BEHAVIOUR OF TiB₂-COATING ON GRAPHITIZED CARBON CATHODES DURING LABORATORY ALUMINIUM ELECTROLYSIS

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ABSTRACT

Graphitized carbon materials were coated with alumina-bonded TiB₂ (TINOR). The coating thicknesses were 0.45, 0.8 and 1.1 mm. One sample had a 1.2 mm coating on one half and 0.2 mm on the other half. Traction test of baked samples before electrolysis showed strong adherence of the coating. The samples were used as cathodes in a laboratory cell, and electrolysis was carried out for 200 hours with an aluminum pool and a fluoride electrolyte. The coating was penetrated by aluminum and to a lesser extent by the electrolyte. A 100 – 300 μm aluminum carbide layer was formed between the coating and the substrate, but did not lead to delamination. The standard 1.1 mm TINOR 2000™ coating performed best with complete wetting and an intact coating.

INTRODUCTION

The TiB₂ TINOR coating has been applied on 14 different smelters throughout the world. The main ingredients of the TINOR coating are a slurry of TiB₂ in colloidal alumina which is brushed on carbon in several layers. The colloidal alumina is transformed into a solid binder by heating and the TINOR coating aluminized. The coating has been steadily improved with respect to adherence to the carbon and between the successive TiB₂ layers and with respect to the wetting of liquid aluminum. This is accomplished by adding chemical modifiers to the coating. The present TINOR 2000™ coating is typically a 1.1 mm crack-free coating.

The TiB₂ coating accomplishes wetting between liquid aluminum and the cathode which is expected to lead to the following improvements in aluminum electrolysis:

- Slower and more controlled sodium penetration;
- Improved cathode current distribution;
- Lower cathode voltage drop;
- Improved current efficiency;
- Less sludge formation;
Increased resistance towards abrasion/corrosion.

The last point has become increasingly important for the modern high amperage cells that use graphitized cathodes. With the low electrical resistance of graphitized cathodes the current density will be higher at the block ends (1). High current density combined with low abrasion resistance lead to life-determining excessive wear at the ends of the cathode blocks (2-3).

The present study was to determine the performance of the TINOR 2000™ coating on commercial graphitized cathode materials during laboratory electrolysis. Partial coating and varied TiB₂ coating thickness were also investigated. In addition the coating adherence before electrolysis was tried measured.

Coating Adherence Before Electrolysis

Traction tests were carried out with a 1.5-mm TINOR 2000™ coating applied on different substrates. The coating was applied on 15 mm Ø carbon samples and heat-treated. After cooling, the coating was fastened to a copper rod with Araldite (Fig. 1). An Araldite that polymerized very rapidly was used, and electron mapping confirmed that the Araldite did not penetrate through the coating.

A 3-mm horizontal hole was drilled in the copper and in the carbon rod. Rods were put through the holes and the copper rod was fastened to a rack while a bucket was fastened to the carbon sample. The bucket was filled with lead and then gradually with water.

The sample specifications and the summary of the tests are given in Table 1.

Table 1. Adherence Test Results. Fully Graphitized Samples.

| Commercial graphitized cathode | Density (*) | Maximum load (**) |
|-------------------------------|------------|------------------|
| European source (1)           | 1.61 g/cm³ | 48 kg            |
| European source (2)           | 1.58 g/cm³ | 44 kg            |
| Russian source                | 1.64 g/cm³ | 42 kg            |

(*) Apparent density determined by geometric measurements.
(**) Max. load before substrate rupture.

All samples broke in the carbon material, so it can be concluded that for all coated samples, the adherence was larger than

\[ 42 \cdot 9.87 / 0.0075^2 \cdot \pi = 2.3 \text{ MPa} \]

The experiment can be used to estimate the tensile strength of the materials:
(42/48) \[ \frac{9.87}{(0.0075^2 \cdot \pi - 0.003 \cdot 0.015)} = \frac{3.2}{3.6} \text{ MPa} \]

which are reasonable results.

Cylindrical carbon samples; 75 mm \( \phi \times 20 \) mm were coated and tested by electrolysis with different configurations of TINOR coating on graphitized cathode from Europe and Russia. The coated cathode was placed at a graphite crucible bottom and held in place by TINOR used as a glue. A dense alumina tube of 90 mm outer diameter and 7 mm thickness was used as the lateral wall lining.

EXPERIMENTAL

Cathode Materials and Set-up

Cylindrical carbon samples; 75 mm \( \phi \times 20 \) mm were coated and tested by electrolysis with different configurations of TINOR coating on graphitized cathode from Europe and Russia. The coated cathode was placed at a graphite crucible bottom and held in place by TINOR used as a glue. A dense alumina tube of 90 mm outer diameter and 7 mm thickness was used as the lateral wall lining.
The following samples were studied:

1.2 mm coating on one half and 0.2 mm on the other half. European graphitized cathode; 0.45 mm coating. European graphitized cathode; 0.80 mm coating. European graphitized cathode; 1.1 mm (Standard TINOR™). Russian graphitized cathode.

Cell start-up:

- The green coating was protected by an aluminum sheet of 2 mm thickness. Aluminum shots corresponding to about 20 mm of metal liquid were placed on the AI protection sheet.
- A quantity of 1.2 kg of fluoride electrolyte was loaded on the top of the cathode and the AI shots.
- The cell is heated up from room temperature to 940 °C during 24 hours. The aluminizing of the coating occurs in-situ by liquid AI from about 700 °C.
Electrolysis test conditions:

- Anodes: An inert MOLTECH metallic anode of 20 mm diameter and 20 mm height was used to provide a stable anode throughout the experiments.
- Total current: 15 A, which corresponds to a nominal current density at the coated cathode surfaces of 0.5 A/cm².
- The coated cathode was protected by an aluminum pool of 20 to 30 mm.
- Electrolyte composition: 14 wt% AlF₃ excess / 4 wt% CaF₂ / 8 wt% Al₂O₃ (close to saturation to reduce the dissolution of the alumina lining in the test cell). Operating temperature: 940 ± 5 °C.
- Alumina feeding: Calculated on the base of current efficiency of 60%.
- The bath composition and alumina content was analyzed and adjusted every day by adding NaF, and by adjusting the feeding rate.
- Aluminum tapping: Done every 2 days to maintain the aluminum pool height in the range of 20 – 30 mm.
- Test duration: 200 hours.
- Before the cell was cooled down most of the aluminum was spooned out of the cell. This procedure made the cutting procedure easier.
- After cooling the cell was cut in two halves. For the sample with partial coating the cut was perpendicular on the interface between the thin and thick coating.

The aluminum addition procedure was not fully mastered for samples 1 and 2 and the voltage varied from 4.2 to 6.5 volt. The cell voltage was very stable for the last two samples and was 3.5 ± 0.1 volt.

RESULTS

Fig. 3 shows a picture of the cut-through crucibles after the experiments for samples 1, 3 and 4. The partially coated sample 1 is cut perpendicular to the thick and thin interface. The areas as cut-out from element mapping are also shown. Fig. 4 gives the element mapping for the areas shown on Fig. 3. The present element mapping is in black and white'. Table 2a gives element analysis of 5 locations shown in Fig. 4 e and f.

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* Coloured pictures with intensity scale can be obtained from the authors (oye@material.ntnu.no).

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Table 2a. Element analysis. (Sample 3). Weight % (not adjusted to 100%).

| Loc. No. | C   | K   | O   | F   | Ti  | Na  | Al  | Total | Comment          |
|---------|-----|-----|-----|-----|-----|-----|-----|-------|------------------|
| 1       | 13.3| 2.2 | 5.3 | 8.2 | 0.0 | 6.7 | 60.7| 96.3  | Area 2, gray layer |
| 2       | 11.9| 2.0 | 15.6| 3.2 | 0.0 | 1.5 | 61.1| 95.4  |                   |
| 3       | 13.4| 1.2 | 10.9| 3.3 | 0.0 | 1.5 | 63.7| 94.0  |                   |
| 4       | 6.2 | 0.0 | 1.0 | 0.0 | 0.3 | 0.0 | 93.1| 100.7 | Area 2, Al globule |
| 5       | 4.1 | 8.3 | 21.1| 25.1| 0.0 | 12.8| 31.1| 102.6 | Area 3, salt globule |

Table 2b. Element analysis. (Sample 3). Atomic-% (adjusted to 100%).

| Loc. No. | C   | K   | O   | F   | Ti  | Na  | Al  | Total | Comment          |
|---------|-----|-----|-----|-----|-----|-----|-----|-------|------------------|
| 1       | 24.7| 1.2 | 7.4 | 9.7 | 0.0 | 6.5 | 50.5| 100.0 | Area 2, gray layer |
| 2       | 21.9| 1.1 | 21.6| 3.8 | 0.0 | 1.5 | 50.1| 100.0 |                   |
| 3       | 25.2| 0.7 | 15.4| 3.9 | 0.0 | 1.5 | 53.4| 100.0 |                   |
| 4       | 12.9| 0.0 | 1.6 | 0.0 | 0.1 | 0.0 | 85.4| 100.0 | Area 2, Al globule |
| 5       | 7.0 | 4.3 | 26.9| 26.9| 0.0 | 11.3| 23.5| 100.0 | Area 3, salt globule |
Fig. 3 a) Sample 1. 1.2/0.2 mm coating.

Fig. 3 b) Sample 3. 0.8 mm coating.

Fig. 3 c) Sample 3. 0.8 mm coating from above.

Fig. 3 d) Sample 1. 1.1 mm coating

Fig. 3. Cut-up samples after 200 hours of electrolysis. The marked area was taken out for element analysis.
4 a) Sample 1. 1.2 mm coating. Area 1.

4 b) Sample 1. 0.2 mm coating. Area B.

4 c) Sample 2. 0.45 mm coating.
4 d. Sample 3. 0.8 mm coating. Area 1

4 e. Sample 3. 0.8 mm coating. Area 2.

4 f. Sample 3. 0.8 mm coating Area 3.
4 g. Sample 4. 1.1 mm coating. Area A.

4 h. Sample 4. 1.1 mm coating. Area B.

4 i. Sample 4. 1.1 mm coating. Area C.
DISCUSSION

Reliability of the element mapping and quantitative analyses.

Table 2 a,b shows element analysis in 5 different localities. This analysis was done to check the reliability of the element mapping. The weight % data is calculated without any adjustments. The total weight % is reasonable close to 100% which gives credence to the analysis. The composition in atom % is adjusted to 100%.

Location 1-3 (Fig. 4e) is within the gray layer on the CP picture underneath the TiB_2 coating. The averages for the three analyses are:

- C: 23.9 at %
- K: 1.0 at %
- O: 15.8 at %
- F: 5.8 at %
- Na: 3.1 at %
- Al: 51.3 at %

A charge balance with respect to excess aluminum excluding carbon:

\[ [\text{Al}] - (1/3) (2 [\text{O}] + [\text{F}] - [\text{K}] - [\text{Na}]) = 40.2 \text{ at-%}. \]

If all excess aluminum is bond as Al_4C_3, then \( (3/4) \cdot 40.2 = 30.2 \text{ at-% C should be present. This means excess Al as C is analyzed to 23.9 at-%. It can hence be concluded that the major constituent of this layer is Al_4C_3 even though electron mapping does not show C in this area. Some aluminum metal could also be present. In location 4 (Fig. 4e) the main constituent is metallic aluminum as expected. Location 5 (Fig. 4f) is expected to be electrolyte. A cation/anion balance confirms this.

Cations: \( 3[\text{Al}]+ [\text{K}] + [\text{Na}] = 86.1 \text{ at-%} \)

Anions excluding carbon: \( 2[\text{O}] + [\text{F}] = 80.7 \text{ at-%}. \)

If the carbon is counted as anions (Al_4C_3) the anion balance is \( 80.7 + 4 \cdot 7.0 = 108.7 \text{ at-%}. \) It is concluded that area 5 consists mainly of electrolyte, possibly with a small amount of Al_4C_3 and C.

Generally it can be concluded that the layer found underneath the TiB_2 is Al_4C_3 except for sample 1, which rather surprisingly indicates TiC under the thick coating (Fig. 4a). This is unusual as TiC cannot be formed from TiB_2, C and Al_4C_3. (TiC can however be formed from TiO_2, C and Al. Some TiO_2 may have been formed in the coating by penetration of oxygen into the interface between the thick and thin coatings and then been reduced by aluminum and transported to the TiB_2 – C interface and reacted to TiC).

Stability of the TINOR coating.

Sample 1. 1.2 mm / 0.2 mm coating

Fig. 3a and b shows the cut-up cell after electrolysis. About 27 mm of the thick coating is intact (Fig. 3a to the left) while 10 mm of the thick coating has delaminated. A thin coating is present in the middle (Fig. 3a).
Fig. 4a shows element mapping of the thick coating under the wetted Al (Area A in Fig. 3a). A 1 mm TiB$_2$ coating is found. A very thin vein has delaminated. Al has penetrated into the TiB$_2$ coating and a 300 µm layer of TiC is present underneath. A much smaller layer of electrolyte is also present under the coating below the TiC layer. Fig. 4b shows element mapping of the thin coating (Area B, Fig. 3a). This coating is electrolyte as the main constituents are bath elements (F, Na and Al). Only traces of Ti and B could be detected.

**Sample 2. 0.45 mm coating**

Inspection of the cut-through crucible showed only partly Al-wetting*. A sample where wetting is observed was cut out for element mapping. A 0.35 mm TiB$_2$ coating is present and a 200 µm coating is seen underneath, probably Al$_4$C$_3$ (Fig. 4c). Aluminum has penetrated into the coating. The TiB$_2$ coating is probably not present in the areas without Al-wetting.

**Sample 3. 0.8 mm coating**

Fig. 3b shows a cut-through picture of the crucible after electrolysis. Fig. 3c is taken from above. About 2/3 of the bottom is wetted by aluminum. Delamination and corrosion are present at the edges. The central areas are completely wetted. Figs. 4d-f give element mapping in the areas shown in Fig. 4b. The TiB$_2$ coating is present in all pictures. The thickness varies from 0.3 mm to 0.7 mm (Figs. 4d-f). Some TiB$_2$ is found as particles in the aluminum above the coating. (Figs. 4d and e). In area 1 (Fig. 4d), near the corroded edge, a vein of up to 300 µm is present underneath the TiB$_2$ coating. This layer is probably Al$_4$C$_3$. Aluminum has penetrated into the coating. Some electrolyte has also penetrated. In area 2 (Fig. 4e), an electrolyte layer of about 250 µm thickness is present underneath the TiB$_2$ coating, and underneath the electrolyte layer, there is again a 100 µm layer, which is probably Al$_4$C$_3$. In area 3 (Fig. 4f) only a small amount of electrolyte has penetrated through the coating, but a 150 µm layer, also probably Al$_4$C$_3$, is seen.

**Sample 4. 1.1 mm coating.**

Fig. 3d shows a cut-through picture of sample 4. Complete aluminum wetting is observed. Fig. 3d also gives the area where samples were cut out for element mapping, and Figs. 4g-i give the result. A 0.9 mm TiB$_2$ coating is found in all the three pictures as seen from the Ti and B mappings (Figs. 4g-i). A 100 µm vein of Al is present between the coating and the carbon substrate. This vein is probably Al$_4$C$_3$. The carbon surface is irregular and has probably also some large pores and TiB$_2$ has partly penetrated into the material. Aluminum has penetrated into the TiB$_2$ coating. Some electrolyte (Na and F mapping) has also penetrated into the coating and is partly concentrated in the lower point of the coating. Fig. 4h shows some delamination of the TiB$_2$ coating in the upper part of the coating. This delamination is partly filled with electrolyte. But the general feature is an intact coating being completely wetted by aluminum.

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*Unfortunately no photo is available.
CONCLUSION

The baked coating before electrolysis adhered strongly to the graphitic substrate. Traction tests give breakage in the graphitized material rather than in the coating substrate interface.

The electrical resistance of the coating is low and stable as demonstrated especially for the 0.8 and 1.1 mm coating. The formation of the 100 – 300 μm layer of Al₄C₃ did not lead to any increased resistance.

The thin coating (< 0.5 mm) is far less effective than the thick coating. Partial surface oxidation during the start-up (under industrial conditions with insufficient protection by Al sheet), could lead to partial loss of coating thickness by dissolution of the binder matrix in cryolite (about 0.3 - 0.4 mm) before total aluminization occurred. However, a thin coating may be effective if oxidation during start-up can be avoided. In a prior work of a hanging cathode tests, it was shown that a thin coating worked well. The aluminizing was done by dipping the cathode in a molten aluminum bath without access to oxygen before placing it in the cell. There was no oxidation and therefore the effectiveness of the thin coating was observed.

Electrolysis tests for 200 hours with a partial coated cathode resulted in disappearance of the thin coating, as well as 10 mm of the thick coating. The interface between the thin (or no) coating and the thick coating is a weak area and may cause delamination. However, 27 mm of the thick coating was still present. Only partial wetting and edge delamination are observed with coating thickness up to 0.8 mm.

The standard 1.1 mm TINOR 2000 gave complete wetting and the coating is intact with only a 100 μm layer of Al₄C₃ underneath. The formation of Al₄C₃ does not lead to delamination.

ACKNOWLEDGEMENT

We appreciate the element mapping and element analysis carried out by Morten Raaness, Department of Materials Science, Norwegian University of Science and Technology.

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