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DETERMINATION OF THE EFFECT OF PITCH-IMPREGNATION ON CATHODE EROSION RATE

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Abstract

A number of smelters have adopted or have trialed high density, pitch impregnated cathode blocks as one measure to counter the trend in decreasing cell life due to line current increases. To date the true benefits of pitch impregnated cathode blocks are not fully understood and therefore a joint collaboration between SEC CARBON Limited and the Light Metals Research Center has endeavored to understand the effect of pitch impregnation on cathode block performance. The initial results of this project showed that pitch impregnated cathode blocks had no benefit in regards to electrochemical wear resistance, and it was proposed that this was due to the pitch impregnation increasing the reactivity of the cathode material [1]. This paper reports on recent work conducted to firstly characterize the difference between the pitch impregnation phase and other phases present in the bulk cathode matrix and secondly to understand the relative reactivity of these phases under electrolysis conditions.

Introduction

The use of graphitized cathode blocks has become wide spread in the aluminium smelting industry as these low electrical resistivity blocks allow the for higher amperages at lower cathode voltage drops. This can result in significant increases in production while minimizing the impact on energy efficiency. Although the benefits of increased line current (production) have been realized it has come at the detriment of decreasing pot life due to increased erosion rate.

The correlation between increases in amperage and increased erosion rate has been studied extensively and it is generally accepted that the electrochemical formation and subsequent dissolution of aluminium carbide is one of the dominant erosion mechanisms in graphitized cathode materials. The electrochemical formation of aluminium carbide has been found to be accelerated with increasing cathode current density the mechanism shown in equation 1 [2-6].

$$3\,C_{(cathode)} + 4\,AlF_{3\,(diss)} + 12\,e^- = Al_4C_{3\,(s)} + 12\,F^-_{(diss)} \qquad (1)$$

Although the mechanism in equation 1 shows the consumption of cathode carbon, this reaction alone does not lead to significant erosion as the aluminium carbide formed will act as a passivating layer protecting the cathode surface from further attack. For erosion to occur the formation mechanism needs to be coupled with a subsequent dissolution mechanism. Work carried out by Ødegård et al. showed that aluminium carbide readily dissolves in the presence of a cryolitic melt through equation 2 below [7].

$$Al_4C_{3\,(s)} + 5\,AlF_{3\,(diss)} + 9\,F^-_{(diss)} = 3\,Al_3CF_8^{3-}{}_{(diss)} \qquad (2)$$

In industry the correlation between the erosion of graphitized cathode blocks and current is not only evident by lower overall pot life but also by the W-shape wear patterns observed in decommissioned pots as shown in Figure 1. This wear pattern is due to local increases in current density as the current takes the shortest path through the low resistivity blocks to the collector bars. In the areas of high localized current density the rate of aluminium carbide formation is higher which when coupled with higher fresh bath recirculation in the same areas will lead to increased localized erosion rates shown.

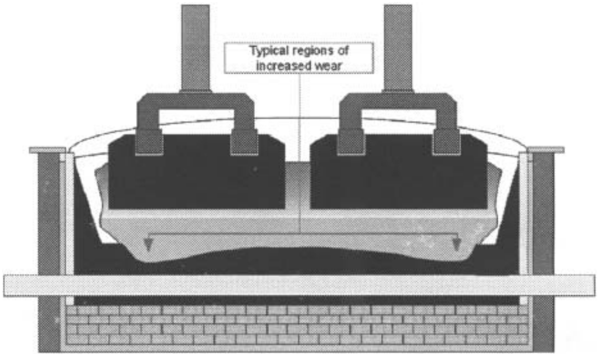

Figure 1: W-Shape wear patterns in modern aluminium cells

It should be noted that aluminium carbide formation is not solely limited to the surface and it has been found by Rafiei et al. and Patel et al. that electrochemical aluminium carbide formation can occur within the pores of the cathode structure which can lead to internal weakening and particle detachment which can result in pitting and ultimately cathode failure [3, 4, 8].

Electrochemical aluminium carbide formation and dissolution is not the sole mechanism contributing to cathode erosion. Physical erosion is also a major contributor and is extremely important in graphitized cathode blocks which are generally softer than other cathode types. Physical erosion occurs due to the movement of sludge, bath and metal over the cathode surface. It is the alumina in the sludge which is the most detrimental to the cathode as it is hard and naturally abrasive [9].

In recent years, efforts in graphitized cathode block development have mainly concentrated on increasing abrasion resistance and reducing internal electrochemical wear mechanisms by increasing cathode density, mainly through efforts to reduce open porosity. This has mainly been done through formulation optimization and/or pitch impregnation.

Pitch impregnation has been a major avenue of development for a number of cathode manufacturers around the world. It involves forcing pitch into the pores of the cathode material, with subsequent baking and graphitization to reduce the open porosity. The use of this densification technique does result in improved physical and mechanical properties such as increased density, increased flexural strength and reduced electrical resistivity, however it was reported by Sato et al. that it can adversely affect the wear resistance of the material [1].

Sato et al.'s findings showed that when non-pitch impregnated and pitch impregnated cathode samples were tested in laboratory scale electrochemical erosion experiments the pitch impregnated samples generated higher erosion rates (as shown in Figure 2) [1]. This indicated that pitch impregnated samples have higher susceptibility to electrochemical aluminium carbide formation and dissolution.

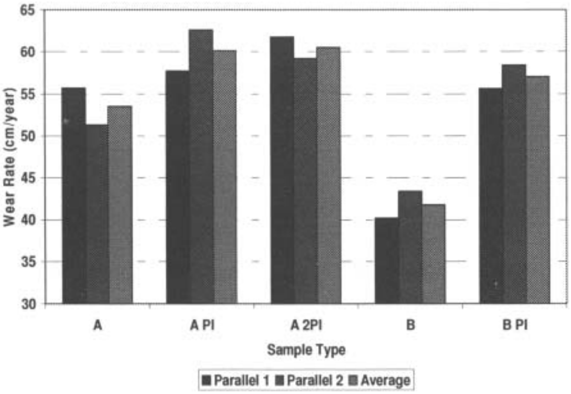

Figure 2: Laboratory erosion rates with rotating cathode. 48 hour electrolysis at a cathode current density of 1 A/cm^2 with rotation speed of 80 rpm. A and B represent different formulation types

Although with the pitch impregnated samples a definite increase in electrochemical erosion was found, the mechanism leading to the increased erosion rate was still unclear. It was suggested however that the impregnation pitch used could have a higher reactivity than the bulk cathode matrix and therefore cause increased erosion. With this in mind the work reported here was designed as a continuation of the work reported by Sato et al. [1] to try and understand the mechanisms leading to the increased erosion rate after graphitization of cathode materials with pitch impregnation.

The two main areas investigated and reported in this paper were:

- Characterization of the impregnation pitch material to determine any differences between this and regular binder pitch which could help explain an increase in reactivity.
- Determine the relative electrochemical reactivity of the pitch impregnation phase and the standard binder pitch phase under electrochemical testing conditions.

Characterization

To understand the possible reasons for greater reactivity in the impregnation pitch phase a greater understanding on its structure was required, especially in terms of how different it is from phases found in a non- pitch impregnated cathode material.

It was decided that comparisons will only be made between the impregnation pitch material and a standard binder pitch material as these are the phases that will likely have the highest reactivity in a cathode block in terms of aluminium carbide formation (via equation 1).

The impregnation pitch and binder pitch selected were standard pitch types produced by a Japanese maker. Table I shows that the properties of the two pitch types are significantly different with the impregnation pitch having lower viscosity, softening point and toluene and quinoline insoluble fractions. For impregnation pitches, viscosity, softening point and very low quinoline insolubles content are highly important as this will determine the ease of pitch penetration and target pore size range reduction for the impregnation process.

Table I: Properties for the impregnation and binder pitches.

	Impregnation Pitch	**Standard Binder Pitch**
Softening Point (ºC)	77	97
Fixed Carbon (%)	51.5	57.5
Toluene Insoluble (%)	12	33.5
Quinoline Insoluble (%)	<0.1	11.5
Viscosity (mPa.s)	20 at 200 ºC	800 at 160 ºC

From these pitch types four samples with varying heat treatments were analyzed using x-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM). The four samples investigated are outlined in Table II.

Table II: Binder and impregnation pitch samples

	Sample Forming Method
Binder Pitch Calcinated	Normal binder pitch, heat treated to 1000ºC and then crushed
Binder Pitch Graphitized	Normal binder pitch, heat treated to 2800ºC and then crushed
Impregnation Pitch Calcinated	Impregnation pitch, heat treated to 1000ºC and then crushed
Impregnation Pitch Graphitized	Impregnation pitch, heat treated to 2800ºC and then crushed

Characterization - XRD Results

XRD was used to determine the degree of graphitization of the samples shown in Table II. As the degree of graphitization increases the carbon peak measured by XRD will become narrower because the sample is more crystalline.

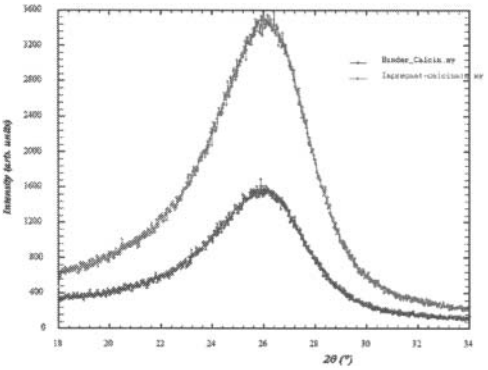

Figure 3: XRD pattern for calcined binder and impregnation pitches

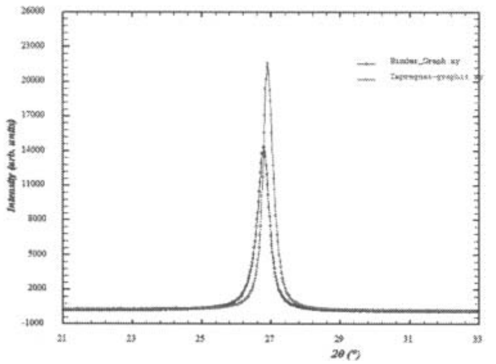

Figure 4: XRD pattern for graphitized binder and impregnation pitches

From the spectra (Figures 3 and 4) the full width half maximum (FWHM) can be used to determine the peak width, infering the crystallinity (L_c). From the results shown in Figure 3 and Table III the calcined pitches have relatively low and similar crystallinities. This shows that heat treatment to 1000ºC has minimal effect on the graphitization of both samples.

The graphitized sample results (heat treated to 2800ºC) in Figure 4 and Table III show that the degree of graphitization increases dramatically for both samples. However, it was found that the graphitized impregnation pitch had the highest L_c value, indicating the greatest degree of graphitization and crystallinity.

Table III: XRD results for binder and impregnation pitches heat treated to 1000 and 2800ºC

Material	B (rad)	Lc, (Å)
Binder Pitch Graphitized	0.00785	254.3
Impregnation Pitch Graphitized	0.00606	360.7
Binder Pitch Calcinated	0.0737	20.5
Impregnation Pitch Calcinated	0.0724	21.4

The high crystallinity found in the graphitized impregnation pitch is particularly interesting when directly compared with a standard non-impregnated graphitized cathode block sample. The L_c for the standard cathode block was found to be 306 Å, which is lower than the graphitized impregnation phase, thus showing that if the sample was impregnated there will be a definite difference in the phases present in the bulk. This difference in phase properties could lead to the adverse affects noticed in the pitch impregnated cathode samples previously tested.

Samples Development for Environmental Scanning Electorn Microscopy (ESEM) and Electrochemical Wear Analysis

Custom cathode samples were required so comparisons could be directly made between the graphitized impregnation pitch and binder pitch. To achieve this, two samples were developed which contained 60 wt% of either the powdered impregnation pitch phase or binder pitch phase (Sample U and V respectively). Each sample type contained the same aggregate filler coke material type and grain size fractions (40 wt%) thus making the primary difference between each sample the powdered pitch phase and therefore any differences in measured electrochemical wear rate could be attributed to this.

Along with samples U and V, a third sample W, was produced which contained powdered coke material for its 60 wt% fraction. This sample represented a material which approaches commercial cathode formulations and was used for comparison. The production steps for all test samples are outlined in Figure 5.

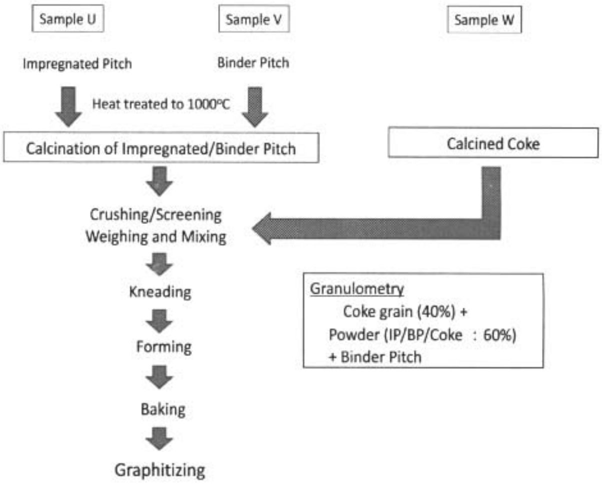

Figure 5: Production steps of test samples for determining electrochemical reactivity of impregnation pitch

Table IV shows some of the resulting properties for the test samples U, V and W.

Table IV: Properties of specialized samples

	Sample U	Sample V	Sample W
Bulk density (g/cm^3)	1.567	1.667	1.599
Electrical resistivity (μΩm)	13.3	12.9	12.1
Young's Modulus (GPa)	4.45	6.47	6.49

Characterization - ESEM Results

One property difference thought to have a significant effect on the final performance of the cathode block was the difference in thermal expansion between the graphitized impregnation phase and the graphitized binder phase. Phases with higher degrees of graphitization such as the graphitized impregnation pitch will have higher thermal expansion coefficients and therefore when heated could expand and widen finer pore networks, potentially increasing the exposed surface area and thus the reactivity of the material.

To test this hypothesis, ESEM analysis with in-situ sample heating was conducted to determine if any microscopic structural changes could be observed when the samples U (impregnation pitch rich) and V (binder pitch rich) were heated from room temperature to 800 ºC. Samples were heated in the presence of reducing gas atmosphere to eliminate oxidation of the sample at high temperature.

Figure 6 and 7 show room temperature ESEM images of samples V and U respectively. The images show a difference in texture between the two samples with Sample U having a more ordered structure as evident by distinct and preferentially orientated graphite platelets. This is a direct reflection of the higher graphitization state of the impregnation pitch material as confirmed by the XRD results.

Although structural differences were seen between the different materials at room temperature, when the samples were heated slowly to 800 ºC, very little to no quantifiable structural change could be observed in either sample. This can be seen when comparing the U sample in Figure 7 (room temperature) and Figure 8 (800 ºC) where images appear almost identical, with little difference in pore size and no significant evidence of opening up of graphene layers. Although these results disprove the hypothesis that was being tested, they do allow us to conclude that surface area changes due to thermal expansion are not likely the cause of the increased wear rate observed in the impregnated cathode samples.

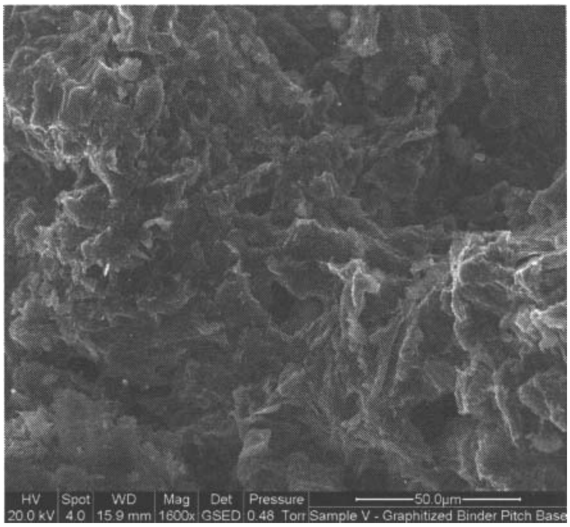

Figure 6: Sample V, graphitized binder pitch rich sample – Room Temperature

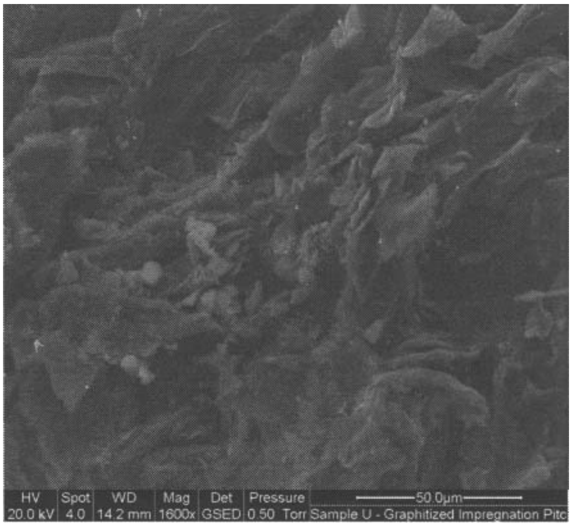

Figure 7: Sample U, graphitized impregnation pitch rich sample – room temperature

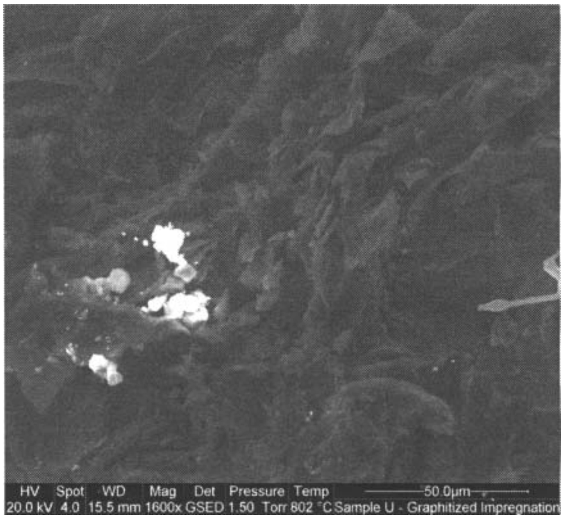

Figure 8: Sample U, graphitized impregnation pitch rich sample – 800ºC

Determination of Electrochemical Reactivity of Impregnation Pitch

Through controlled laboratory electrolysis experiments the electrochemical wear rate (in cm/year) of cathode materials was measured and compared to determine the relative electrochemical reactivity of samples U, V and W.

The laboratory electrolysis configuration (Figure 9) used in this set of experiments was an inverted cell configuration where the cathode sample was centrally suspended in a graphite crucible which acts as the anode for the experiment. This configuration was used as it promotes electrochemical wear because the sample is not protected by an aluminium pad and therefore is always exposed to fresh bath. In all experiments, a sintered alumina cone was used to direct aluminum away from under the cathode sample to the anode where aluminium re-oxidation would take place. The cone also provided an extra source of alumina so the cell did not require feeding at any point during the experiment. During the entire experiment the cathode was rotated at 80rpm to promote mass transfer of aluminium carbide to the bath.

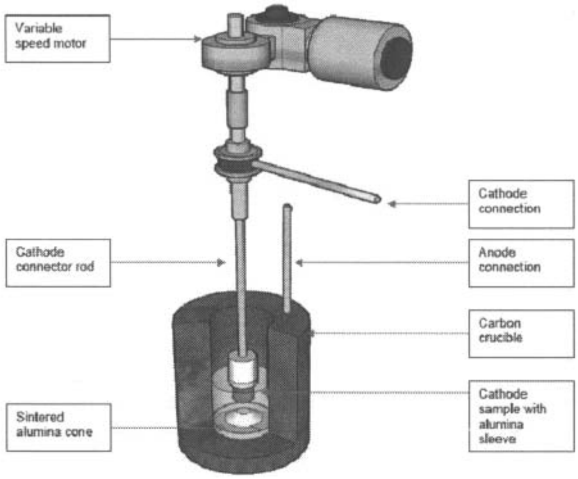

Figure 9: Experimental set up for laboratory electrolysis wear testing with rotating cathode

Experimental parameters such as bath composition, current density and experiment time can be found in Table V.

Table V: Experimental conditions for laboratory electrolysis of cathode materials.

Bath Composition	Weight Percent (%)
Cryolite	78.7
Alumina	9
Aluminum fluoride	7.8
Calcium fluoride	4.5

Aluminium added at start	26g
Cathode current density	1 A/cm^2
Electrolysis time	48 hours
Cathode immersion depth	38mm

For each sample type, two samples were tested to ensure reproducibility of results. Figure 10 gives a summary of the erosion rates found after 48 hour laboratory electrolysis.

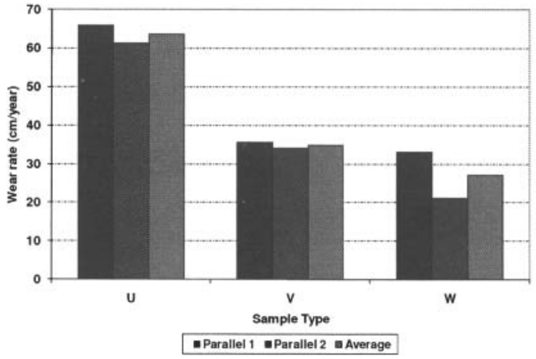

Figure 10: Erosion rates for samples U, V and W

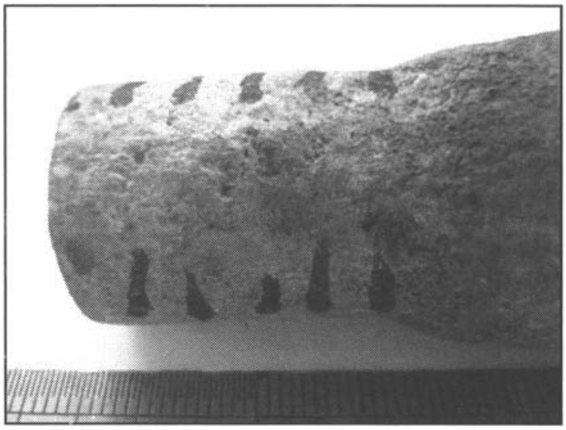

Figure 11: U sample – 60 wt% impregnation pitch powder

Figure 12: V Sample – 60 wt% binder pitch powder

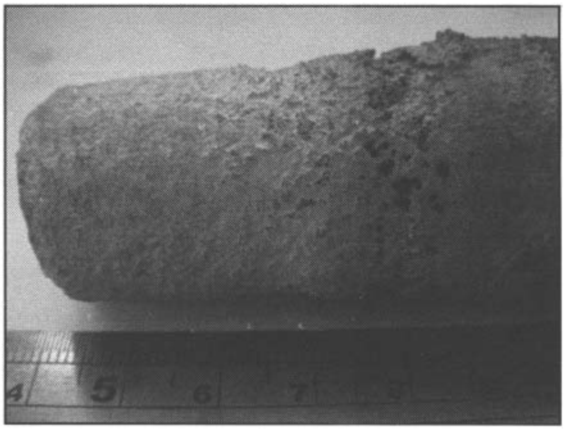

Figure 13: W Sample – 60 wt% coke powder

Results show that sample U produced a significantly higher wear rate (nearly double) under identical conditions than samples V and W. This confirms the theory that the graphitized impregnation pitch phase has a higher electrochemical reactivity than the graphitized binder pitch phase and also the graphitized coke phase of sample W. This in agreement with the results reported in Light

Metals 2010 where it was stated that pitch impregnation had an adverse effect on the results.

Although these wear results confirm the proposed hypothesis that the impregnation phase has a higher reactivity than the binder pitch phase or the coke phase, it however also goes against the general accepted theory that highly ordered graphite structures will have lower reactivity than the less ordered structures. The reason for the higher reactivity in the highly ordered graphitized impregnation phase is still unclear and more experimentation will be carried out to determine the acting mechanism. It is clear however, from the ESEM results that the driving mechanism relates to the chemical reactivity of the material rather than structural aspects such as increased porosity and surface area due to differing physical properties of the pitch impregnation material.

More work on the actual mechanism causing the increased reactivity will be carried out and reported at the Light Metals Conference.

Conclusions

- Graphitized impregnation pitch was found to have a higher degree of graphitization than graphitized binder pitch and also standard graphitized cathode block material. This indicates that within impregnated cathode blocks a definite phase differential exists.

- Cathode samples which contained 60 wt% powdered impregnation pitch wore significantly more than the powdered binder pitch sample. This implies that the impregnation pitch has a higher electrochemical reactivity than the other samples tested.

- The higher electrochemical reactivity of the impregnation pitch phase can not be attributed to increased surface area due to structural changes of this phase during heating. It is therefore concluded the increased reactivity is due to the chemical reactivity of carbon phase itself.

References

1. Sato.Y, Patel.P, and Lavoie. P, *Erosion Measurements of High Density Cathode Block Samples Through Laboratory Electrolysis with Rotation.* TMS (The Minerals, Metals and Materials Society), Light Metals 2010, 2010. p. 817 - 822

2. Keller.R, Burgman.J.W, and Sides.P.J, *Electrochemical Reactions in the Hall-Heroult Cathode.* TMS (The Minerals, Metals and Materials Society), Light Metals 1988, 1988: p. 629-631.

3. Patel.P, Hiltmann.F, and Hyland.M, *Influence of Internal Cathode Structure on Behavior during electrolysis, Part II: Porosity and Wear Mechanisms in Graphitized Cathode Materials,* TMS (The Minerals, Metals and Materials Society), Light Metals 2005, 2005. p. 757 - 762

4. Rafiei.P, Hiltmann.F, Hyland.M and Welch.B, *Electrolytic Degradation Within Cathode Materials.* TMS (The Minerals, Metals and Materials Society), Light Metals 2001, 2001. p. 747 - 752

5. Sørlie.M and Øye.H.A, *Cathodes in Aluminium Electrolysis.* 2nd Edition ed. 1994, Dusseldorf, Germany: Aluminium-Verlag.

6. Wilkening.S and Reny.P, *Erosion Rate Testing of Graphite Cathode Materials.* TMS (The Minerals, Metals and Materials Society), Light Metals 2004, 2004: p. 597-602.

7. Ødegård.R, *On the Formation and Dissolution of Aluminium Carbide in Aluminium Cells.* Aluminum, 1998.

8. Rafiei.P, Hiltmann.F, Hyland.M and Welch.B, *Sub-Surface Carbide Formation Contributing to Pitting and Accelerated Cathode Wear.* in *Al Smelting Conference.* 2001. Queenstown: Univeristy of Auckland.

9. Liao.X and Øye.H.A, *Method for the Determination of Abrasion Resistance of Carbon Cathode Materials at Room Temperature.* Carbon, 1996. 34(5): p. 649 - 661.