Cathode Wear Based on Autopsy of a Shutdown Aluminium Electrolysis Cell

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Abstract

To investigate cathode wear, an autopsy of a shutdown aluminium electrolysis cell was conducted. The original lining consisted of a fully impregnated and graphitized carbon block and the cell was shut down after 2461 days operation. The cell was cleaned down to the surface of the carbon cathode, revealing the profile of the cathode wear. Generally, the cathode wear was uneven across the cell with typical potholes. At a finer length scale, the wear was characterized by small "pitholes" resembling wide shallow pitting corrosion. Samples of the cell lining were obtained by drilling cylindrical samples at different locations in the cell. These samples were analysed with respect to phase composition and microstructure by a combination of X-ray computed tomography, optical and electron microscopy. The findings are discussed in relation to the current understanding of the underlying mechanism(s) for cathode wear.

Introduction

Cathode wear is one of the most important factors in determining the cathode life of an aluminium reduction cell [1]. Factors such as carbon type, amperage levels, bath chemistry, and cathode design as well as other factors play an important role in cathode wear [1], making cathode wear a complex phenomenon. Introduction of the more graphitized cathode bottom blocks coupled with higher amperage levels and more acidic baths in the aluminium industry seems to have accelerated cathode wear [1, 2]. Even though laboratory tests show that graphitized blocks are inferior to their more amorphic counterparts in terms of mechanical wear [3], its usage in the aluminium industry is on the rise [2]. This is largely because of their properties such as low sodium expansion and high electrical and thermal conductivity, which contributes to increased productivity and energy efficiency [4]. Despite the beneficial attributes, it is observed that cathode life is reduced in line with the introduction of graphitized blocks [1]. The reduction in cathode life is attributed to the higher degree of uneven cathode erosion observed on graphitized blocks. The observed wear rate in industrial cells can be ranked as: graphitized > graphitic > anthracitic carbon [1].

Measurements by Tabereaux et al. [5] showed that the highest cathode block erosion was located under the anodes towards the sidewall of the cell, and that the wear under some anodes was deeper than under others. They also found almost no erosion in the centre of the cell. This uneven form of cathode erosion leads to the most common erosion pattern observed in modern high-amperage prebaked anode cells called the W or WW wear pattern [1, 4, 6]. Another detrimental form of uneven cathode erosion observed in industrial cells is formation of single potholes or tunnelling potholes [1, 7, 8], often leading to early pot failure or failure by tap out [1].

Replacing potlinings and disposing off the spent potlinings (SPL) imposes extra costs for smelters [1]. All attempts to understand the mechanisms behind cathode wear so as to implement the necessary actions to improve cathode life, is therefore of great importance.

Autopsy of spent potlinings have been an important tool for understanding the mechanisms behind cathode erosion on both macro and micro scales over the past years [9-11]. The autopsy process involves a combination of various activities including visual inspection, cavity measurements, imaging and samples collection from different locations of interest on the spent potlining and analysing these samples using different microscopic and X-ray techniques, amongst others. Øye and Sørlie [1] have given a detailed outline of a procedure for an autopsy.

In this paper we present an autopsy of an impregnated and graphitized carbon bottom lining obtained from a cell of a prebaked technology and side-by-side configuration that was shut down after 2461 days in operation. Beside visual observations and measurements of wear, samples from the autopsy were analysed by a combination of light and scanning electron microscopy and X-ray computed tomography.

Experimental

Autopsy and Sample Preparation

The autopsy was conducted on a spent potlining (D068) from one of Hydro's SU4 cathode technologies [12, 13]. The autopsied pot was about 4 meters wide and 15 meters long with a cavity of about 53 cm. The bottom lining comprised 19 fully impregnated and graphitized carbon blocks (TG2). The cell was operated on an amperage of 313 kA for 2461 days. Six of the collector bars had been cut prior to the planned shutdown to prevent iron contamination or tap out from the cell. Before the autopsy was conducted, the pot was allowed to cool over a couple of days in an enclosed and dry area, thereby avoiding any contact with water. Bath and metal were carefully removed from the spent potlining leaving the exposed surface of the carbon cathode. The surface was then vacuum cleaned to reveal all the details such as cracks, potholes, metal plugs, sludge, etc. The individual cathode blocks were also numbered with a marker for easy documentation.

Locations of interest all over the cathode bottom block were photographed. The locations of interest for this autopsy were the locations with excessive wear on the cathode blocks, such as near the ends of the cathode blocks, potholes, wide shallow pittings and other abnormal observations.

To obtain the wear pattern on the cathode bottom block, a laser, an aluminium bar and a ruler were used. Each of the individual cathode blocks were measured from one end to the other at regular intervals of 40 cm. The potholes that were observed were also measured to determine their depths and diameters. The data obtained were used to characterize the appearance of potholes on each of the cathode blocks. Figure 1 is a picture of the measurement setup on the cleaned spent potlining.

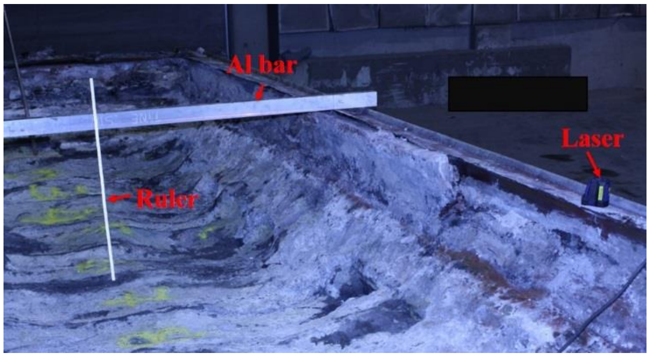

Figure 1. Illustration of the measurement of the wear profile of the spent potlining. The blocks are numbered with yellow markings.

The samples from the spent cathode were obtained by drilling into the lining at different locations of interest using an electrical drilling machine. The drilling machine could drill core samples up to a depth of 10 cm and a diameter of 5 cm. Before the drilling commenced, all the sample locations were marked with a yellow marker. All the autopsy samples were vacuum packed and sealed after the drilling to avoid reactions with moisture. During sample preparations, a thin bath film detached from the surface of two samples and the thickness of the films were measured using a dial indicator.

Laboratory Analysis

The cathode samples were analysed using X-ray computed tomography (CT scan). The CT data was acquired by a Nikon XTH225ST instrument (cone beam volume CT). A tungsten reflection target was used with an acceleration voltage of 140 kV and a current of 135 µA. The imaging was done with an integration time of 1 second, amplification of 18 dB, with 3142 projections per 360º. The distance from source to sample was 226.7 mm, distance from source to detector was 1124.8 mm, detector size 400x400 mm, resulting in a voxel size of 40.2 µm. The images were exported as 16-bit TIFF and processed in the public domain software ImageJ. The autopsy samples were used without any particular preparation apart from inserting it into a plastic container to provide stability while in the chamber of the CT scanner.

For the microstructural and chemical analysis, the autopsy samples had to be cut into smaller samples, imbedded into epoxy overnight and mechanically polished to obtain a smooth surface. Optical microscopy was performed using the REICHERT MeF3A optical microscope whilst Electron microscopy was carried out using the Hitachi S-3400N Scanning Electron Microscope. EDS (Energy Dispersive X-ray Spectroscopy) mapping with AZtec was used to analyse the elements present.

Results

Visual and Macroscopic Observations

A picture of the spent potlining showing the wear pattern and the location of the two pothole samples used for the CT scanning is shown in Figure 2. A 3D plot of the measurements of the cavity gave an indication of the wear pattern, this was similar to the laser scan wear profile observed by Skybakmoen et al. [13]. The 3D plot is shown in Figure 3.

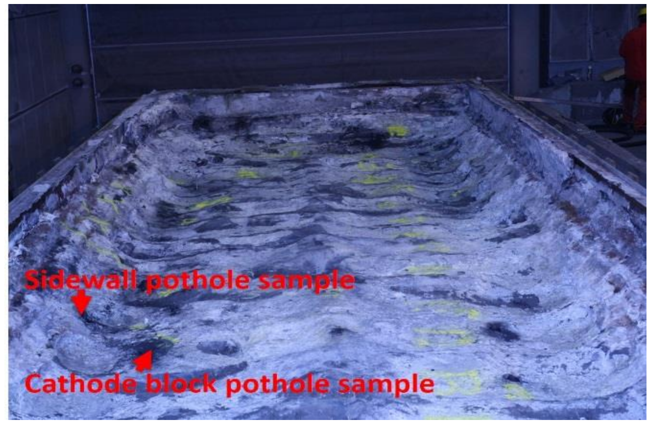

Figure 2. Picture of the spent potlining showing wear profile and locations of the pothole samples used in the CT scanning reaction front analysis.

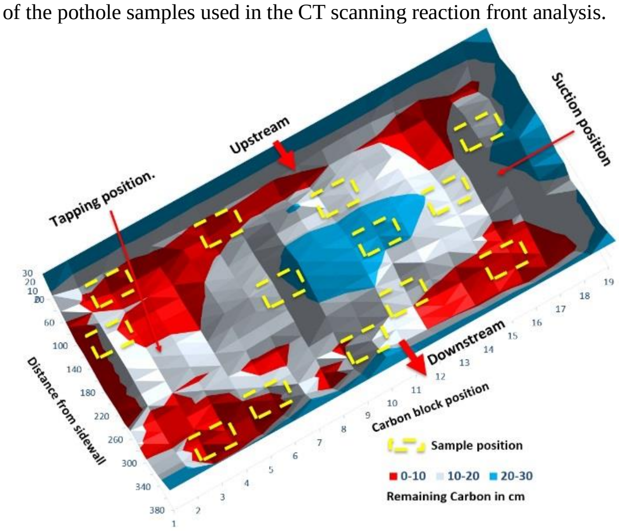

Figure 3. Top view of the wear pattern of the autopsied cell. The yellow dotted rectangles show the sample positions.

Generally, non-uniform wear was observed all over the cathode surface and the cathode blocks were observed to be more worn than the ramming joints between them. The most severe wear was near the outer ends of the cathode blocks on both sides (upstream and downstream) of the cell. The wear towards the centre of the cell was generally less pronounced, however, moving away from the centre, another area of relatively high wear on both sides of the centre of the cell was observed. This wear was, however, less than the one observed near the ends of the cathode blocks. This very high – low – high - very low – high – low - very high wear pattern of cathode erosion observed across the cathode block from side to side is the WW wear pattern. Some of the wear near the ends of the cathode block were deep and could be described as large potholes. These large potholes measured up to about 50 cm in diameter and about 7-10 cm in depth. A closer examination revealed a high degree of wide shallow pitting at the surface within each pothole. A picture of the wear near the ends of the cathode blocks showing the high number of wide shallow pitting within the large potholes is displayed in Figure 4.

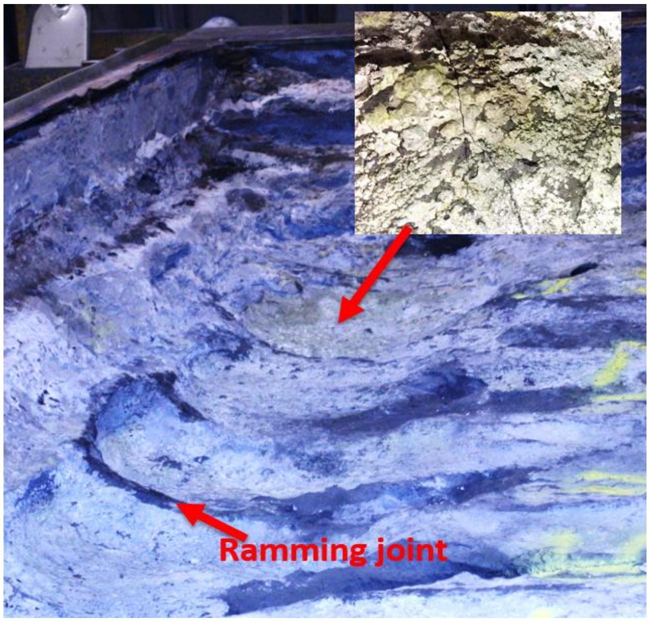

Figure 4. Cathode wear along the ends of the cathode blocks showing wide shallow pitting corrosion within. One can also see the less worn out ramming joint between the more worn out blocks.

Two patterns of erosion, all showing high levels of wide shallow pitting corrosion, were observed near the ends of the cathode blocks. It was observed in most instances that the erosion continued to a certain depth and then stopped before getting to the collector bars whilst in a few instances it was observed that the erosion continued all the way to the collector bars with just millimetres of carbon material remaining. Another observation was the relatively high wear pattern towards the tapping position as compared to the suction position and the considerably high level of bottom ledge and sludge/muck at the suction position. The centre canal towards the suction position had the least cathode wear.

Wide shallow pitting with varying diameter (2-5 cm) and depth (1-2 cm) were observed over most of the surface of the cathode blocks. At some locations, typically along the sidewall, one could observe a cluster of these pittings that had joined to form a pothole with diameters of up to 12 cm and depth of 6-7 cm. A pothole showing the relatively smaller pittings within is shown in Figure 5.

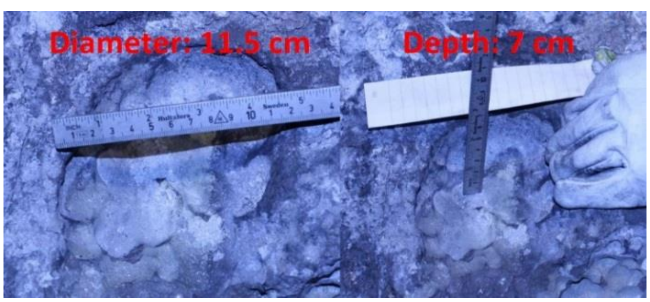

Figure 5. A pothole showing the smaller pittings that joined to form it. The diameter and depth are also shown.

A thin layer of bath was observed covering the whole cathode surface. A picture showing this thin layer of bath that was detached from the autopsy samples is shown in Figure 6. Six different measurements of the thickness of this thin layer gave an average thickness of 636±200 µm. Yellowish aluminium carbide was also observed, especially at locations towards the ends of the cathode blocks where the erosion was highest and between the ramming joints and the cathode blocks. Aluminium carbide was clearly visible on the carbon cathode blocks as shown in Figure 6.

Figure 6. Autopsy samples showing the detached thin bath film. The yellow colour at the surface is aluminium carbide. Aluminium carbide could be observed under the detached thin bath layer on the sample to the left.

Laboratory analysis

CT scanning analysis, making use of a computer-processed combination of several X-ray images obtained from different angles to produce tomographical images of specific areas of a scanned object, was used to investigate the distribution of different phases present in the cathode. The phases were identified as different shades of greys. For the cathode samples analysed, the bath component corresponds to the white areas while the carbon components are reflected in different forms of grey. Analysis from the CT scanning demonstrated that the porosity of all the autopsy samples were fully impregnated with bath. The CT scan point to a relatively higher amount of bath within the ramming joints than the fully impregnated and graphitized blocks, probably due to the higher porosity in the ramming joints. CT scanning image showing bath impregnation is displayed in Figure 7.

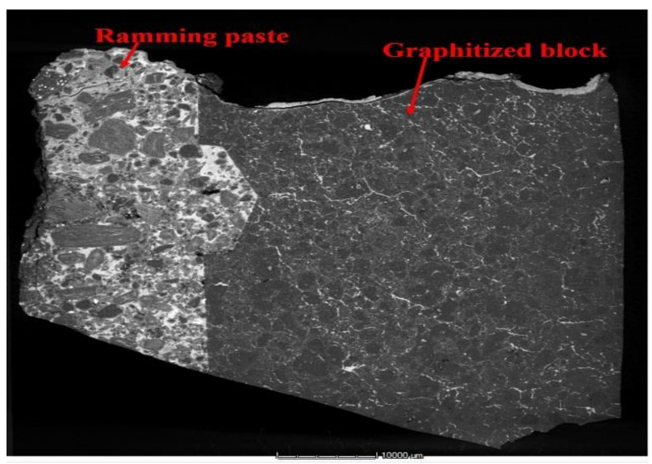

Figure 7. CT scanning image showing bath impregnation within the ramming joints and the fully impregnated and graphitized block. The white is bath and the greys are carbon components.

The CT scanning technique was also used to investigate the reaction front along the edges of the carbon/aluminium carbide interface in two of the pothole samples prepared by drilling. It was observed from the CT scanning images that the cathode block pothole sample had a rougher reaction front than the sidewall pothole sample. Figures 8 and 9 shows the CT scan at the cathode surface for these two pothole samples.

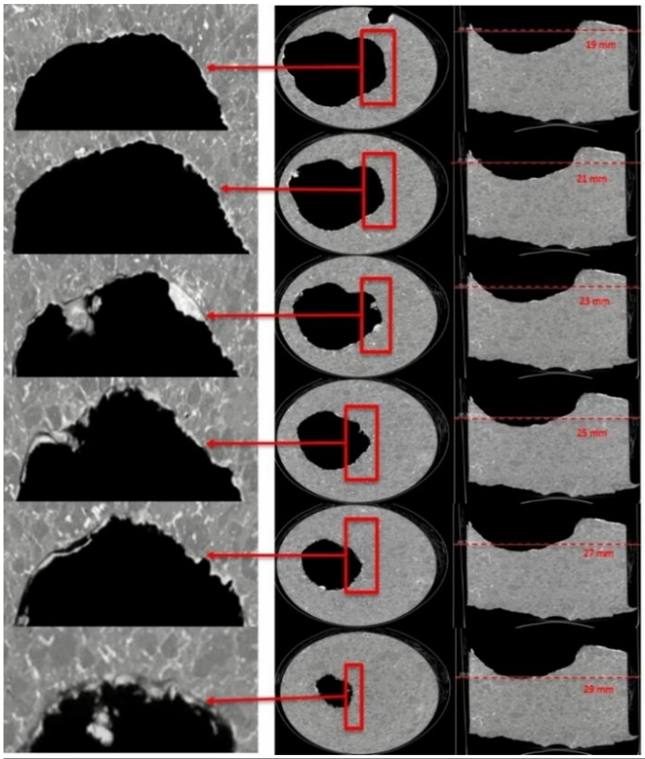

Figure 8. CT scan of pothole sample taken on the fully impregnated and graphitized cathode block showing reaction front along the edge within the pothole.

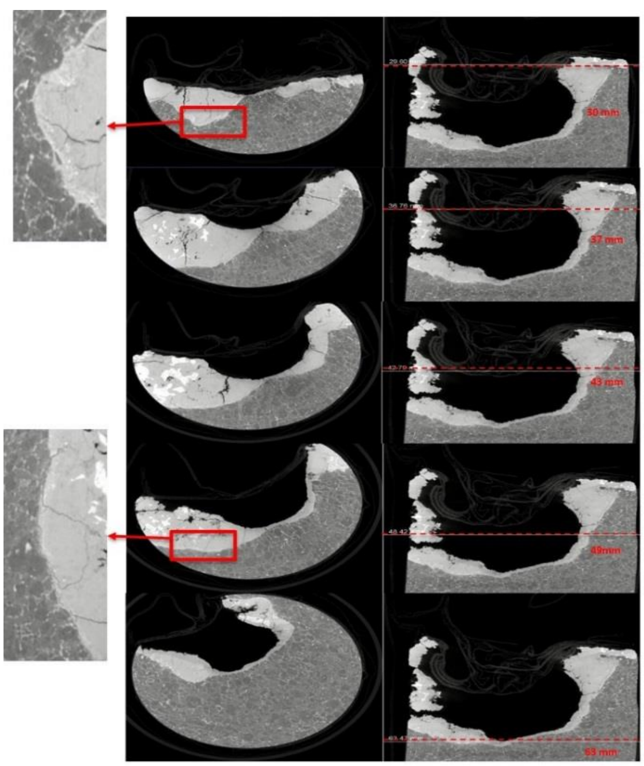

Figure 9. CT scan of pothole sample taken 50 cm from the sidewall showing the reaction front along the edge within the pothole.

Optical microscopy was combined with scanning electron microscopy and EDS to investigate the microstructure and phases present in the bath film and near the cathode surface. An observation that was made from the different cathode samples analysed was the absence of aluminium in direct contact with carbon. Where aluminium was observed, it was seen as floating fragments, see Figure 10. The aluminium carbide layer was also observed in its hydrated form as a distinct layer rich in oxygen on the EDS mapping images.

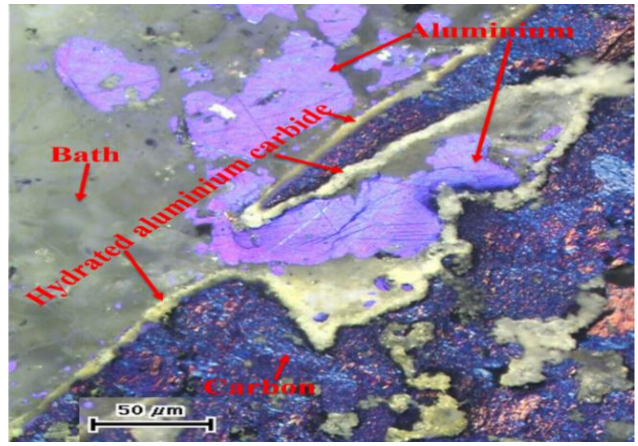

Figure 10. Light microscopy picture of an interface between carbon, bath and aluminium showing fragments of aluminium and a defined layer of hydrolysed aluminium carbide.

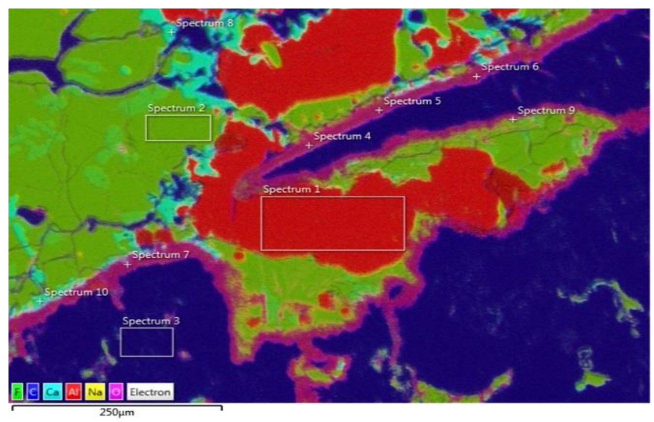

Figure 11a. EDS mapping of the interface described in Figure 10.

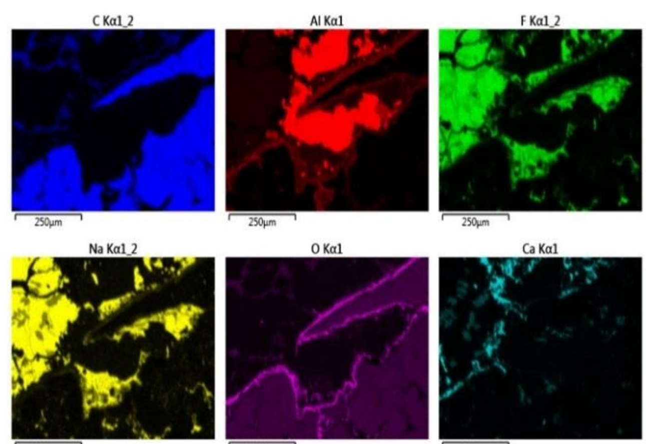

Figure 11b. EDS mapping of the interface described in Figure 10 showing the individual elements present.

Discussion

In line with other autopsy investigations [1, 4, 5, 10, 11, 13] the typical WW pattern was also observed in this study. Cathode erosion mechanisms are proposed by many authors [1, 5, 14-21] to be controlled mainly by the formation, dissolution and transport of aluminium carbide.

Evidence of the limited wettability of aluminium on the carbon cathode as observed from the cathode samples and the role of wide shallow pitting corrosion as a precursor for pothole formation are important experimental observations in the present autopsy. The presence of a thin layer of bath all over the cathode surface and the high level of bath impregnation by both the fully graphitized and non-graphitized parts of the bottom lining, as observed from the CT scanning images, suggests that the molten electrolyte wets the carbon cathode block well. Bath impregnation, which follows the wetting of carbon cathode by the bath, is assumed to occur fast after the cell has been put online due to the sodium activity [1, 15].

Aluminium has been assumed to wet carbon the same way as the molten electrolyte when current is applied to the cell and electrochemical cathode reactions are initiated [1, 22, 23]. However, the almost total absence of aluminium in contact with the carbon cathode, as observed by microscopy, seems to question the extent to which aluminium wets the carbon cathode at all during electrolysis. In the present study, there were no observations of carbon in direct contact with aluminium on any appreciable level, indicating that aluminium wets the carbon significantly less than the molten bath. It can be argued that direct contact between carbon and aluminium should result in carbide formation due to the favourable conditions for the carbide forming reaction (Gibbs energy of -147 kJ at 970 °C) [1], Reaction 1.

$$Al(l) + C(s) = Al_4C_3(s) \quad (1)$$

If this is an important wear mechanism, aluminium should have been observed on top of the carbon and the carbide layer, which was not observed. In the present autopsy, a thin bath film on top of both the carbon cathode and the carbide layer was observed. Most likely a thin bath film may have been present all the time from the start-up of the pot with bath [1]. If this is indeed the case, the aluminium metal will have reduced chances to wet the carbon cathode, making direct carbide formation a less likely scenario.

Electrochemical wear leading to possible dissolution of carbon may explain the pothole formation mechanism observed in the two pothole samples used in the CT scanning analysis. The wide shallow pitting corrosion seems to have different formation rates in different parts of the cell. The high degree of wide shallow pitting corrosion observed within the locations of relative high erosion near the ends of the cathode blocks, as shown in Figure 4, as well as other parts of the cell, may suggest that wide shallow pitting corrosion is the most dominant cause of cathode erosion. It can also be assumed that the mechanism is electrochemical in nature due to the high current densities at the locations with highest wear.

The absence of carbon particles in the samples analysed may suggest that wide shallow pitting of cathode blocks arises from electrochemical induced wear resulting in dissolution of the carbon cathode without particle detachment. This may be because both the binder and the aggregate phase are fully graphitized and there is no preferential binder phase dissolution leading to particle detachment as proposed for cathode blocks with amorphic binder phases [1] .

As most of the wide shallow pitting corrosion seems to be both restricted in width and depth, it is a good indication that this initiating pitting stops or slows down at some depth. The real cause for this is presently not determined, but a plausible explanation may be that bath components are involved in both the initiation and the slow down. A possible mechanism is that bath is slowly depleted of aluminium, resulting in two slow down mechanism. One is that the wear is less in more basic bath (lower activity of aluminium for the formation of aluminium carbide) and, secondly, the fact that more basic bath may freeze out due to a higher melting temperature. When neighbouring wide shallow pits reduce the depth of the first pit, the process may start over again, creating new shallow pits within the original pit.

The presence of smaller pittings within the larger potholes, as shown in Figure 5, supports it that this is a central mechanism for pothole formations. Figure 5 shows that potholes seem to form from individual pittings joining under the right conditions. This kind of pothole formation is different from a single pothole formed as a result of chunks breaking off due to weaknesses or defects in the carbon lining [1]. The smaller wide shallow pitting seems to form as a result of electrochemical induced mechanisms. The circular nature of these pittings may suggest that convective patterns set by metal pad movement, or whirlpool effect on the metal pad close to the carbon surface, due to high current densities, play a part in their formation [1, 7].

The convective patterns set up by the metal pad movement during metal tapping may also play a part in cathode erosion. This may contribute to the relatively high erosion towards the tapping position as compared to the suction position. Higher velocities within the metal pad movements during metal tapping will induce convective movements within the bulk of the bath. This may in turn introduce fresh bath to the locations with carbide leading to increased carbide dissolution and transport, which is suggested to be a prerequisite for cathode erosion [1, 16, 21]. The considerably high levels of bottom ledge and sludge/muck observed at the suction position may explain the relatively low erosion rates observed there. The extensive bottom ledge and sludge/muck that is accumulated may also be a result of a colder zone or a more stagnant flow at this location [12]. The high level of bottom ledge or sludge may protect the carbon cathode block from erosion by reducing the access of fresh bath that enhances the dissolution of the carbide layer at this location. A frozen bottom ledge or muck may also prevent the transport of the formed carbide to the bulk bath, thereby creating a saturation zone for aluminium carbide and thus reduce its formation.

The high magneto-hydro-dynamic (MHD) forces caused by the high current densities near the ends of the cathode blocks, and the close proximity of bath being transported along the side ledge, may also explain the higher wear observed near the ends of the cathode blocks. The higher MHD forces will induce local flow patterns and the close proximity of bath being transported along the side ledge will ensure presence of fresh bath that will enhance carbide dissolution and transport. Enhanced formation, dissolution and transport of aluminium carbide at these locations may enhance the formation of individual wide shallow pits, which may merge faster with neighbouring pits, collectively creating the larger potholes.

Some of the earlier proposed theories for cathode wear may explain the W wear pattern [6]. However, the WW wear pattern, also observed during the present autopsy, is not easily explained by many of the prevailing theories. This is especially true for the W wear pattern close to the centre of the cell. A mechanism related to the anodes may contribute to the centre W wear pattern. Gas released from under the anodes will create additional bubble-induced flow. This bubble-induced flow may cause more turbulence at the bath/metal interface in the centre of the cell with the possibility of more bath entrainment and transport to the cathode surface. In addition, the centre space between the anodes, to allow room for centre feeders, may cause a different metal flow pattern compared to cells without centre feeders and no centre canal. In addition, the additional edge current along this centre canal may contribute to higher current densities in this area. These mechanisms will be investigated using CFD (computational fluid dynamics) and MHD models in the future.

Conclusion

CT scanning images demonstrated that the porous ramming joint were more filled with bath than the graphitized and fully impregnated cathode blocks. However, both were completely infiltrated by molten bath. The absence of any appreciable amounts of aluminium in direct contact with the carbon cathode suggests that electrochemical induced wear is the main mechanism behind cathode wear in industrial cells. The high level of wide shallow pitting at locations with high erosion rates further suggests that fully impregnated and graphitized blocks tend to wear by the formation of these shallow cavities. A possible mechanism for the W wear pattern towards the centre of the cell is suggested. The mechanism involves a bubble-induced flow caused by gas release under the anode leading to turbulence at the bath/metal interface in the centre of the cell and/or a flow pattern at the bottom of the cell caused by the two anode rows being arranged with a space between to accommodate the centre point feeders.

Acknowledgements

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