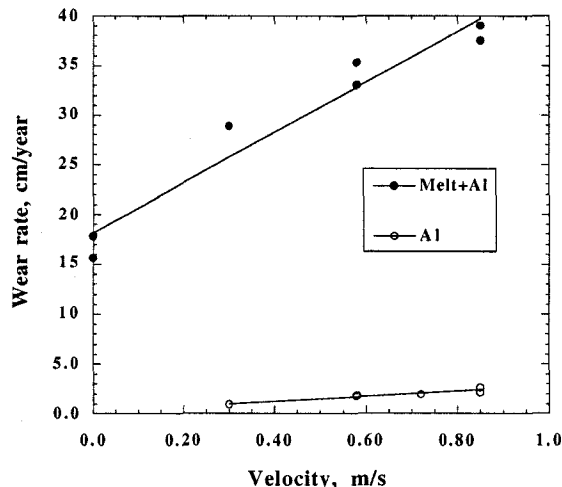


Figure 4: Wear rate of CS graphite as a function of velocity in aluminium and in cryolitic melt with 5-6 wt% aluminium without electrolysis. Melt A, t=990 °C, test time=2 hours.

When excess alumina is added to the above alumina-saturated melt with aluminium, the wear process becomes 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 chemical 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.

Figure 5 shows the wear rate of CS graphite as a function of the alumina content in cryolitic melts with 5-6 wt% aluminium.

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 chemical corrosion due to carbide formation and dissolution. It

is also seen that the wear in the slurry increases significantly with temperature. This is probably due to 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 alumina addition seems to be the physical barrier or poor surface mixing through alumina layer formation.

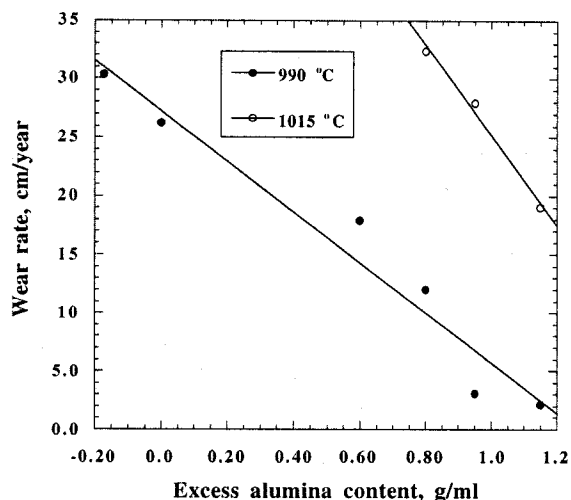


Figure 5: Wear rate of CS graphite as a function of alumina content in cryolitic melts with 5-6 wt% aluminium. Melt A, $t=990\text{ }^{\circ}\text{C}$, $V=0.55\text{-}0.60\text{ m/s}$, test time=3 hours.

The density and cohesiveness of the alumina layer were found to decrease with the number of times the slurry was used, and the wear increases, as shown in Figure 6. The slurry becomes more and more dirty with the times 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 times used, this is probably because the porosity of alumina particles decreased with the times used through solution and precipitation 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 defects, 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.

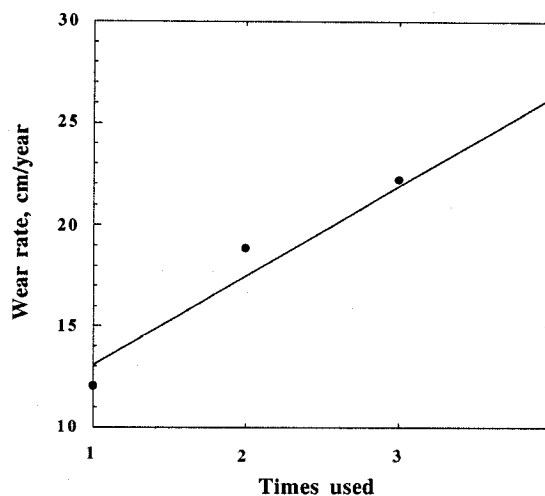


Figure 6: Wear rate of CS graphite as a function of the number of times used. Melt A with 5.65 wt% aluminium, $A_c^E=0.80\text{ g/cm}^3$, $t=990\text{ }^{\circ}\text{C}$, each test time = 3 hours.

3.4 Chemical Corrosion under Polarization

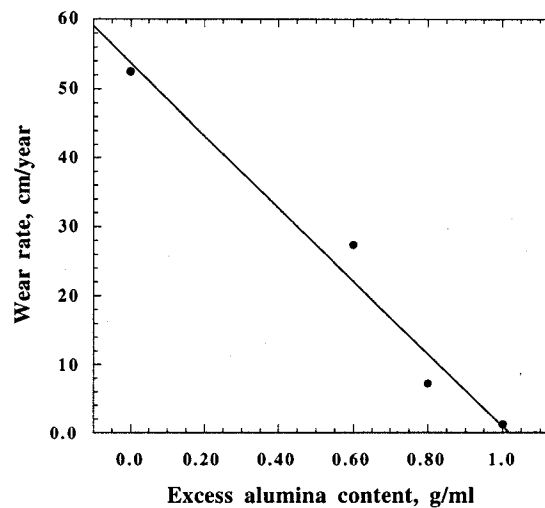


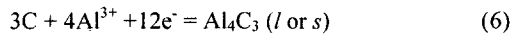
Figure 7: Wear rate of CS graphite as a function of excess alumina content under polarization. Melt A, $t=990\text{ }^{\circ}\text{C}$, $V=0.55\text{-}0.60\text{ m/s}$, $\text{CCD}=0.21\text{ A/cm}^2$.

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.[11] of 9.1 mm/week in industrial cells and Gudbrandsen et al.[12] 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 solution, the removal of the alumina layer is difficult.

The wear rates of CS graphite in alumina-saturated cryolitic melts with or without Al₄C₃ added are shown in Table IV. The immersed length of the sample was about 28-30 mm for all the experiments here. The total surface area and total wear are used for the calculation of an average current density for experiments with two samples connected in the 50 mm holder and the 20 mm holder respectively, since their wear rates are similar. An average current efficiency for carbide formation (Carbide CE) is also calculated. It is then assumed that the only wear mechanism is the half cell reaction



The carbide current efficiency is then the part of the current that can be attributed to this reaction. The apparent density of CS graphite used here is about 1.80 g/cm³. The electrochemical equivalent is then 62.2 mm³/A-h. The carbide current efficiencies are calculated according to this equivalent.

Graphic representations of the wear rates for these eight experiments are shown in Figure 8 (the average wear rate is used if two samples are involved in one experiment).

The effect of Al₄C₃ concentration on the wear rate is limited, as the carbon cathode was worn away at a similar rate in the carbide-oversaturated melt and in the corresponding carbide-free melt under similar conditions (Compare Experiments 2-4 with Experiments 6-8 in Table IV). The possible explanation is that the wear product in Reaction (6) is solid carbide and that a dissolution mechanism is not operative since dissolved carbide cannot be formed in the carbide-saturated melt. This is different from what is suggested by Gudbrandsen et al. [12] that the cathode wear is caused by cathodic carbon dissolution and

that no solid carbide is present at electrolysis temperature. The solid carbide formed according to Reaction (6) is probably particles which easily detach from the cathode. The dissolution of carbide is slow and the melt is probably under-saturated with carbide once the electrolysis is started. The melt is well stirred so that the concentration difference of carbide makes limited contribution to the mass transfer, and hence to the carbide dissolution and cathode wear.

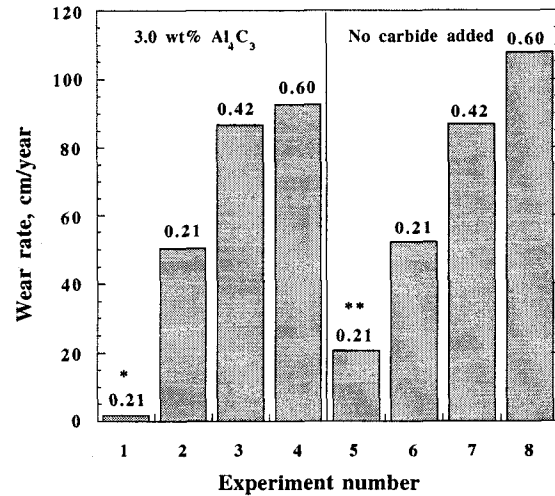


Figure 8: Wear rates of CS graphite in Melt A with or without Al₄C₃ addition, numbers on the bars denote the current density, A/cm².

* Excess alumina was added ($A_c^E = 0.80 \text{ g/cm}^3$).

** Started electrolysis when the melt was viscous.

Table IV Wear of CS Graphite in Cryolite-Based Bath with or without Al₄C₃ Addition
Bath A, T=980 °C, V=0.60 m/s, Test Time = 3 hours

Experiment	1		2		3		4		5		6		7		8	
	1#	2#	3#	4#	5#	6#	7#	8#	9#	10#	11#	12#	13#	14#		
Sample																
Holder	20	50	20	50	20	50	50	20	50	20	50	20	50	50		
Current, A	4		4		8		6	4		4		8		6		
CCD, A/cm ²	0.21		0.21		0.42		0.60	0.21		0.21		0.42		0.60		
Al ₄ C ₃ , wt%	3		3		3		3	0		0		0		0		
Cell voltage, V	4.8-5.1		3.0-3.2		5.0-5.2		4.0-4.2	4.6-4.8		4.6-4.8		6.3-6.5		5.1-5.3		
Wear rate, cm/year	2.33	1.19	48.03	52.71	80.89	92.43	92.76	23.30	18.28	53.71	50.45	83.36	90.28	107.8		
Carbide CE %	1.46		41.82		35.97		28.14	17.26		43.23		36.04		32.60		
Carbide CD, A/cm ²	0.003		0.087		0.151		0.169	0.037		0.091		0.151		0.196		
Note	New slurry A _c ^E = 0.80 g/cm ³		New melt		Used bath in Expt 2		New melt	Started electrolysis when melt was viscous		New melt		Used melt in Expt 7		New melt		

The cell voltages listed in Table IV should be viewed with some caution since the contact resistance between the carbon brush and the shaft may vary significantly from experiment to experiment. However, the difference between experiments with carbide addition and that without carbide addition is seen. The cell voltage in the carbide-free melt is significantly greater than that in the carbide oversaturated melt when the total current and alumina concentration are the same. The cell voltage is comprised of three components:

- The cell and melt resistance contribution.
- The electrochemical decomposition voltage.
- The electrode polarization.

Since the current densities employed here are large enough for aluminium deposition, the following two parallel cell reactions are expected to occur:

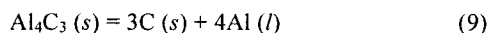
- Carbide formation at the cathode and oxidation at the anode which should occur at 0 volt plus overpotential:



- Aluminium deposition and carbon monoxide evolution (dioxide evolution is also possible since the anodic current density is uneven although the average is very low) for the carbide-free melt which should occur at about 1.1 volts plus overpotential:



For the carbide-oversaturated melt, the overall reaction should be the following:



The standard voltage for reaction (9) is calculated to 0.127 V at 970 °C[3].

The cell voltage difference observed by Gudbrandsen et al. [12] where the cell voltage difference between period 1 (corresponding to carbide-free melt) and period 3 (corresponding to carbide-saturated melt) is about 1.4 volts.

The carbide current densities (Carbide CD) in Table IV are calculated by multiplying the current density by the corresponding carbide current efficiency. The results show that the limiting current density for carbide formation may exceed 0.20 A/cm² (Experiments 4 and 8). This value is higher than that found by Gudbrandsen et al, probably because the samples are rotating in the present study, while Gudbrandsen used static samples. More experiments with higher current densities are needed to find out the limiting carbide current density.

Experiment 1 shows that excess alumina strongly suppresses the wear in carbide saturated melt. The current efficiency is the lowest among the experiments with electrolysis.

A solid crust was observed after Experiment 5, indicating that a solid crust can be formed when the electrolysis is started in a viscous melt, and this crust can remain for a long time even though the viscosity is decreased since the melt is kept at a high temperature for a long time. The crust is probably rich in cryolite whose melting point is about 30 °C higher than the test temperature.

4. Ranking

4.1 Resistance to Chemical Corrosion

The wear rates of CS graphite and anthracitic carbon in cryolitic melt with or without electrolysis are given in Table V.

Table V Wear Comparison of CS Graphite (G) and Anthracitic Carbon (A) in Cryolitic Melts at 980 °C, Melt A, $V=0.55$ m/s

Expt	1		2		*3		*4	
	G	A	G	A	G	A	G	A
CCD, A/cm ²	0.15		0.21		0		0	
A_c^E , g/cm ³	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 V 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 [13].

4.2 Resistance to Physical Abrasion

When no aluminium is added or electrolysis performed, the chemical corrosion disappears. The ranking results between CS graphite and anthracitic carbon in such systems are given in Table VI.

Table VI shows 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 which is similar to the result at room temperature test[1,2].

With two samples moving in the same path, the ranking experiments were found to give 30-60% less wear rate than the velocity effect experiments where two samples moved in different paths.

Table VI Ranking of CS Graphite (G) and Anthracitic Carbon (A) in Cryolitic Melt-Alumina Slurries without Aluminium and without Electrolysis, $V=1.58-1.75$ m/s

Expt	1		2		3		4	
	G	A	G	A	G	A	G	A
Sample	G	A	G	A	G	A	G	A
A_c^E , g/cm ³	0.90		1.15		0.85		1.10	
Melt	A		A		B		B	
T , °C	960		990		980		1015	
Weight loss, mg	29.3	6.3	49.3	7.9	47.8	8.5	73.6	14.8
Wear rate mm ³ /h	2.09	0.51	3.52	0.64	3.41	0.69	5.26	1.20
Wear rate cm/year*	1.99	0.48	3.35	0.61	3.24	0.66	4.99	1.14
Relative wear rate**	0.241		0.182		0.213		0.228	

* The wear rate is calculated according to density and test time, the density of graphite is 1.75 g/cm³, anthracitic carbon 1.54 g/cm³.

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

5. Conclusions

1. The chemical corrosion is a much stronger wear process than the physical abrasion. It is suppressed in alumina slurries. The density, viscosity and cleanness 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. The concentration of Al₂O₃ has little influence on the wear rate of the carbon cathode in electrolysis of well-stirred cryolite-based melts. This indicates that the wear mechanism is probably through solid carbide formation and removal, and that carbide dissolution is slow.

3. Graphite and anthracitic carbon have approximately the same resistance to the chemical corrosion due to carbide formation.

4. 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.

5. It is generally known from smelting experience that graphitic materials are less wear resistant than anthracitic materials. In spite of that chemical wear is found to be larger than physical wear, it appears that physical wear is the most important wear mechanism for cathode materials. Because of the parallelity of physical wear in cryolitic melts and in SPT, the easy room temperature test is recommended for evaluation of cathode materials. It is, however, expected that the room temperature testing exaggerates somewhat the difference between materials. Further studies with more materials will be carried out.

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Reference

1. X. Liao and H. A. Øye, "Method for Determination of Abrasion Resistance of Carbon Cathode Materials at Room Temperature," *Carbon* **34** (1996), 649-661.
2. X. Liao and H. A. Øye, "Determination of Abrasion Resistance of Carbon Cathode Materials at Room Temperature," *Tribologia-Finnish Journal of Tribology* **15** (3) (1996), 3-34.
3. W. L. Worrell, "Carbothermic Reduction of Alumina: A Thermodynamic Analysis," *Can. Met. Quart.* **4** (1965), 87-95.
4. K. Grjotheim and H. Kvande, Introduction to aluminium electrolysis (2nd edition, Aluminium-Verlag, Düsseldorf, 1993).
5. X. Liao and H. A. Øye, "Increased Sodium Expansion in Cryolite-based Alumina Slurries," *Light Metals* (1998).
6. E. Rabinowicz, *Friction and wear of materials* (2nd ed., USA, 1995).
7. X. Liao and H. A. Øye, "Enhanced Sodium Expansion in Carbon Cathode Materials due to Presence of Alumina Slurries," *Aluminium* **73** (1997), 528-531.
8. E. A. Hollingshead and J. A. Brown, "Rate of Solution of Carbon in Molten Aluminium under a Cryolite Melt," *Light Metals* (1982), 625-634.
9. R. Ødegard, Å. Sterten and J. Thonstad, "On the Solubility of Aluminium Carbide in Cryolitic Melts," *Light Metals* (1987), 295-302.
10. R. Ødegard, Å. Sterten and J. Thonstad, "On the Solubility of Aluminium in Cryolitic Melts," *Met. Trans.* **19B** (1988), 449-457.
11. M. P. Taylor, B. J. Welch and J. T. Keniry, "Influence of Changing Process Conditions on the Heat Transfer during the Early Life of an Operation Cell," *Light Metals* (1983), 437-447.
12. H. Gulbrandsen, Å. Sterten and R. Ødegård, "Cathodic Dissolution of Carbon in Cryolitic Melts," *Light Metals* (1992), 521-528.
13. M. Sørli and H. A. Øye, *Cathodes in Aluminium Electrolysis* (2nd edition, Aluminium-Verlag, Düsseldorf, 1994).