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INVESTIGATION OF THE CATHODE WEAR MECHANISM IN A LABORATORY TEST CELL

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Abstract

Cathode wear has become one of the major challenges for the life time of high amperage aluminum reduction cells due to the use of graphitized cathodes. The fundamentals of the cathode wear are still a matter of debate, and a laboratory procedure for testing of cathode materials is desired. Here, we present a laboratory electrolysis cell, which has been designed for cathode wear tests of industrial cathode materials. The formation and transport of aluminum carbide have been considered to be an important factor for cathode wear, and the laboratory test cell was designed in such a way that the cathode is exposed directly to the electrolyte. Aluminum carbide formed at the cathode may dissolve directly into the electrolyte. Here we present the study of the cathode wear of a commercial high density graphitic material, where the influence of the cathode surface morphology, diffusion and hydrodynamics in the electrolyte, have been in focus. The cathode wear and the penetration of electrolyte into the cathode were investigated by optical and electron microscopy. The influence of current density, hydrodynamics and transport of carbide in the electrode are discussed in relation to the experimental results.

Introduction

One of the key issues in the aluminum smelting industry is to improve production capacity and increase energy efficiency. Graphitized cathode blocks combine excellent thermal and electrical properties (increased electrical conductivity) and are the state of art cathode material in modern high-amperage cells [1]. The benefits of increasing the line current and productivity need to be weighted against higher material costs and lower wear resistance. Today, the increased wear rate is one of the decisive factors for decreased lifetime of the Hall-Héroult cells, and it is crucial to find the mechanism(s) for the wear and especially the strongly non-uniform so-called "W" or "double W" wear pattern [1-4]. A significant body of research has been conducted, but the fundamentals are still a matter of debate. It is generally agreed that both, the formation and transport of aluminum carbide are important factors for the cathode wear, but so far the formation mechanism is mainly based on theoretical considerations [5].

Al_4C_3 is formed at the carbon-molten aluminum metal interface according to reaction (1),

$$4\,Al\,(l) + 3\,C\,(s) \rightarrow Al_4C_3\,(s) \qquad (1)$$

This reaction is thermodynamically favored ($\Delta G_{965°C}$= -139 kJ) and should occur at the electrolysis conditions [6], but graphite is known to be poorly wetted (wetting angle Θ>90°) by liquid aluminum and bath components [7]. Thus, reaction (1) produces only small amounts of aluminum carbide without the presence of bath. The protective Al_2O_3 layer on aluminum prevents the direct contact between carbon and metal, but formation of aluminum carbide is enhanced in presence of the molten electrolyte between molten aluminum and carbon [7]. Aluminum is then transported through the cryolite layer, reacts with carbon at the graphite/cryolite interface, and forms Al_4C_3. Here, the mass transfer of aluminum through cryolite would be the rate limiting step [7]. The wetting ability of the carbon cathode and infiltration with respect to bath are known to be influenced by the sodium uptake in carbon [1] as well as the influence of current density [8]. The microstructure of industrial graphitized carbon materials (e.g., size and orientation of crystallites, graphitization degree, pores and cracks) may also contribute to facilitate bath and aluminum penetration.

Aluminum carbide formation due to bath penetration can be described by chemical or electrochemical means according to reaction (2) and (3), respectively [1].

$$4\,Na_3AlF_6\,(l) + 12\,Na\,(\text{in C}) + 3\,C\,(s) \rightarrow Al_4C_3\,(s) + 24\,NaF\,(l) \qquad (2)$$

$$3\,C\,(\text{cathode}) + 4\,AlF_3\,(\text{diss}) + 12\,e^- \rightarrow 3\,Al_4C_3\,(s) + 12\,F^-\,(\text{diss}) \qquad (3)$$

The importance of reaction (2) was questioned since carbide was found in cracks, where electrolyte and aluminum metal were present, but not in pores [9, 10]. Rafiei et al. [11] proposed that the driving force of carbide formation increases with increasing current density. Wilkening and Reny [12] proved that the electrochemical reactions highly contribute to the cathode wear. It was proposed that the direct contact between molten aluminum and carbon does not lead to significant wear at the cathode surface. The reaction would continue until a stable carbide layer is formed acting as a protective layer against further attack [1, 13].

Rødseth et al. [14] studied the solubility of carbon in aluminum of industrial cells and its effects upon the casting process. It was shown that the metal is not saturated with carbon. Explanation was given by earlier work of Ødegård et al. [15]. They found that the carbon solubility (in form of carbide) in aluminum metal is two order of magnitudes lower then the solubility in cryolite, which increases with the cryolite ratio (CR) to a maximum of 2 wt% (at CR=1.8). It was suggested that Al_4C_3 dissolves in the bath according to reaction (4):

$$Al_4C_3\,(s) + 5\,AlF_3\,(\text{diss}) + 9\,NaF\,(l) \rightarrow 3\,Al_3CF_8^{3-} + 9\,Na^+ \qquad (4)$$

Convection (e.g., of the metal pad) inside the pot might be responsible for transporting the carbide saturated bath film to the bulk bath, while exposing continuously "fresh" bath to promote the dissolution of aluminum carbide.

Laboratory tests have also been introduced to investigate the wear mechanism and the influence of the type of carbon material on the wear [12, 13, 16]. Typical wear rates in electrolysis cells are in the range of 2-6 cm/year [17]. To reproduce this in a laboratory cell would require long and unpractical electrolysis times. This was solved by using the inverted cathode configuration [10-12, 18], where the cathode is directly exposed to cryolitic bath. This enhances the average wear rates in the order of 50 cm/year, which is approximately one order of magnitude higher compared to industrial cathodes with metal pad protection [18].

The experimental set-up is based on a test design used by Patel [18] and Sato et al. [13]. Several modified cells have been tested, and the most promising one is used here. Previously, this test was designed to study and rank different commercial cathode materials [16], where the test cell parameters were kept constant in between each test. Here, the set-up was used to study the wear mechanism, and the results are compared with computer simulations.

Experimental

Laboratory test cell

The experimental set-up is shown in Fig. 1. It consisted of a graphite crucible placed on a graphite supporter in the isothermal zone of the furnace. Nitrogen, used as inert carrier gas, was flushed from below, and the system was kept as gas-tight as possible with an outlet gas collection into a fume hood. The crucible was positively charged acting as an anode, and contains cryolitic bath and molten aluminum metal. The negatively charged cathode sample was immersed into the electrolyte, whose composition was 74.8 wt % cryolite, 12.0 wt% AlF_3 (cryolite ratio = 2.14), 8.2 wt% Al_2O_3 (saturated at 960 °C) and 5.0 wt% CaF_2. The aluminum carbide solubility in this melt was calculated to be 0.7 wt% [15]. The electrolysis temperature was set to 960 °C and kept constant during the experiment by an external temperature controller. A heat resistant steel rod was used to conduct current to the cathode. In order to establish similar conditions as in industrial cells, the cathode was rotated at a constant speed of 50 rpm during the electrolysis. The cathodic current density used was 1 A/cm^2 and the electrolysis time was 24 hours. The cell voltage, current and temperature (measured inside the crucible wall) were recorded during the experiment.

After the experiment the furnace was turned off while maintaining the nitrogen atmosphere. The steel rod with the cathode was lifted out of the bath and allowed to cool in the colder part of the furnace.

Materials preparation and characterization

A commercial high density graphitic carbon block was used as the cathode. The test pieces were 30 mm in diameter and 80 mm long. In order to prevent non-uniform current distribution and wear as observed in [13], it was considered to be important to define the exposed area accurately. Each end of the cathode specimen was covered by an insulating material (Si_3N_4), defining a uniform 30 mm high cylindrical area exposed to the electrolyte, as shown in Figs. 2 and 3, respectively. With this set-up it was possible to prevent high current densities at the bottom of the cathode and to achieve accurate data on wear relative to the current density.

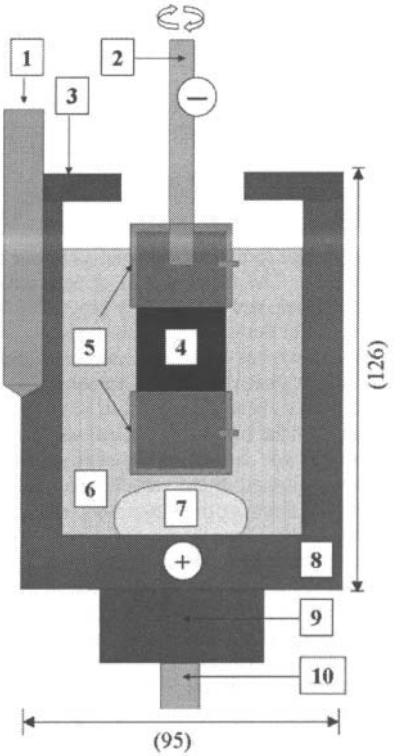

Fig.1: Schematic drawing of the experimental set-up with a vertical rotating cathode. The dimension of the graphite crucible is given in round brackets with the unit [mm]. 1) thermocouple, 2) rotating cathode connecting rod, 3) lid of sintered alumina, 4) cathode sample, 5) Si_3N_4 linings covering both ends, 6) bath/electrolyte, 7) aluminum metal (100 g), 8) graphite crucible/anode, 9) graphite support, 10) anode lead.

Two different cathode surface morphologies were used. The dimensions and appearance of the samples for ranking the different cathode materials is shown in Fig. 2. Those samples are referred to as type 1 in the following. For studying the wear mechanism two types of slots were cut into the surface around the periphery as shown in Fig. 3. Those samples are labeled type 2.

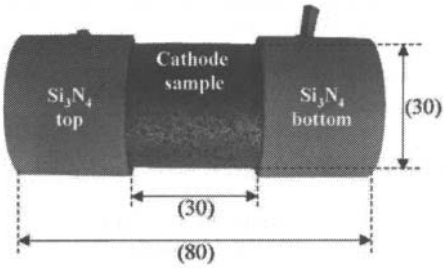

Fig. 2: Image of the cathode sample with Si_3N_4 covered ends (type 1). The dimensions in millimeters are given in brackets.

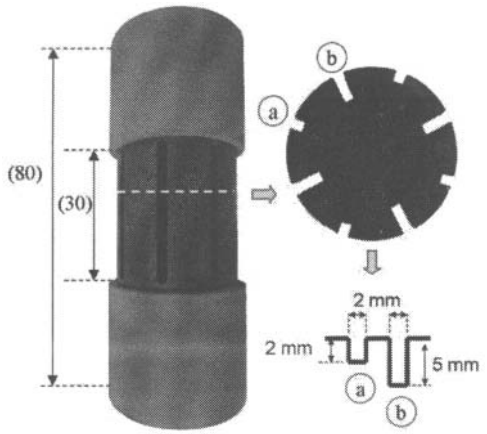

Fig. 3: Image of the cathode with slots and with Si_3N_4 covered ends (type 2). The dimensions in millimeters are given in brackets. Eight vertical slots with two different depths were cut evenly distributed around the periphery. Four slots were 2 mm wide and 2 mm deep (a) and the other four slots were 2 mm wide and 5 mm deep (b).

The weight, apparent density and open porosity of each specimen were measured before the test. After the test the remaining bath at the cathode surface was carefully removed with a knife, avoiding loss of carbon. The average diameter of type 1 samples was determined before and after the experiment using a caliper as well as image analysis methods described in detail by [16].

Type 1 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 Fig. 4. To expose the cross section, the tested samples were dry cut into slices with 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 ground down to 10 µm using silicon carbide paper (P220-P2000). Afterwards, the samples were polished (Struers Rotoforce-1) using diamond sprays (6, 3, 1 and ¼ µm) on satin woven acetate cloths (Struers). During grinding and polishing, 100 % ethanol was used as a lubricant to avoid reactions in contact with water. Finally, the samples were coated with carbon to reduce the problems with charging. The same preparation procedure was carried out with the virgin material. The electron beam spot size was broadened to 30 µm to avoid Na evaporation. The content of the major components C, Al, O, F and Na was recorded. Type 2 cathodes were investigated by using the caliper before and after the test. In order to study the wear profile, they were cut, embedded, ground and polished similar to type 1 cathodes.

Computer Simulations

In order to evaluate the experimental findings, two 2D stationary electric field and hydrodynamic models using FEM simulation were performed. Experimental data from industrial measurements and the laboratory set-up were incorporated. The models themselves are preliminary and serve as a pre-study towards a more sophisticated reproduction of the laboratory wear test by computational methods.

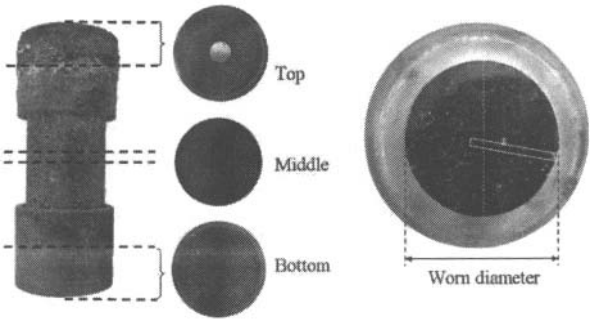

Fig. 4: The sampling position and preparation of worn cathode cross sections. The white box in the embedded and polished slice represents the area for EPMA investigations.

The set-up of the 2D stationary electrical model of the wear test sample including the two types of slots is depicted in Fig. 5. Here, the model is composed of two materials with different electric and magnetic properties. To avoid diverging electrical fields at interacting corners, all sharp edges of the slots where slightly rounded to 0.0001° also with the perspective that no physical object with perfect corners exists. The set-up for the 2D stationary hydrodynamic model used in the simulation is depicted in Fig. 6. All the simulations were performed by using COMSOL Multiphysics® 4.2 [19]. The software includes physics interfaces for modeling static electric fields as well as currents by using the AC/DC module and hydrodynamics (incompressible laminar fluid flow) by using the Fluid Flow module. The mathematical background for these modules is described in [19].

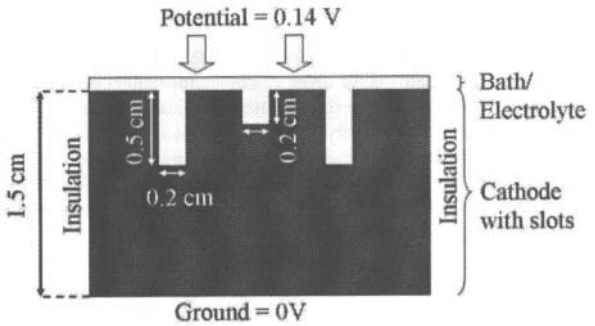

Fig. 5: 2D model geometry of the cathode with two types of slots filled and covered with a layer of bath/electrolyte. The boundary conditions and dimensions are given.

Important material data were density, viscosity and electrical resistivity for the involved materials. The electrical resistivity for bath/electrolyte and carbon cathode was given as 204 S/m and $1.25 \cdot 10^{-5}$ S/m [1], respectively. The dynamic viscosity of the bath/electrolyte was 2.42 Pa·s and the density was 2200 kg/m^3 [1]. The circular motion of the cathode sample was simulated by specifying the vector components of the speed (u, v) and transforming the rotation value of 50 rpm into [m/s] using the initial radius of 0.015 m.

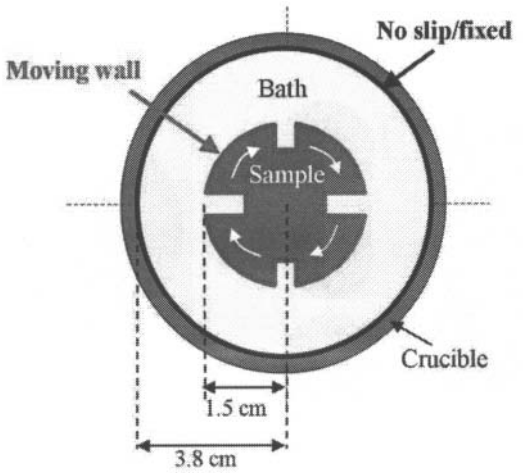

Fig. 6: 2D geometry of the top view of the wear test. The cross section includes the rotating sample with two types of slots and the surrounding bath/electrolyte. The boundary conditions and dimensions are given.

Results

The cross sections of four different wear test durations (24 h, 1 h, 10 min and 2 min) of type 1 samples were examined with EPMA, primarily to determine the depth of penetration. The results of the cross sections at the top, middle and bottom position for each type 1 cathode were relatively similar. The measurement was performed from the surface to the center of the sample. Here, the micrograph and element distribution of Na and F, which is representing the bath components, is presented in Fig. 7. The layer of surrounding bath and probably the subjacent thin layer of aluminum carbide on the cathode surface were removed to measure the diameter as previously mentioned. Thus they are not present in the surface micrograph in Fig. 7. After 24 h it is evident that the electrolyte has penetrated the entire cathode and no bath front could be identified. In order to obtain more data on the bath penetration rate the wear test times were gradually reduced. Even after a wear test time of only two minutes the entire cathode was infiltrated with bath. The individual carbon grains can clearly be distinguished from the infiltrated bath in the cracks and pores of the carbon cathode material. Aluminum carbide was mainly found at the surface and in the pores.

Fig. 8 shows the type 2 cathode after the wear test including the sampling position. For type 1 cathodes the wear was quite uniform over the whole length of the exposed area, which indicates a fairly even current distribution. This has recently been reported by Tschöpe et al. [16]. The same was observed in the exposed area of type 2 cathodes, but during the experiment the bottom lining fell off. In this region, a higher wear rate was observed. For the caliper method only the exposed area (assuming an intact bottom lining) was considered. Therefore, only slices from the upper region towards the top Si_3N_4 lining were cut and prepared as described in the experimental section. The polished slices of virgin and tested cathode are shown in Fig. 9a and 9b, respectively. Superimposing them on top of each other visualizes the worn area, which is indicated by the red (dark grey) color in Fig. 9c.

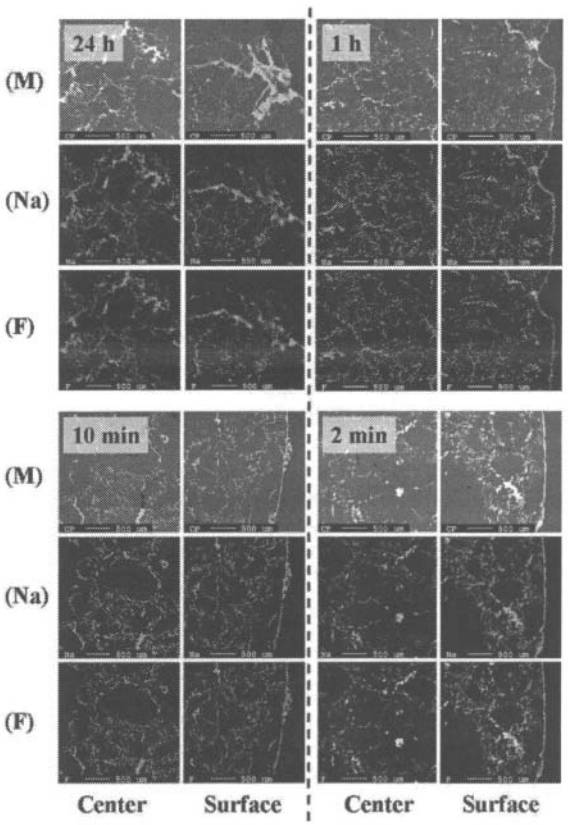

Fig. 7: Micrograph (M) and element distributions of Na and F at the surface (right) and the center (left) for the 24 h, 1 h, 10 min and 2 min wear test duration. The area maps are scaled and the lighter the color the higher the content (intensity of the grey-scale).

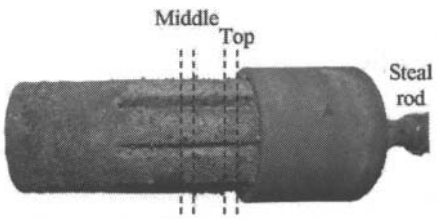

Fig: 8: Type 2 sample after the test including the sampling position (not in scale). The yellow color at the surface is aluminium carbide.

A graphical presentation of the wear observed for the cathode (Fig. 9) is further depicted in Fig. 10. From both figures it is evident that the cathode cylinder surface is worn to a greater extent than the cathode at the bottom of the slots. Furthermore, the 2 mm slots appear to be deeper worn at the wall and bottom compared to the 5 mm slots. It is also interesting to note the systematic preferred wear which occurred at one side of each slot (Fig. 10, edge 1). The wear profile shows clearly that the rotation of the cathode had a detrimental effect on the slot wear. The white arrow in the center of the slice illustrates the rotation direction (Fig. 10).

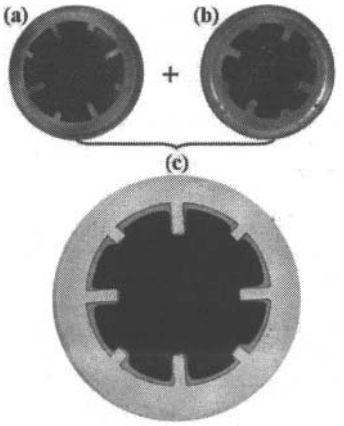

Fig. 9: Images show the specimen before (a) and after (b) the test. Both where superimposed to receive image (c). The blue/light grey area in (c) corresponds to the wear of the specimen after 24 h electrolysis.

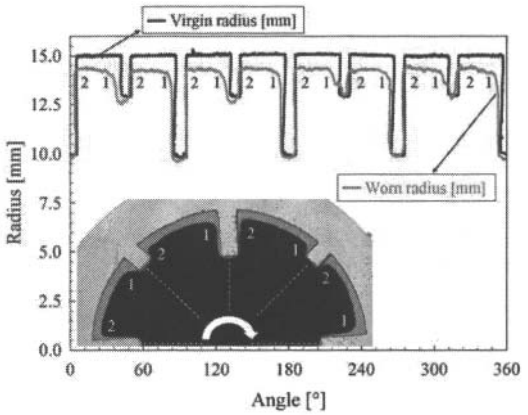

Fig. 10: Graphical representation of the cathode surface shown in Fig. 9. The angle is plotted versus the radius around the periphery of the virgin and worn cathode sample. The two curves are shifted relative to each other for better visibility. The numbers 1 and 2 are used to describe the different wear patterns of the left and right corners of the slots.

Discussion

After an electrolysis time of 24 hours the specimens are penetrated with bath to the center, which was in line with expectation. Lowering the exposure time to two minutes in contrast showed that sodium infiltrates the cathode material fast and induces the bath penetration, since no concentration gradients could be identified. Therefore it is suggested to run the test either shorter than 2 min, where the practicability of the test has reached its limit or at a lower current density. Experiments without polarization are also considered for future experiments, to see if the sodium up-take and bath penetration into the carbon materials take place without the presence of electrochemical reactions, but with the presence of molten Al in contact with molten electrolyte.

By superimposing the tested (b) profile onto the virgin (a) the worn area in the cross section is clearly illustrated (see Figs. 9 and 10). The interpretation of the wear profile is not straight forward, since it could be either influenced by the current density or fluid flow around the rotating cylinder or both. Experiments to separate both effects have not been performed, and will be followed up in future work.

Fig. 11 shows the simulated current density distribution of the bath inside the slots and at the surface of the cathode. The highest current density can be observed at the edges of the slots (corner 1 and 2). Inside the 2 mm slot the current density is higher compared to the 5 mm slot. This corresponds well with the wear pattern shown in Fig. 9. The influence of the current at bottom of the slots is hard to compare with the experimental findings. It should be kept in mind that the virgin sample might be slightly different compared to the tested sample due to the inhomogeneity of the carbon material. Moreover, the fabrication of the slots depth implies an uncertainty during machining, while the width is quite accurate machined. Here more experience, through a number of similar experiments, need to be gained. Due to the difference in current density the higher wear occurs at the cathode surface rather than at the bottom of the slots, which is supported by the simulations in Fig. 11. The consistently higher wear of corner 1 in Figs. 9 and 10 cannot be explained by the current density without considering the influence of the hydrodynamics during the electrolysis.

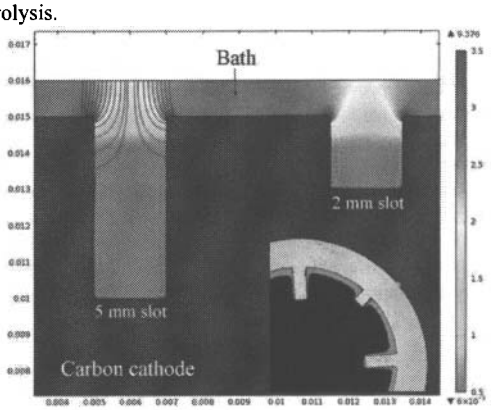

Fig. 11: FEM-simulations of the current density distribution of the bath inside slots of two different depths (2 and 5 mm) shown as surface/contour plot [A/cm^2] at stationary conditions. The red/dark grey color in the scale bar indicates high and green/light grey color low current density.

The simulated velocity magnitude [m/s] in the vicinity of the two types of slots is shown in Fig. 12. The rotation direction of the cathode is clockwise. The simulation illustrates the motion of bath relative to the cathode. The higher velocity and thereby higher material transport at the corners labeled 1 relative to the edges 2 is evident, which explains the more severe wear at the corners 1. The difference of the flow pattern at both corners is not large due to the relatively low flow rate. Corner 1 can be regarded as a stagnant point. The flow slows down or stops, because the cathode rotates against the bath. This might induce swirls causing an increased material transport away from corners 1 into the boundary layer or bulk material. The bath inside the deeper slots is considered to be stagnant relative to the rotation of the cathode sample. Therefore the bath inside the slots moves with almost the same speed as the rotating cathode. The exchange of saturated bath (containing dissolved carbide) with fresh bath, causing a material transport, is limited. This become more likely the deeper

the slot is. The convection of the bath is ranked as follows: outer surface >>> 2 mm slot >> 5 mm slot. Increased wear follows the same order, which can clearly be seen in Figs. 9 and 10. From Fig. 12 it is suggested that future simulations should be performed with a higher mesh density. Furthermore, it is planned to study the same models in ANSYS to compare both simulations among each other and with experimental results to establish a sophisticated and reliable wear test model.

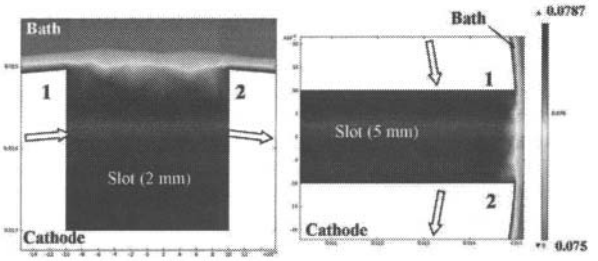

Fig. 12: Simulation of the velocity magnitude surface [m/s] at stationary conditions for the two slots depth. The dark grey color indicates high and the light grey low speed.

Conclusion

The wear test showed considerable wear of the cathodes after 24 hours as shown previously [16]. The penetration of bath into the cathode was shown to occur already after 2 min electrolysis in the present test, which shows that the sodium intercalation and bath penetration was most probably occurring already before polarization of the cathode. By introducing slots into the cathode surface it was shown that the wear was significantly influenced by both the hydrodynamics and the current density. The interpretation of the experimental data could be supported by computer simulations.

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