

CRITICAL REFLECTIONS ON LABORATORY WEAR TESTS FOR RANKING COMMERCIAL CATHODE MATERIALS IN ALUMINIUM CELLS

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Keywords: Cathode wear, Aluminium electrolysis, Wear test, Aluminium carbide, Carbon cathode, Modelling

Abstract

The lifetime of high amperage cells with graphitized carbon cathodes is mainly determined by cathode wear. Several attempts have been made to investigate cathode wear in laboratory test cells, but the underlying mechanism is still a matter of discussion. This is reflected in the fact that test methods enabling the ranking of different commercial cathode materials are still to be developed. In the present paper we report on a laboratory test cell where the cathode is directly exposed to the electrolyte, which accelerates the wear rate by an order of magnitude relative to the wear rate in industrial cells. In this study three different commercial carbon cathode materials have been tested; graphitized carbon, high density graphitized carbon, and anthracitic carbon. No significant differences in wear rate could be detected under the test conditions used. Possible reasons for this unexpected result are discussed, and suggestions for modifications of the test cell are provided.

Introduction

To date, tremendous efforts have been made to improve the performance of the Hall-Héroult process [1]. New methods and technologies have been developed for operation and control, and better materials have been made available. As a consequence the specific energy consumption has been reduced, and the amperage and particularly the current density have steadily increased. The latter has resulted in new requirements for the cathode materials, and new materials have been requested by the industry [2]. A gradual change from anthracitic carbon to the state-of-the-art graphitized materials has occurred over the past decades. This has allowed for energy savings due to increased electrical conductivity. However, the benefits of increasing the amperage and productivity need to be weighted against higher material costs and lower wear resistance.

Nowadays, cathode wear is one of the main factors limiting the service life of aluminium electrolysis cells. Wear is generally defined as net removal of material from a surface [1]. The cathode blocks in aluminium cells wear unevenly, and the maximum wear is up to several cm per year. Recorded wear pattern can be strongly non-uniform, and the profile of a used cathode may be “W”-shaped or even “double W”-shaped due to a higher material removal along the periphery of the cell [2-6]. To extend the potlife and thus the smelter’s profitability it is crucial to understand the wear mechanism(s).

It is generally agreed that formation, dissolution, and transport of aluminium carbide are all important factors for cathode wear [2]. In terms of dissolution, it has been shown that the aluminium metal is not saturated with carbon. This is because the carbon (carbide) is transported across the two boundary layers at the metal-bath interface before being oxidized by the anode gas. The solubility of carbon in aluminium is 105 ppm counted as aluminium carbide at 960 °C [7]. The solubility in the electrolyte is two orders of magnitude higher; values up to 2 wt% (at CR = 1.8) are reported [8], while the solubility in industrial bath is about 1 wt%. If a bath film is present at the top of the cathode carbon, metal convection might be responsible for transporting the carbide saturated bath film to the bulk bath, while a continuous supply of “fresh” bath to the cell bottom promotes the dissolution of aluminium carbide. It has been shown that the carbide concentration in the electrolyte is very low [9].

The formation of aluminium carbide can be described by chemical or electrochemical means, but the underlying mechanisms suggested are mainly based on theoretical considerations and still a matter of debate.

Several authors have worked on designing laboratory test methods in order to study the wear and wear rates and to rank the different commercial carbon cathode materials. In 2007, some of the available methods were summarized by Skybakmoen *et al.* [10]. They concluded that the exact mechanism(s) behind the uneven wear profile can so far not be explained. Furthermore, the tests described were not able to rank cathode materials based on their apparent density. This is in contrast to observations made by the industry stating that slower wear rates were achieved by using a denser graphitized block.

In the following, we give a short description of some of the work which has been published since 2007 on wear tests and discuss our latest attempt based on the “inverted cell” configuration designed by Rafiei *et al.* [11]. A slightly modified set-up was used for further wear test studies by Patel *et al.* [12, 13]. Graphitic and graphitized materials with different granulometries were investigated to determine the effect of porosity and pore size distribution under varying electrolysis conditions. The results showed a strong influence of the current density and bath chemistry on the wear rate. The effect of porosity was opposite on the two materials; high wear rates were observed for the dense graphitic material, while the wear rate was lower for the dense graphitized material. Dense graphitized cathode carbon was

suggested to be the best choice regarding electrochemical behaviour.

Pitch impregnation is one of the densification techniques used in the industry. Sato *et al.* [14] and later Patel *et al.* [15] continued the work on the inverted test cell by concentrating on pitch impregnated cathode samples. Nevertheless, an adversely effect on the wear resistance was found.

Vasshaug *et al.* [16, 17] also used the principle of the “inverted cell” set-up to study the wear mechanism(s) using a synthetic graphite material. Both ends of the sample were covered with sintered alumina tubes to ensure a defined exposed area and a uniform current distribution. The electrolysis was performed at different bath compositions, cathodic current density, duration, rotation speed, and presence of aluminium and their influence on the wear rate was investigated.

Lately, Tschöpe *et al.* [18-20] continued using the experimental set-up based on the cell design by Patel and Sato *et al.* [14, 15] to study the wear phenomena by modifying the cathode surface morphology. The attempt was to separate the effects of electrochemical and physical wear on the wear rate. This work is ongoing, and recent results are going to be published [20].

As listed above, several types of reversed polarity cell set-ups were tried and extensive studies have been performed aiming at understanding the wear mechanism(s). However, the establishment of a standardized test for the ranking of commercial cathode materials requires consistent test parameters for comparison. So far no such standard test exists.

Experimental

Laboratory Test Cell

A schematic drawing of the experimental set-up is shown in Figure 1. The main parts and installation are described elsewhere [19].

The whole assembly was heated to operating temperature of 960 ± 5 °C at a heating rate of 350 °C/h, and kept constant during the experiment by an external temperature controller. A heat resistant steel rod was used to conduct current to the cathode. The cathodic current density (i_c) was set to 1 A/cm² except for the experiment without polarization. To establish similar conditions as in industrial cells, the convection was induced by rotating the cathode during electrolysis. The angular speed was kept constant at 5.24 rad/sec (= 50 rpm). The electrolysis time was 24 hours for each experiment. The cell voltage, the temperature (measured inside the crucible wall), and the current were recorded continuously during electrolysis.

After the experiment, the furnace was turned off while the nitrogen atmosphere was maintained. The steel rod with the cathode sample was lifted above the bath surface before solidification.

Materials Preparation and Characterization

Three commercial carbon cathodes were tested: A) graphitized carbon, B) high density graphitized carbon, and C) anthracitic carbon (70 % electro-calcined anthracite and 30 % graphite). The test pieces were 30 mm in diameter and 80 mm long.

It was considered important to have an accurately defined cylindrical cathode area in order to prevent non-uniform current

distribution and wear. Thus, each end of the cathode specimen was covered by an insulating material (Si₃N₄), leaving a uniform 30 mm high cylindrical area exposed to the electrolyte, as shown in Figure 1. With this set-up it was possible to prevent high current densities at the bottom of the cathode and to achieve wear data that could easily be related to the current density. The weight, apparent density, and open porosity of each type of specimen were measured before the test, and the materials are compared in Figure 2.

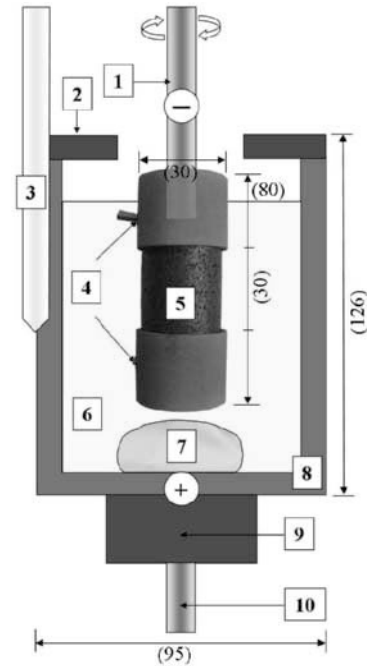


Figure 1. Schematic drawing of the experimental set-up with a vertical rotating cathode. The dimension of the graphite crucible (mm) is given in parentheses. 1 - rotating cathode connecting rod, 2 - lid of sintered alumina, 3 - thermocouple, 4 - Si₃N₄ linings covering both ends, 5 - cathode sample, 6 - electrolyte, 7 - aluminium metal (100 g), 8 - graphite crucible/anode, 9 - graphite support, 10 - anode lead.

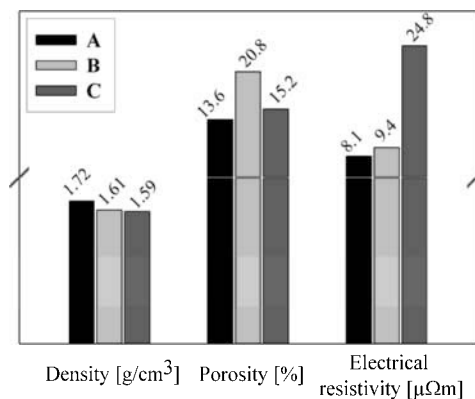


Figure 2. Comparison of density, porosity and electrical resistivity data for the tested cathodes: A) high-density graphitized; B) graphitized, and C) anthracitic material.

After the test the remaining bath at the cathode surface was carefully removed using the backside of a knife, avoiding loss of carbon. The average diameter of the samples was determined before and after the experiment using the calliper method; the positions are indicated in Figure 3 a).

Besides the ranking, some of the cathodes were investigated in order to identify the chemical composition and in particular the sodium and bath concentration gradients in the cathode after electrolysis. The sample preparation is illustrated in Figure 3 b). To expose the cross section, the tested samples were dry cut into slices using a diamond saw. Area mappings of the element composition were performed by electron probe micro analysis (EPMA) using a JXA-8500F Hyperprobe JOEL (EPMA/WDS) apparatus. Before image analyses, the slices were embedded into epoxy (Struers Epofix) and wet-ground with silicon carbide papers to P4000 ($< 5 \mu\text{m}$). Afterwards, the samples were polished using diamond sprays (3, 1 and $\frac{1}{4} \mu\text{m}$). During grinding and polishing, 100 % ethanol was used as a lubricant to avoid reactions due to contact with water. Finally, the samples were coated with carbon to reduce charging interference. The same preparation procedure was carried out with the virgin material to perform EPMA, macro- and microstructure imaging. The electron beam spot size was broadened to $30 \mu\text{m}$ to avoid Na evaporation. The content of the major components C, Al, O, F and Na was recorded. Light microscopy (LM) and low voltage field emission scanning electron microscopy (LVFESM) were used to examine the virgin carbon material.

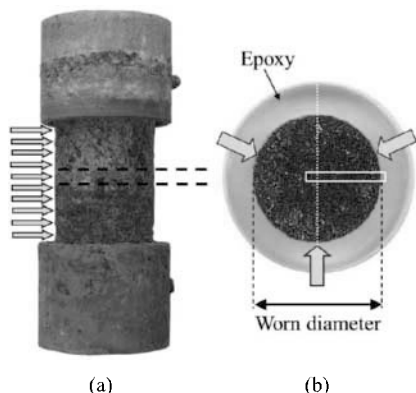


Figure 3. Sampling positions (a) and preparation of worn cathode cross sections (b). The arrows indicate the placement of the calliper to determine the average diameter: 10 times along the height repeated for 3 positions around the circumference at an angle of 120° . The white box in the embedded and polished slice (b) represents the area for EPMA investigations.

Results

The results of the wear tests for the three cathode materials are shown in Figure 4. The dimensional changes were recalculated to cm/year . All three materials tested possess similar average wear rates: 50.9 cm/year (material A), 46.5 cm/year (material B) and 54.0 cm/year (material C). There is no trend with respect to density, porosity, electrical resistivity, or type of cathode. In fact, the results point to a lower wear resistance of the anthracitic material. The wear is fairly reproducible, as shown by the

standard deviations σ in Figure 4, and is as expected 10-20 times accelerated compared to industrial aluminium reduction cells.

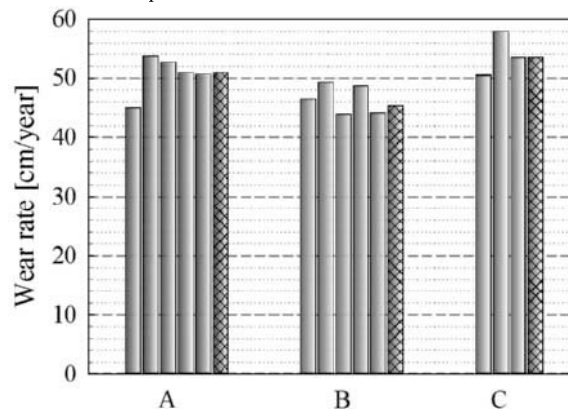


Figure 4. Wear rate in $[\text{cm/year}]$ for the three commercial cathodes: A) high-density graphitized; B) graphitized, and C) anthracitic material after 24 h electrolysis. The textured bar shows the corresponding average value and the standard deviations are $\sigma_{(A)}=3.0$, $\sigma_{(B)}=2.1$ and $\sigma_{(C)}=3.1$.

Figure 5 shows the appearance of each tested cathode material before and after 24 h of electrolysis. Consistent wear profiles were observed, without indications of grain pull out or pitting. The uniformity of the wear over the whole length of the exposed area was proven by the image analysis method earlier described by Tschöpe *et al.* [18]. As intended, this indicates a fairly even current distribution, as recently been reported [18]. In the course of the work, the image analysis data was continuously compared to calliper measurements. Similar results were observed, leading to the preference of the latter, which is a less time consuming procedure. Ratvik *et al.* [21] have shown that the sodium uptake proceeds rapidly during start-up and reaches saturation within 60 min; this goes for samples of amorphous, graphitic, and graphitized cathode material. Cathode expansion due to sodium penetration is small compared to the wear and was therefore not considered when determining the wear rate.

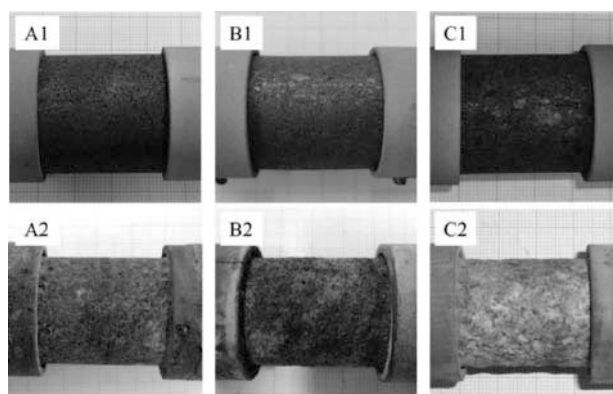


Figure 5. Cathode samples for the measurement of the average diameter before A1-C1 and after the wear test A2-C2: A) high-density graphitized, B) graphitized, and C) anthracitic material.

Three cross sections, prepared and measured as shown in Figure 3, were examined with EPMA in order to find the depth of sodium

and bath penetration. The measurement was performed on the same used cathode material (A), but with different experimental scenarios:

- Set 1: Virgin sample for comparison
- Set 2: Standard ranking sample (24 h electrolysis time)
- Set 3: Reduced test durations (1 h, 10 min and 2 min)
- Set 4: Without polarization (24 h electrolysis time)

The micrographs and element distribution of Na and F (represents the bath components) of set nos. 1, 2, 3 (the 1 h and 10 min tests were published in [19]) and 4 are displayed in Figure 6.

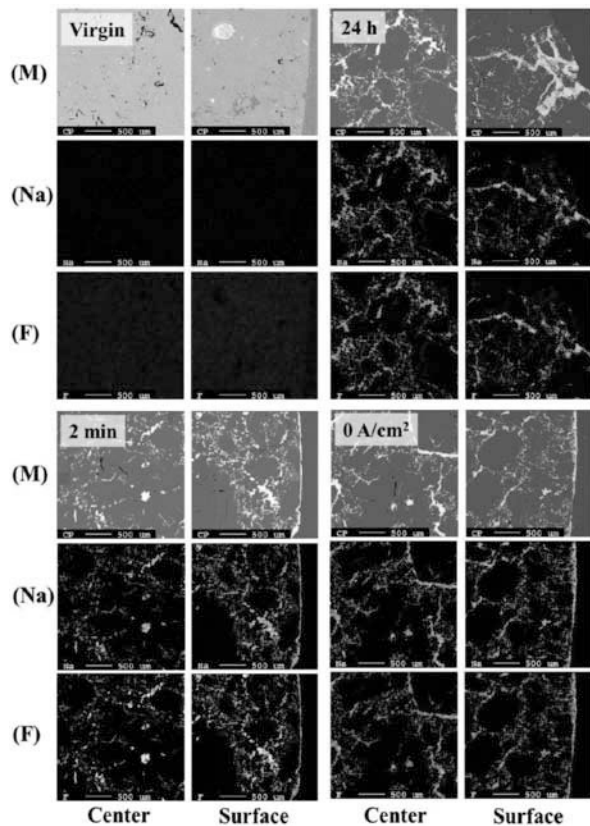


Figure 6. Micrograph (M) and element distributions of Na, and F at the surface (right) and the center (left) for the virgin, 24 h, 2 min, and no polarization wear test. The area maps are scaled in such a way that lighter colour represents higher content (intensity of the grey-scale).

By comparing the virgin and standard ranking sample (Set 2), it is evident that the electrolyte has penetrated the entire cathode after 24 h, and no bath front could be identified. The penetration rate was further investigated by gradual lowering the wear test times until the practical lower limit was reached. Results of the Set 3 samples were recently published [19]. It was concluded that sodium infiltrates the cathode material at a high rate and induces bath penetration by improving the wetting between electrolyte and carbon, since the entire cathode was infiltrated and no concentration gradients could be identified even after the short exposure time of 2 minutes. Therefore, it was suggested to perform a 24 h test without polarization (Set 4). Also this non-polarized sample was fully penetrated. In all samples individual

carbon grains could clearly be distinguished. Area scanning of those carbon grains at high resolution revealed neither a sodium gradient nor a sodium concentration in general; see Figure 7. The infiltrated bath was only found in the cracks and pores of the carbon cathode material. Aluminium carbide was mainly found at the surface and inside the pores.

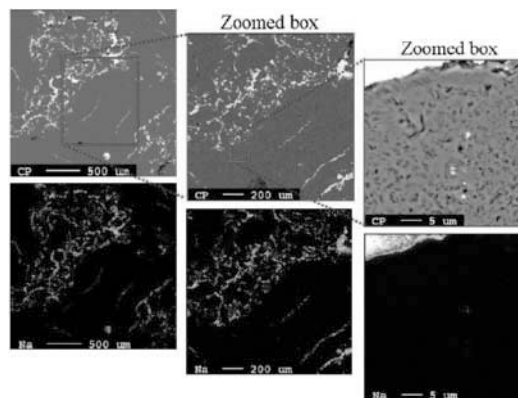


Figure 7. Micrograph and element distribution of sodium taken from a carbon grain at three different magnifications. The scanning positions are indicated by the red-coloured box. The area maps are scaled such that lighter colour represents higher content (intensity of the grey-scale).

The macro- and microstructure of the virgin cathode samples A, B and C are shown in Figure 8. At high magnification (see Figure 8 d), the cathodes A, B and C appear to be very similar, because they are all made up of oriented graphite sheets of similar size. Binder and aggregates are hard to distinguish. Only the anthracitic material in Figure 8 a-c) shows inorganic glassy grains surrounded by binder at a lower magnification.

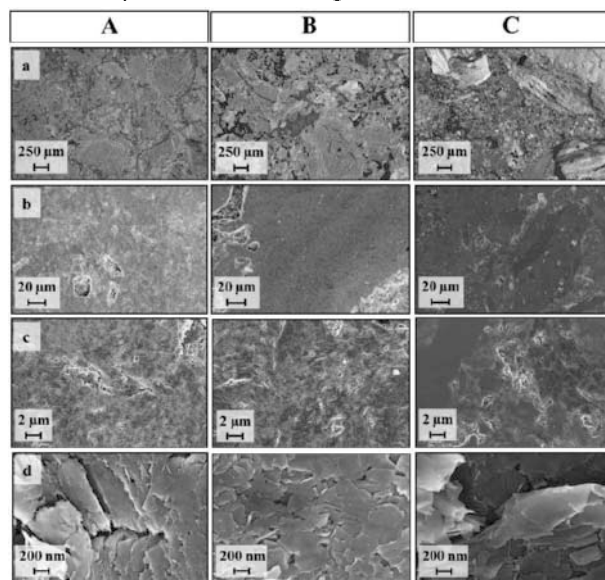
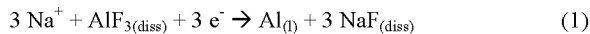


Figure 8. Optical microscope (a) and high resolution imaging (b-d) of virgin samples of A) high-density graphitized; B) graphitized, and C) anthracitic cathode material.

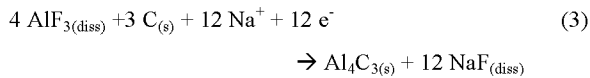
Discussion

Care was taken to repeat the same procedure for each experiment in order to minimize unsystematic errors. This is reflected in Figure 4, where it is evident that the obtained wear rate is reproducible for each material. However, the results from the present test cell, like other test methods presented in the literature [10, 14], show that ranking of different materials has not been made possible. Different wear rates have been observed in industrial practice, however. In the author's opinion, the only possible interpretation is that the test methods developed so far do not reflect the conditions in a real cell. This can be related to the chemical environment, the current density, or other factors influencing the wear rate, such as the existence (or not) of a bath film between the metal and the cathode. It is possible that the work in this field hitherto has been too much focused on developing an accelerated test, without knowing the underlying mechanisms. In the following, some possible wear mechanisms and reasons for the discrepancies between laboratory tests and industrial observations will be discussed. The discussion is based on the high resolution images, observations made in the laboratory, and earlier explanations suggested in the literature [2].

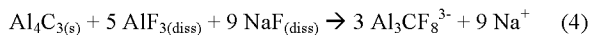
As generally agreed, the main wear mechanism is related to formation (either chemical or electrochemical in nature) and dissolution of aluminium carbide. Experiments without polarization revealed that although the sample was infiltrated with bath components, no carbon consumption was detected. This leads to the conclusion that the electrochemical reaction occurring at the surface is indeed needed to cause aluminium carbide formation at surfaces exposed to electrolyte, at least under the condition that no aluminium layer is present. This might be different if the cathode surface is covered. Al and Al_4C_3 were observed underneath the lower electrically insulating lining in the test cell, as shown in Figure 9. Formation of aluminium might take place at the cathode surface according to reaction (1) below and penetrates downwards together with cryolite into the gap between cathode and the Si_3N_4 tube by gravity. According to Novak *et al.*, [22] chemical formation of aluminium carbide can occur at operation temperatures when cryolite is present, as shown by reaction 2. This also explains why only electrolyte was found underneath the upper lining.



At the cathode surface, between the upper and lower lining the following electrochemical reaction will take place [2]:



According to Ødegård [8] the aluminium carbide will then dissolve in the bath:



The solubility of aluminium carbide in the bath under the test conditions was calculated to be 0.7 wt%. However, more carbon is removed from the cathode than what can actually be dissolved in the bath as aluminium carbide. It is, therefore, considered that the reverse reaction can take place at the crucible wall (anode) forming carbon dust and leaving the bath undersaturated in

aluminium carbide during electrolysis. Examination of the bath filled crucibles after the test revealed considerable amounts of carbon dust mainly at the crucible walls and on the bath surface.

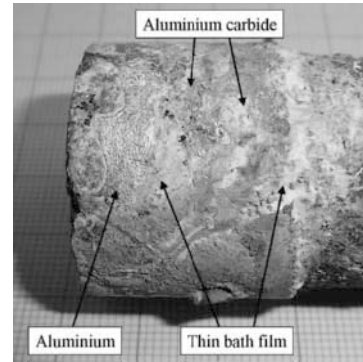


Figure 9. Cathode surface underneath the lower lining.

As seen in Figure 5, fields of Al_4C_3 were visible on each cathode surface after testing. This suggests that the dissolution of carbide is slow and dependent on the rate of reoxidation at the anode.

An Al_4C_3 layer forms readily on the exposed cathode surface in the presence of carbon, aluminium and fluoride. The formation proceeds until a certain thickness is reached. If the cathode is stationary the carbide formation will reach a steady level, and the rate determining step for the wear will be dissolution of the reaction product into the bath. Rotation is intended to increase the mass transfer, but it was proven that a threshold speed exists [20]. A speed of up to 50 rpm is assumed to be too low to contribute much in increasing the dissolution rate into the bath. By using the slot morphology, as conducted in previous experiments, it was shown that the wear rates were similar in tests with 50 rpm rotation as in tests without rotation [20]. Increasing the speed up to 125 rpm led to a 55 percent increase in the wear rate [20]. In this case, the rotation influences mass transfer rate at the cathode surface, permitting more aluminium carbide to be formed due to a larger area fraction of "fresh" cathode surface, and also speeding up the diffusion flux of $\text{Al}_3\text{CF}_8^{3-}$ away from the cathode. Oxidation of carbide at the anode may also be rate determining in the laboratory cell, but not in an industrial cell. Given that the same experimental conditions are applied, the above mechanisms would probably affect the wear rate to the same extent, independent of the material.

The above suggestions may explain why the wear rate is independent of the carbon material, and in particular, when the different cathodes possess relatively similar microstructures as shown in Figure 8. It is suggested that a ranking of cathode materials in the present test cell and conditions is not possible.

Nevertheless, it was proven that this set-up can be used to study the wear mechanism(s) in detail by performing parameter studies as shown by Tschöpe *et al.* [19, 20]. Previous investigations with the focus on performing parameter studies using similar test cells revealed that parameters like the current density, bath chemistry, granulometry, and physical wear in general influence the wear rate [2, 10, 16, 17 and 19].

However, still the question remains, why does the industry observe different wear rates than what we can observe in the laboratory test cells? Here we like to draw your attention to a fact

that may seem trivial, but to the authors' opinion it is crucial for explaining this difference. As mentioned in the introduction; to cope with the industry's request to improve the smelters productivity, the cathode materials have gradually been replaced. Graphitic and lately graphitized cathode blocks are used instead of anthracitic blocks. This made it possible to increase the amperage of the cells, because the new materials have higher electrical conductivities. At the same time, an increase in the wear rate has been observed, and the industry ranks the wear resistance of the cathode blocks as follows: anthracitic > graphitic > graphitized. Here, it is fair to say that the industry ranking is made without considering the different conditions under operation. Anthracitic materials operated with a lower current density and a relatively uniform cathodic current distribution, while the graphitized blocks are performing at much higher current density and non-uniform current distribution along the block.

Testing the same materials under standard conditions revealed that the wear rate does not depend on the type of material. The cathode wear seems not to be directly related to the chemistry of carbide formation. It is rather indirectly affected, in so far that an increase in current density enhances the carbide formation and thus the wear rate.

Therefore, industrial observations made at cells operated under different conditions might be misleading when compared to laboratory tests, which are performed under standard conditions.

Conclusion

Our laboratory study for ranking cathode materials was carried out under realistic conditions concerning electrolyte composition, temperature, current density, and other factors possible to control in a laboratory experiment. However, there are still discrepancies with respect to industrial experience. The rate of carbon removal from the cathode surface is unrealistically high. The accelerated wear rate is probably caused by the absence of a protective aluminium layer, leading to direct contact between the cathode surface and the electrolyte. This allows the test to take place within a reasonable time frame, which is suitable for laboratory investigations.

It was proven that the observed wear was reproducible. Non-conducting linings at each end of the specimen ensured a uniform current distribution along the exposed cathode surface area. Nevertheless, it was found that the wear rate is not material dependent. Therefore, a ranking of the three different cathode blocks tested, by using the presented cell design and under standard conditions, is not possible.

Possible reasons and the cause of discrepancies with industrial observations have been discussed.

Acknowledgement

The present work was carried out in the project Durable Materials in Primary Aluminium Production (DuraMat), financed by the Research Council of Norway, Hydro Primary Metal Technology, Sør-Norge Aluminium (Soral), and Elkem Carbon. Permission to publish the results is gratefully acknowledged. Special thanks go to Ms. Dian Mughni who performed some of the wear test experiments during her summer job at NTNU.

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