

## Development of Technology for Producing a Wettable Coating on a Carbon Cathode by Electrodeposition

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### Abstract

The article deals with the technology of producing an aluminium-wettable coating in the process of electrolysis of cryolite-alumina melts. This technology has been implemented under laboratory conditions by electrodeposition of boron on the surface of the carbon-titanium cathode.

The presence of a 100-500 µm near-surface layer of boride-carbide compounds, synthesized in the process of a 20-42 hour electrolysis, is confirmed by X-ray diffraction and SEM-EDS analyses.

### Introduction

Many problems of the existing electrolysis technology, including high power consumption, are connected with the fact that carbon blocks are not wetted with aluminum. Almost all aluminum companies in the world have been trying to solve this problem for the last 60 years by creating a cell with a drained cathode. However, Dr. Evans, discussing the issue [1], noted in 2007, "... large-scale projects spanning a couple of decades, involving TiB<sub>2</sub> and composites thereof, have failed to achieve widespread commercial acceptance." The main reason for that, in our opinion, is chemical and mechanical degradation of compact and composite coatings on a cathode in the aggressive means of electrolysis.

Attempts were taken to solve the problem in a different way. The way seemed to be more simple, cheaper and feasible. We talk about the method of electro-deposition or high-temperature electrochemical synthesis of wettable coatings on a carbon cathode from cryolite-alumina melts. The impulse for these attempts and systematic research was given by D. W. Townsend in a patent published in 1991. The patent proposes synthesis of borides of high-melting metals on a drained carbon cathode by doping the cryolite-alumina melt with oxide compounds, such as TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> [2]. It is not known if the patent has been commercially used.

Since 1993, D. Kaptay and S.V. Devyatkin, under laboratory conditions, started to research on synthesis of borides of high-melting metals from molten salts. They were among the first researchers who set a goal of proving the possibility of electrodeposition of TiB<sub>2</sub> from Na<sub>3</sub>AlF<sub>6</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> melts [3, 4]. Their attempts to create wettable coatings on carbon and metallic cathodes ended at the laboratory level [5-8].

In thorough and systematic work, Makyta and his colleges took an attempt to do electrodeposition of a compact diboride coating on molybdenum and graphite cathodes from Na<sub>3</sub>AlF<sub>6</sub>-K<sub>2</sub>TiF<sub>6</sub>-KBF<sub>4</sub> and Na<sub>3</sub>AlF<sub>6</sub>-B<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> melts at 960 °C and the cathode current density of 0.25-1.0 A/cm<sup>2</sup> [9]. All the attempts with melts of different composition ended in producing TiB<sub>2</sub> coatings

of low quality and low cohesion to a molybdenum cathode, and production was only possible at 0.25 to 0.50 A/cm<sup>2</sup>. In all other cases, powder-like TiB<sub>2</sub> and white crystal sediment were synthesized. It seems that the authors took thorough but unsuccessful steps to produce a compact TiB<sub>2</sub> coating with good cohesion on metallic and graphite surfaces. The unsuccessful results were taken as the impossibility of high-temperature electrodeposition of a diboride coating from cryolite melts.

Taking into account the previous unsuccessful attempts, other authors [10] set the same ambitious goal in 2008 to do electrodeposition of a diboride coating on graphite from the cryolite-alumina melt. As a result of research and experiments, a layer of products was produced on a cathode. These products were a mix of electrolyte and its components, calcium borides (CaB<sub>6</sub>) and low titanium oxides (TiO, Ti<sub>2</sub>O<sub>3</sub>). By X-ray diffraction and SEM-EDS analyses, it was discovered that there was only 15 wt.% of powder-like TiB<sub>2</sub> conglomerate of dendritic morphology; it is underlined that varying in the melt composition, current density, and the boron- and titanium-containing components nature doesn't allow the coating morphology be improved. However, it has been proven that samples immersed into molten aluminum are wetted with aluminum.

So, we can say that until now production of compact coatings by electrodeposition from cryolite melts at densities higher than 0.1 A/cm<sup>2</sup> has not been achieved yet. Therefore, this is one of the reasons why there is no commercial technology for a cell with a drained cathode.

We could name a few reasons for the unsuccessful results of such long research, but the main reason is that the surface of composite materials is not homogeneous – it has many micro- and macro-inequalities, cracks, and pores. On such a surface of a cathode-graphite cathode, it is impossible to create equal distribution of current and, as a result, equal, front, and layer-by-layer production of a synthesized phase.

In this regard, we are proposing a new method of production and sustenance of a wettable coating on carbon blocks of the cell [11]. The proposed technology is about having a chemical reaction of the initial reagents (Ti + 2B = TiB<sub>2</sub>) on the carbon surface and on the near-surface layer of the cathode. Conditions for the reaction are created during the process of electrolysis of cryolite melts doped with boron-containing components. The number of these components is limited by the requirements for aluminium purity. Another component of a wettable coating, titanium, is doped into the composition of carbon blocks at the stage of their production.

In fact, boronizing of a near-surface titanium-containing layer occurs. Formation of a wettable coating, in this respect, takes place in synthesis (synthesis of compounds) stages – first, in the Ti-B-C system, then in the TiB and the TiB<sub>2</sub> systems. Therefore,

the near-surface layer of a carbon cathode will consist of layers. (Formation takes a long time.) The outer surface will be boronized to  $TiB_2$ ; the next one will consist of compounds close to the composition of  $TiB$ . Deeper layers will consist of  $Ti_xB_yC_z$ .

As it can be seen from the above, it is expected to produce a compact, durable, and regenerated  $TiB_2$  layer.

### Experiment

For experiments, carbon samples doped with titanium powder which is added to a green aggregate of the cathode block with the size of  $\varnothing 30 \times 50$  mm. For the melt, commercial cryolite with the CR = 1.78, alumina and boron-containing components of chemical purity were used.

All experiments were conducted at 970-990 °C in electrolyte with the CR = 2.5. These experiments were conducted in the cell, the sketch of which is given in Figure 1. The atmosphere of the cell contained argon during electrolysis. After each experiment, the cathode was taken out of the cell.

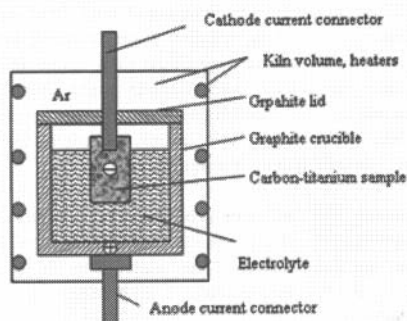


Figure 1. – Cell sketch.

In order to find parameters of electrodeposition-boronizing, 20 experiments were conducted. Joint electrodeposition of aluminum and boron on the carbon cathode under galvanostatic conditions was performed. This paper contains some of the results obtained at the current density of 0.7-1.3 A/cm<sup>2</sup>.

After taking samples out of the melt, samples were photographed, cleaned from electrolyte for an XRD analysis and preparation of specimens for electronic microscopy.

### Experiment results and their discussion

First, we will present experiment DT18 in which only sedimentation (deposition) of aluminum was done. We had the simple goal to create a wettable coating on a carbon-titanium cathode without adding a boron-containing component. In other words, it was necessary to get initial analytical and visual data on the condition of the surface of a cathode. Fig. 2 gives side view and end view of the surface of a sample after a 20-hour experiment.

Separate aluminium semi-drops of different size and low wettability were clearly observed – the angle between the surface of the cathode and metal drops was nearer or greater than 90 °.

Lack of wettability of the carbon sample doped with titanium confirms the need for boronizing the sample surface for generating a  $Ti + 2B = TiB_2$  chemical reaction occurring in the near-surface layer of the cathode.

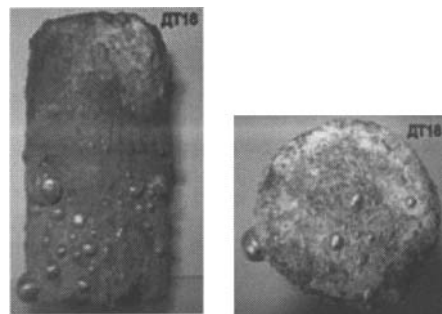


Figure 2. Carbon-titanium cathode after the experiment.

Experiments DT6 and DT9 were conducted under special conditions with primary electrodeposition of boron. (These conditions were difficult for aluminum precipitation on the cathode.) During a 24-hour experiment, only an electrolyte layer and rare droplets of aluminum were found on the cathode. Therefore, after cleaning, the surface of the cathode was easily accessible for taking samples for an XRD analysis. Table I shows the analysis results.

Table I. XRD analysis results of the surface of the DT9 cathode and electrolyte from the cathode surface, wt. %

Phase	DT6		DT9	
	Cathode	Electrolyte	Cathode	Electrolyte
$TiB_2$	2.44	0.47	0.96	1.13
$Ti_3B_4$	0	0.63	0	0
$TiC_{0.981}$	2.30	0	0	0
$Ti_8C_5$	0	0	2.02	0
$CaB_6$	4.26	3.64	1.03	2.51
$TiO_2$	0.58	0	0	0
Ti	1.65	0	0	0
$Na_3AlF_6$	27.7	58.0	28.0	74.8
$Na_5Al_3F_{14}$	17.8	31.3	0	0
NaF	0	0	0	3.02
$Al_2O_3$	1.23	4.71	8.24	5.64
$B_2O_3$	0	0	0	4.68
C	34.6	0.52	49.9	3.22
Al	0	0	2.43	2.32

As it can be seen from the data,  $TiB_2$  and  $Ti_3B_4$  are contained both in the surface layer and electrolyte. It can be assumed that titanium borides, together with electrolyte, were partially removed from the surface of the cathode during cleaning of the cathode. Besides the main components – carbon and electrolyte, the surface of the cathodes contained 2 wt.% of titanium carbide ( $Ti_8C_5$  and  $TiC$ ). The small number of the listed compounds in the cathode is connected with the need for removing an 1 to 2 mm layer for taking samples. The accumulated data prove the theoretical base for the technology of boronizing-electrodeposition. According to this base, formation of a wettable coating is performed in three stages of formation of compounds, first, in the Ti-B-C system, then in the TiB and the  $TiB_2$  systems.

In all other experiments, the initial composition of electrolyte was same, the only thing that was different is the number of dopes done during an experiment for maintaining the concentration of electro-active components in the preset range.

After a 42-hour experiment (DT11), good adhesion of aluminum to the carbon surface immersed into electrolyte was observed.

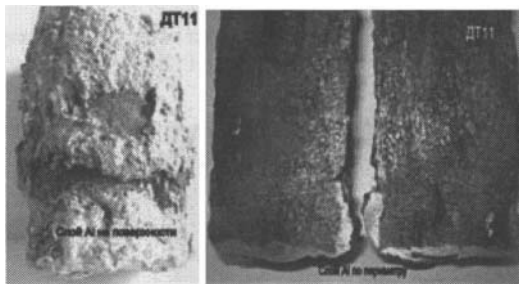


Figure 3. DT11 sample after the experiment (left – Al layer on the surface, right – Al layer along the perimeter).

Samples from the surface of the cathode for an XRD analysis were taken after removing an aluminum layer from the cathode. It seemed that together with the aluminum layer, a layer enriched with  $TiB_2$  was removed – the XRD analysis did not detect this layer. However, the presence of  $TiC$  in the amount of 1.53 % of the mass was observed. The logical assumption would be that outer near-surface layers of the cathode were enriched with  $TiB_2$  compounds, deeper ones – with titanium carbide.

For the SEM-EDS analysis, a sample from the side surface (DT11-B) and a sample from the end side (DT11-T) were taken (Figure 4).

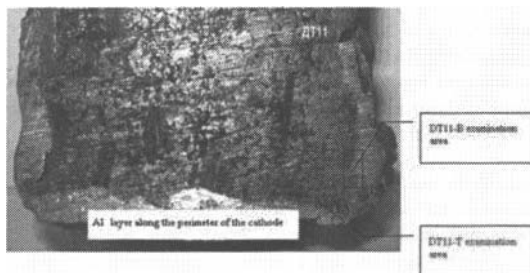


Figure 4. DT11 sample in cross section.

Visually, according to the SEM analysis data for the area of the sample shown in Figure 5, zones of different contrast can be seen. According to the EDS analysis (Figure 6), the joint presence of titanium, boron, carbon between Point 5 and Point 9 of the scanning line can be clearly seen. It proves the presence of compounds in the Ti-B and/or Ti-B-C systems. This area of the joint presence of Ti-B-C is a near-surface layer, 500  $\mu m$  thick, which is located between the aluminium layer and the carbon body. The B:Ti ratio at Points 5, 6, and 7 equal 7.3, 6.4, and 10.0 respectively.

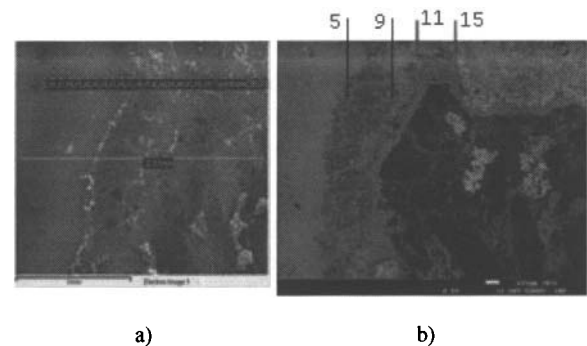


Figure 5. The microstructure of the area of the DT11-B sample ( $\times 55$ ): a) in secondary electrons, b) in back-scattered electrons (composition contrast).

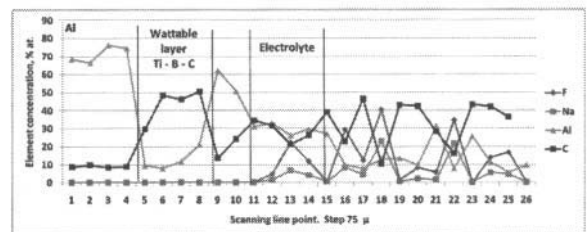
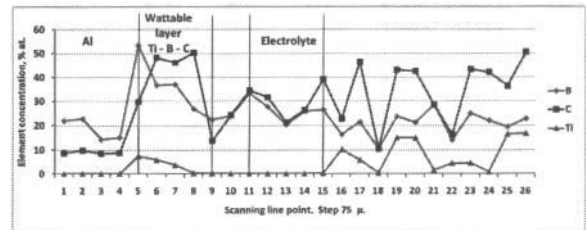


Figure 6. The EDS analysis results along the point spectrum line (see Figure 5).

Then, between the near-surface wettable layer and the carbon cathode body (between Points 11 and 15 of the scanning line), there is a layer of electrolyte-filtrate enriched with NaF. This layer can be visually seen in the figure (composition contrast) of the area microstructure. It seems that it is difficult to explain the presence of this layer between the wettable near-surface layer and the carbon cathode body. An explanation can be given if we look at the whole field of the carbon phase. In this field, electrolyte is concentrated the same way – along the borders of carbon grains, i.e. along the paths of least resistance to impregnation

with electrolyte. The absence of electrolyte in the near-surface wettable layer is most probably explained by the capillary pressure force which makes aluminum go to the pores of the Ti-B-C layer and displace electrolyte. And this phenomenon can be seen as a demonstration of the power of adhesion interaction of the aluminum layer with the near-surface boride layer.

In order to identify observation zones along the whole area, we will examine the results of element mapping of this area. For convenience, the titanium distribution should be distinguished on the map. Red line is external front-faced to the layer of aluminum of the carbon surface. Blue line is the internal front of the titanium distribution.

Next, we will copy the titanium distribution area to other element maps.

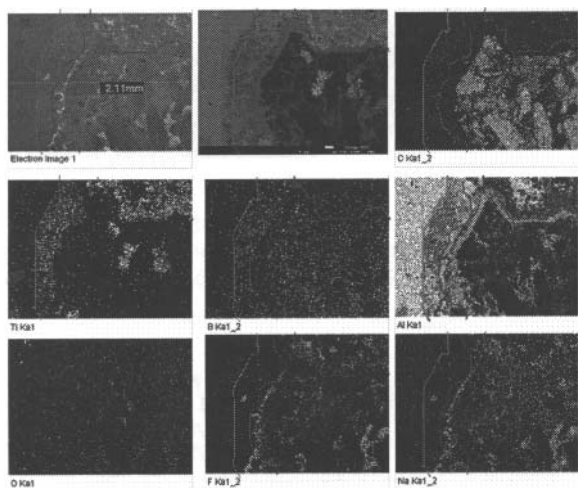


Figure 7. EDS-mapping of the area of the DT11-B.

First, note the clearly observed zone of the joint presence of titanium, boron and carbon residue (between the red and blue lines). The data in Figure 7 confirms that the internal zone behind the red line to the right is the initial borders of the carbon sample. And the area between the red and blue lines is a near-surface layer (100-500  $\mu\text{m}$ ) of wettable compounds with the composition of the triple Ti-B-C system. This area is between the main carbon body of the sample and aluminum. Between the aluminum layer and the Ti-B-C layer there are no other phases and inclusions; it proves that the cathode surface is fully wetted with aluminum.

Before making analyses, the carbon sample taken from the DT11-T cathode end was destroyed. Therefore, an SEM-EDS analysis was performed not on the border (line) of aluminum and carbon, but areas of the surface of this border which remained on the other side. Figure 8 shows the area and points in which the analysis was performed.

At Points 2 and 4, the joint presence of boron and titanium, with no significant presence of other elements, was discovered. The amount of boron exceeds a stoichiometric amount for  $\text{TiB}_2$  – the B:Ti ratio  $\sim 3$ . It fully corresponds to a supposed mechanism of

surface boronizing at which the concentration of an active component decreases from the side of its migration, i.e. from the surface layers to deep inside the cathode.

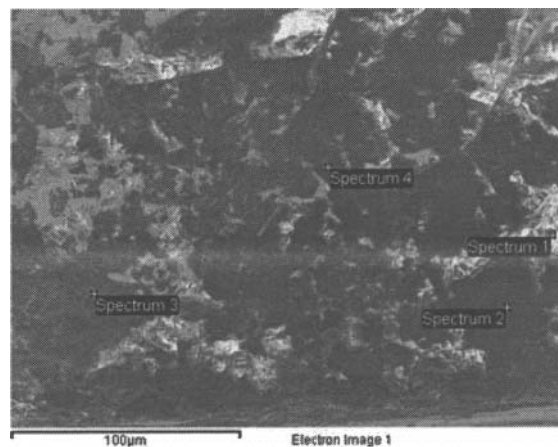


Figure 8. Structure of the wettable cover of the DT11-T sample in secondary electrons ( $\times 500$ ).

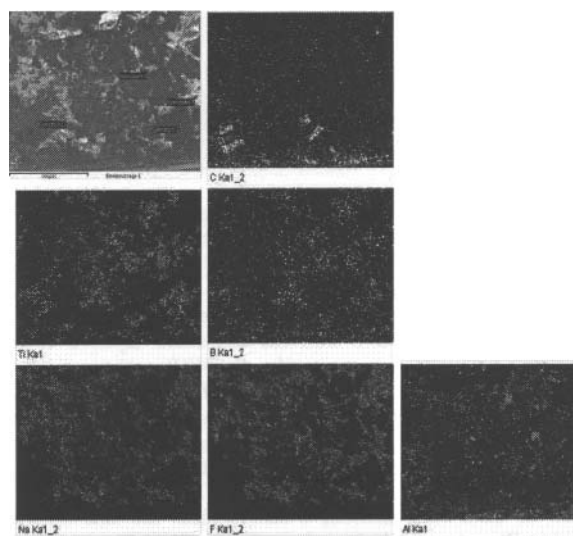


Figure 9. EDS-mapping of the area of the DT11-T sample.

It should be noted that Points 2 and 4 are in the dark field of the microstructure. This field prevails in the area. This field is fully occupied with continuous boron and titanium zones (Figure 9). Gaps of these zones are filled with elements comprising electrolyte (Point 1 in Table II).

Results of the analysis of the DT11 sample (side and end surfaces) discover the reason for the cathode wettability – the presence of boron and titanium in the near-surface layer. Along the thickness, titanium borides don't have a permanent composition which depends on deepness and boronizing time.

Table II. EDS analysis results

DT11-T- All results in atomic%, point spectrums					
Spectr	B	Ti	F	Na	Al
Spectr 1			38.95	36.58	18.17
Spectr 2	73.05	26.03	0.66		0.26
Spectr 3		6.40		0.46	11.66
Spectr 4	73.47	22.80	0.55		3.18

The DT14 carbon-titanium cathode sample (see Figure 10), after the experiment, showed wettability with good adhesion of aluminum to the surface. Therefore, taking samples from the surface (for an XRD analysis) was not possible.

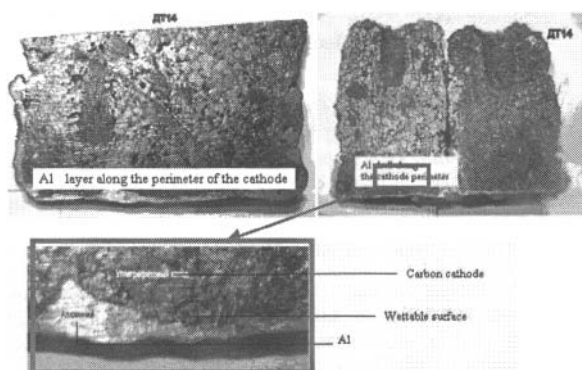


Figure 10. DT14 sample in cross section after the experiment.

Good adhesion of aluminum to the carbon surface can be proved by observation of sequential destruction of the sample cut from the central part of the cathode.

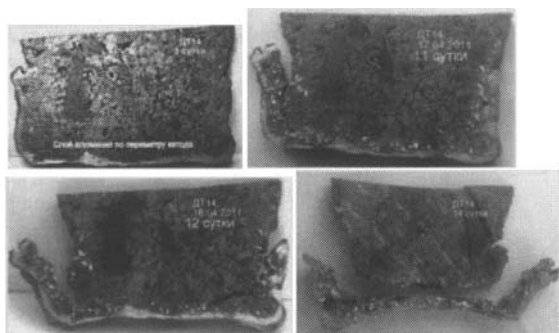


Figure 11. DT14 subsequent destruction (left to right: Day 1, Day 11, Day 12, Day 14).

Visual destruction under the influence of atmospheric moisture started on Day 10-11 (see Figure 11). The notable observation is the place and the path of the crack – along the front of the body of the sample impregnated with electrolyte. There was absolutely no separation of aluminum from the carbon surface. It can be explained by ideal adhesion of aluminum to carbon and no electrolyte layer between Al-C.

Before making analyses, the carbon sample was destroyed. Therefore, a SEM-EDS analysis was performed not on the border (line) of aluminum and carbon, but on areas of the surface of this border which fully remained on the opposite site.

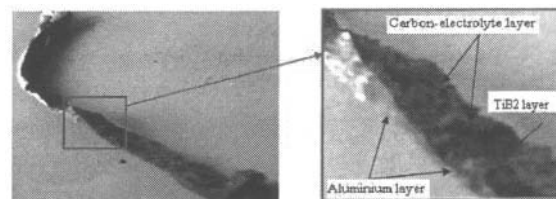
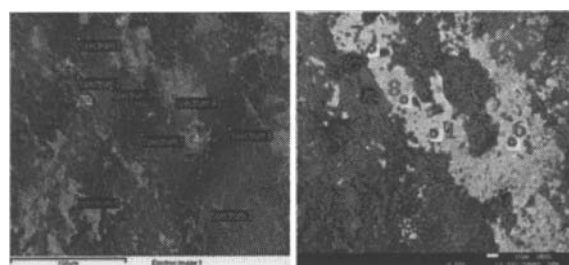


Figure 12. Aluminum shell of the DT14 sample. The area of the near-surface layer joining the aluminum layer from the cathode surface side was selected and zoomed.

On Figure 13 shows microstructure in secondary and back-scattered electrons.



a) b)  
Figure 13. Microstructure of the area of the DT14 sample (x500): a) in secondary electrons; b) in back-scattered electrons (composition contrast).

In this case, polishing of the area (see Figure. 12) was not performed. In the figure, in composition contrast, bright areas belong to the layer that joins aluminum; black areas belong to the next layer under the bright field (layers from bottom to top: Al – bright layer – dark layer).

Table III. EDS analysis results

DT14 Sample, x500, Atomic %, Point Spectrums					
Spectr	B	Ti	F	Na	Al
Spectr 1	62.28	32.09	4.21	0.39	1.03
Spectr 2	38.91		2.06	1.30	33.44
Spectr 3		0.54	50.11	23.86	15.99
Spectr 4			52.63	32.00	14.16
Spectr 5			48.78	37.22	13.01
Spectr 6	74.42	23.26	1.54	0.31	0.46
Spectr 7	59.87	31.44	4.48	0.89	1.92
Spectr 8	66.22	28.68	2.38	0.57	2.15

In Point 1 and Points 6 to 8 located in the bright field of the composition contrast, the joint presence of boron and titanium, without any significant presence of other elements, was discovered. The boron-titanium ratio = 2 to 3. In fact, the bright field of the microstructure belongs to the  $TiB_2$  layer joining aluminium. Above the diboride layer, according to Table III, there is electrolyte with the composition which corresponds to cryolite. This is proven by mapping of the area.

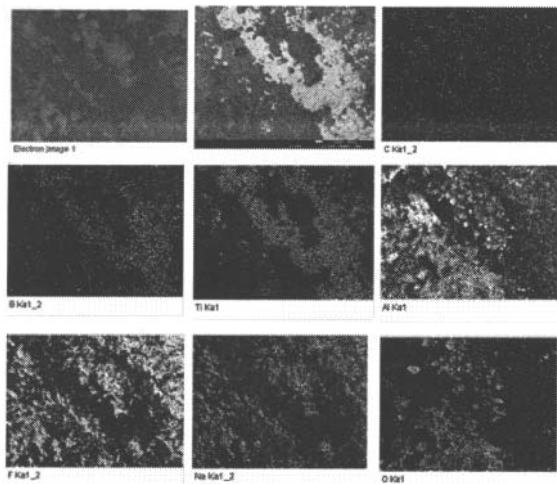


Figure 14. EDS-mapping of the area of the DT14 sample.

Visually, full and concentrated concurrence of the boron and titanium fields is noted. Therefore, we can state that good cathode (DT14) wettability is due to a formed wettable  $TiB_2$  coating.

### Conclusions

1. During visual observation of carbon-titanium samples after electrolysis experiments in the cryolite melt, wettability of the carbon surface with aluminum and good adhesion of aluminum to the carbon surface were observed.
2. The reason for wettability of the cathode with aluminum is confirmed – the presence of a near-surface layer of carbide-boride compounds, 100-500  $\mu m$  thick, synthesized during 20 to 24 hours of electrolysis.
3. By XRD and SEM-EDS analyses, the presence of compounds of the Ti-B-C system, including  $TiB_2$  and  $TiC$ , is discovered.

Thus, under laboratory conditions, a technology for producing an aluminum-wettable near-surface layer on a titanium-carbon cathode during electrolysis of cryolite-alumina melts by the method of boronizing has been developed and implemented.

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