

Application of Boron Oxide as Protective Surface Treatment to Decrease the Air Reactivity of Carbon Anodes

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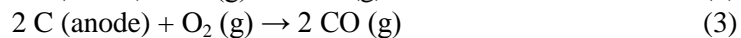
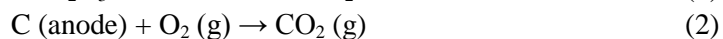
Abstract

Oxidation of carbon anode with air and CO₂ occurs during the electrolysis of alumina in Hall-Héroult cells, resulting in a significant overconsumption of carbon and dusting. Boron is well known to decrease the rate of this reaction for graphite. In this work, the application of boron oxide has been investigated to evaluate its inhibition effect on the air oxidation reaction and to provide an effective protection for anodes. Different ways of impregnation coating have been explored. Impregnated anode samples were gasified under air at 525 °C according to the standard measurement methods. X-ray tomography was used to obtain the microstructural information of the samples before and after air-burning tests. The impregnated samples showed a very low oxidation reaction rate and dust generation.

Keywords: Anode air reactivity; boron oxide anode coating; anode impregnation coating; anode sample gasification; X-ray tomography.

1. Introduction

Anode is consumed in the conventional process of Al production using Hall-Héroult cells in which the overall reaction may be written as equation 1. One of the main factors causing excess anode consumption is oxidation of the anode surface exposed to air during electrolysis. The temperature of the anode exposed to air is comprised between 400 and 600 °C [1]. There are two possible reactions of carbon with oxygen (equations 2 and 3), depending on the reaction temperature.



Air reactivity is one of the most important yet variable characteristics of carbon anodes and together with CO₂ reactivity counts as the highest contribution to carbon overconsumption. The

anode is composed of calcined petroleum coke, recycled anodes (butts) and coal tar pitch. The effects of raw materials, process parameters, and physical characteristics of baked anode on its resistance against air reactivity were widely discussed in the literature [1 - 6]. There is consensus that the burning rate of the binder matrix (pitch + fine) is higher than that of the large coke grains [6 - 7]. This may result in early removal of the binder matrix and detachment of the unburned coke grains from the anode surface, contributing in part to the dusting phenomenon [8 - 10]. Any protection strategy should therefore focus on providing an impermeable physical barrier on the anode external surface or decreasing the intrinsic reaction rate of carbon, especially that of the binder matrix.

Several attempts have been made to provide a physical barrier on anode. As an example, CSIRO claimed to provide a cost-effective coating on anodes, which maintains integrity throughout the life of the anode [11 - 12]. The coating seems to be alumina-based material, which is sprayed on baked anodes. Although this announcement has been made several years ago, the authors are not aware of any further development or industrial deployment of this coating. In the same context, covering the anode by alumina powder is practiced in almost all smelting plants. In addition, some plants practice a simple way to cover anodes by spreading liquid bath (cryolite) on fresh anode just after it is changed. The liquid bath solidifies immediately on the cold anode surface providing a coating, which seems to decrease its air-burning rate. Both alumina powder and solidified bath are porous media and cannot protect the anode efficiently. However, they may reduce air-burning rate by generating an oxygen diffusion barrier around the anode and protect it to some extent.

Another strategy to protect carbon is to decrease its intrinsic reactivity. The oxidation inhibition is achieved by doping carbon with phosphorus and boron [13 - 14]. However, phosphorus is prohibited in the electrolysis bath due to its negative effect on the current efficiency. Basically, three mechanisms are proposed to explain the effect of boron on carbon oxidation reaction:

- a) *Inhibition of reaction by re-distribution of electron densities on graphite, hence reducing its intrinsic reactivity* [15, 16, 18].
- b) *Effect of boron on enhancing graphitization process* [16, 18, 19].
- c) *Formation of boron oxide film and blockage of active sites* [15, 21 - 22].

It is hard to conceive that two first mechanisms (a and b) would be able to contribute to anode protection. The main reasons are:

1. In most experimental work conducted on composite fields, the boron addition level is too high (from 1000 ppm up to several at.%). This high level of boron addition is not allowed in anode, having in mind that all boron will most likely reduce in the bath and enter the aluminum.
2. The change in electron density is basically due to the fact that boron is substituted in the graphite structure. Since the anode baking temperature is much lower than the graphitization temperature, no significant graphitization occurs during baking. Thus, boron effect on carbon graphitization is not conceivable.
3. In boron-doped graphite, boron is always added in the form of *elemental boron* under inert atmosphere prior to graphitization. Considering the cost of elemental boron, such a high level of addition is justified only for very high-value products, which is not the case of carbon anodes.

The formation of boron oxide film and its effect on active site blockage is, however, worth investigation.

Boron oxide is soluble in water making it possible to be coated by impregnation via an aqueous solution. In this context, Moltech published four patents [24 - 27] claiming the impregnation coating of boron oxide to protect anode. In these patents, addition of other functional compounds into the impregnation solution has also been claimed. The experiments conducted by Moltech in laboratory seem to confirm the beneficial effect of this impregnation. Such a beneficial effect has also been confirmed by our own experiments as well as by other authors [29]. It is however strange that this technique has not been deployed in smelters despite the good laboratory results.

Alcan has also published a patent on protection of anode and cathode by boron-containing compounds with different additives such as AlF_3 and refractory compounds [28]. The coating comprises “*preparing a liquid suspension of a boron compound, aluminum fluoride and a lignosulfonate binder and applying the liquid suspension as a protective coating at least to the portion of the anode which is exposed to the atmosphere during cell operation, followed by drying the coating*”. They applied a thick coating layer using a spray gun followed by drying. They claimed a good protection of anode and cathode in laboratory scale.

Some of our own results and internal discussions with industrial partners lead us to believe that the laboratory-scale results do not reflect the real pot conditions. In fact, the laboratory tests are usually performed on small samples, typically 50 mm in diameter and 100 mm in length. The mass before and after reaction is measured and the mass loss is reported as the indication of reactivity. Therefore, no information is obtained regarding the reaction kinetics or the evolution of the reaction over time. In addition, if the impregnation efficiency depends on the sample size, its protection capability will be overestimated for the small samples. It is thus important to understand the mechanism of protection in order to adjust the process parameters for optimum performance.

This work aims at developing a protective coating to decrease the air reactivity of anodes. Focus is made on revealing the impregnation parameters on the efficiency of the process. During the reactivity tests, the mass loss is recorded continuously in order to follow the reaction rate at any time. The samples were also characterized using X-ray tomography in order to obtain the microstructural information before and after air-burning tests. This information helped understanding the carbon gasification mode inside the anode samples.

2. Materials and Methods

2.1 Materials

In this study, all samples were taken from an industrial baked anode. The anode consisted of 65 % calcined petroleum coke, 22 % recycled anode and 13 % pitch, and baked at 1200 °C. Eight samples were cored from different parts of the anode. Most of the samples were taken from the positions that are normally exposed to air attack in an industrial electrolysis cell.

2.2 Air reactivity test

The air reactivity measurements were conducted using a muffle furnace. In the first series of experiments, a small sample of approximately 6 - 7 g was tested, while in the second series a larger sample size (100 g) was used. The samples were impregnated with boron solution under different conditions. The reactivity experiments were performed under isothermal conditions in a flowing air of 4 - 5 L/min. The samples were protected from oxidation during the heating period

by high purity nitrogen. When the target temperature was reached, the sample was held at this temperature for 10 minutes. Then, air was introduced into the reaction chamber. The sample was maintained at the target temperature before being cooled. During the cooling period, the sample was also protected from oxidation using a nitrogen flow. The anode-air reaction was measured over a range of temperatures from 400 to 600 °C. This temperature range corresponds to the conditions in which the anode reacts with the air atmosphere during the aluminum smelting process.

2.3 X-ray computed tomography

Carbon anode images have been obtained by scanning anode cores before and after air reactivity tests using computed tomography (Siemens Somatom Sensation 64). This method is also capable of revealing spatial density distribution in the sample. Considering the anode core dimension (50 mm diameter) the voxel resolution obtained is 0.1 x 0.1 x 0.6 mm³.

3. Results and Discussion

3.1 Anode impregnation

A series of small samples (6 - 7 g) were cut from an industrial anode core and impregnated under different conditions. The dimension of these samples was 19 x 14 mm. Solution concentration and impregnation temperature were varied. The samples were dipped in the solution for 30 minutes, and then dried in air at 100 °C overnight. Samples (1, 2, 3, 4 and 6) were impregnated for a second time under the same condition. Tables 1 and 2 summarize the treatment conditions of 13 samples, including the references (untreated).

Table 1. Impregnation conditions of the samples.

Sample #	Solute Masse (g)	Solvent	Solvent volume (mL)	Concentration (g/mL)	solution temperature
A	Untreated	-	-	-	-
B	Untreated	-	-	-	-
C	Untreated	-	-	-	-
1	9	Water	50	0.180	Boiling
2	1	Water	50	0.020	R. Temp.
3	9.08	Water	50	0.182	Boiling
4	1	Water	50	0.020	R. Temp.
5	1	Water	50	0.020	R. Temp.
6	8.98	Water	50	0.180	Boiling
7	9.03	Water	50	0.181	Boiling
8	9.08	Water	50	0.182	Boiling
9	9.03	Water	50	0.181	Boiling
10	1.05	Water	50	0.021	R. Temp.

Table 2. Impregnation (2) conditions of the samples.

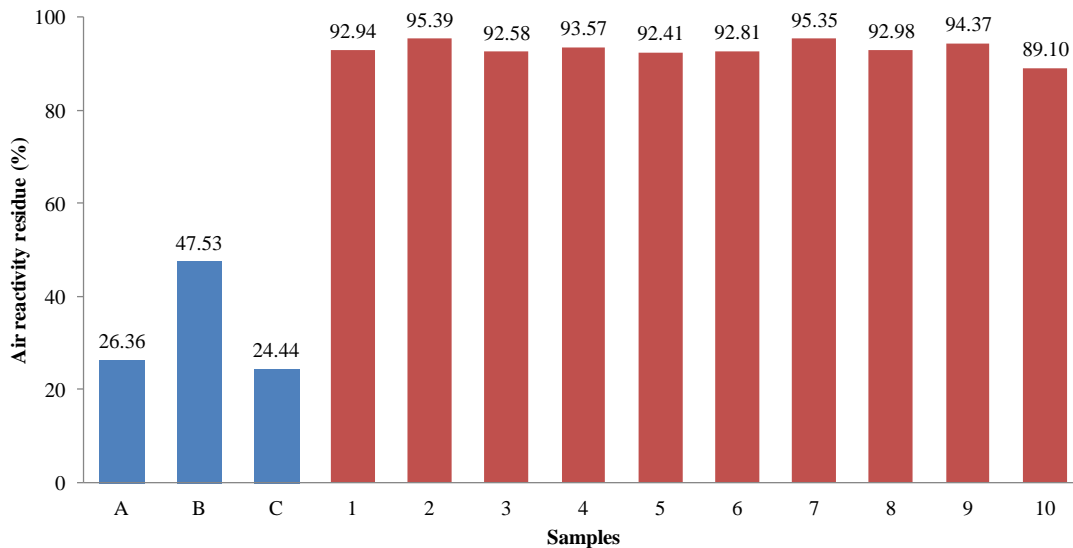
Double-Impregnation					
Sample #	Solute Masse (g)	Solvent	Solvent volume (ml)	Concentration (g/mL)	Solution temperature
1	9.06	Water	50	0.181	Boiling
2	1.02	Water	50	0.020	R. Temp.
3	9.06	Water	50	0.181	Boiling
4	1.03	Water	50	0.021	R. Temp.
6	8.94	Water	50	0.179	Boiling

The air reactivity tests were performed in a muffle furnace with airflow of about 5 L/min. The samples were put in the furnace, heated to 525 °C and maintained at this temperature for 2 hours. The temperature was then decreased to 500 °C over 1 hour and maintained at this temperature for 2 hours. Temperature was then decreased to 450 °C and maintained till the end of the test. Samples were then withdrawn from the furnace and weighed. The residue was calculated according to the following equation:

$$\text{Air reactivity residue} = \frac{100M_f}{M_i} \quad (4)$$

where M_f and M_i are the final and initial mass of the sample, respectively.

Figure 1 shows the air reactivity residue of the treated (1 to 10) and the untreated samples (A, B and C). The results confirmed that the boron treatment has a significant effect on air reactivity of anode samples. The untreated samples showed a high reactivity with a mass loss ranging between 52 and 75 %. The impregnated samples showed much smaller mass loss between 4.5 and 11 %. The best results were in general obtained for the samples impregnated in hot solution (7 and 9), although all the treated samples seem to be efficiently protected. Sample 1, 2, 3, 4 and 6 did not show any difference comparing to the other even with the double impregnation. Therefore, it seems that the anode surface was saturated of boron oxide during the first impregnation.

**Figure 1. Air reactivity of the samples coated by impregnation.**

3.2 Effect of impregnation time

In the second series of experiment, the effect of impregnation time was evaluated. Eight samples were cored from the same anode, the dimension of these samples was (50 x 30 mm). The average mass of the samples was around 100 g. Samples were soaked in a boiling solution with a concentration of 0.17 g/ml using impregnation times varying between 1 and 20 minutes. The coating conditions of samples are summarized in Table 3.

Table 3. Impregnation conditions of the samples.

Sample #	Solute mass (g)	Solvent	Solvent volume (ml)	Concentration (g/ml)	Condition	Dipping Time (min)
1	Untreated	-	-	-	-	-
2	Untreated	-	-	-	-	-
3	53.49	Water	300	0.1783	Boiling	1
4	53.49	Water	300	0.178	Boiling	10
5	48.08	Water	265	0.181	Boiling	1
6	48.08	Water	265	0.181	Boiling	10
7	35.87	Water	200	0.179	Boiling	20
8	36.19	Water	200	0.181	Boiling	20

The air reactivity tests were performed in a muffle furnace with an airflow rate of 4 L/min. The samples were put on an alumina wool, placed on a stainless steel plate, and introduced in the furnace at 500 °C. The temperature was maintained at 500 °C during the entire air reactivity test. In order to follow the reaction rate over the entire reaction time, the samples were weighed every 2 h for the first 24 hours and every 12 h for the remaining time. The gasification was calculated according to the following equation:

$$Gasification = \frac{M_0 - M_t}{M_0} \times 100 \quad (5)$$

where M_0 represents the initial weight of the sample and M_t is the instantaneous weight of the sample at time t.

Gasification percentage as a function of reaction time is shown in Figure 2. Results revealed a remarkable effect of the impregnation time on the air reactivity of the anode. The untreated anode shows high reactivity with a burning rate of about 4 %/h. The anode was totally consummated after 40 hours of reaction. The curves show that the reaction rate decreases by increasing the impregnation time. The resistance of the 1 min impregnated sample was almost doubled compared to that of the uncoated samples. The samples impregnated for 10 and 20 minutes showed lower reactivity with the same reaction rate (about 0.2 %/h) and after 160 h they were consumed only by 70 % and 60 %, respectively. The reaction slightly accelerated for these samples after 20 % gasification. As it can be seen, the sample impregnated for 20 minutes exhibited a remarkable resistance to burning with only 30 % mass loss after 100 h of reaction. Its reaction rate was 20 times lower than that of the untreated sample. A large standard deviation observed in this experiment could be attributed to the inhomogeneity of anode and the small size of the samples.

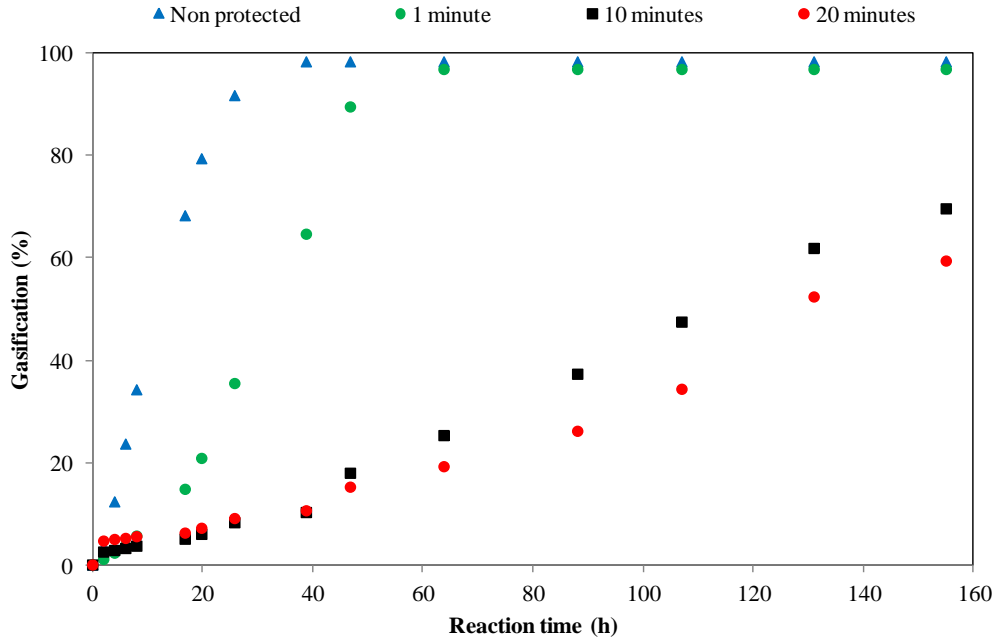


Figure 2. Gasification vs exposure time for samples with different impregnation times.

Figure 3 shows a SEM image of the cross section of an impregnated sample. One can observe crystallized boron oxide slices inside the pores. The protection effect can be explained by this observation, since boron blocks pore surface and limit the access of oxygen. However, the relatively small areas covered by boron oxide cannot explain the significant decrease of reaction rate. Boron oxide is likely also present on the other areas but, due to the limited resolution of SEM, it is not observed.

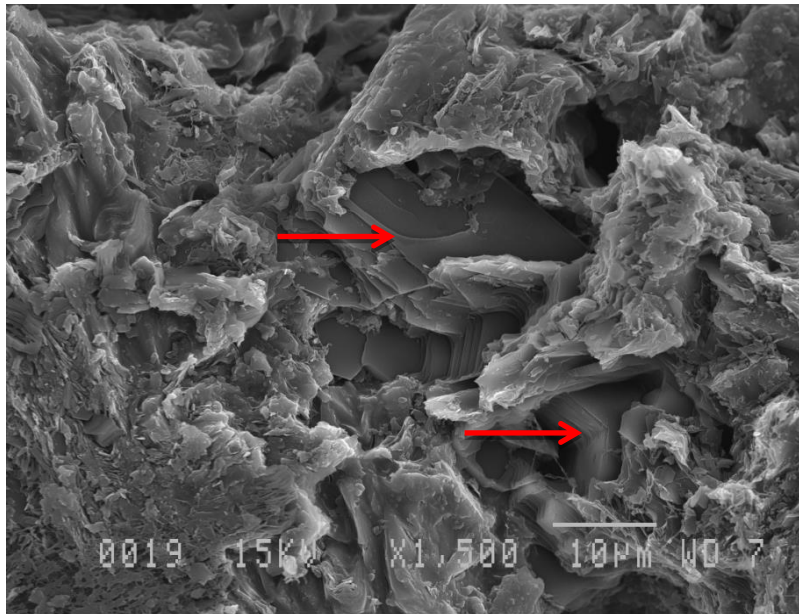


Figure 3. SEM micrograph of a sample cross-section showing the crystallization of boron oxide inside the pores (indicated by arrows).

Figure 4 shows visual aspects of the samples at different reaction times. Figure 4 (a), (b) and (c) show the fresh samples, after 24 h and after 6 days of reaction, respectively. It can be clearly seen that the two reference samples (untreated) are severely reacted after 24 hours of exposure, exhibiting a mass loss of more than 86 %. The entire samples are disintegrated in powder form, which would be considered as dust in a real smelting pot. The mass loss measurements were stopped when the samples were disintegrated. For this reason, the gasification never reached 100 % (Figure 2).

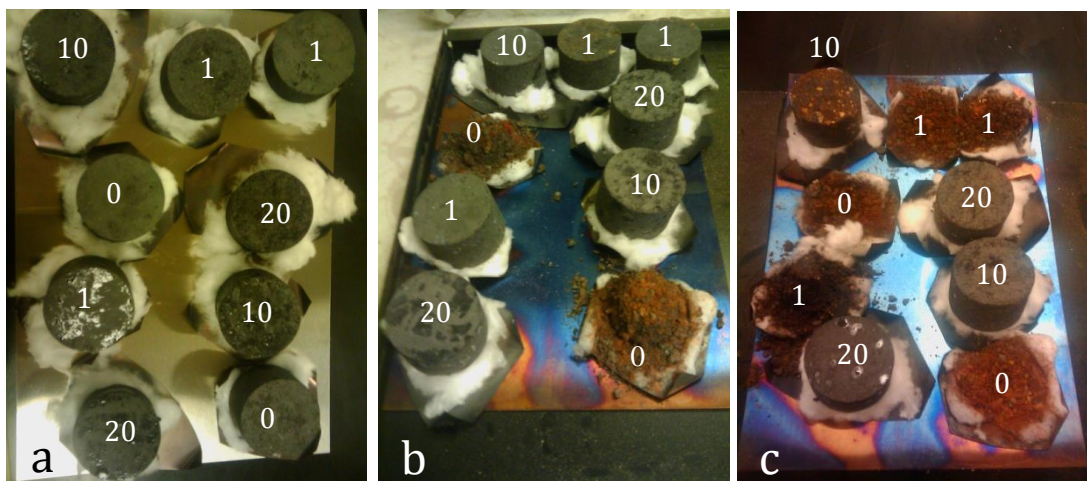


Figure 4. Visual observation of the samples; a) before air reactivity test, b) after 24 h of exposure, c) after 6 days of exposure. The numbers on the samples indicate the impregnation time.

The visual inspection of the samples indicates that after only 24 h of exposure, the untreated samples are disintegrated while the sample impregnated for one minute still seems to be intact, although it exhibited 20 % of mass loss. This sample was disintegrated after 40 h of exposure, generating a large quantity of dust. After 6 days of exposure, however, the samples impregnated for 10 and 20 minutes kept their initial form without any apparent dusting, in spite of more than 50 % of mass loss. This observation suggests that these samples are essentially reacted from the inside while the outer surface is still resisting. This could mean that longer impregnation times not only decrease the overall reaction rate, but also decrease dust emission.

3.3. Boron loading during impregnation

Another series of large-size samples (50 mm in diameter) was prepared in order to get additional information about boron loading and its effect on air reactivity of anode. The standard core samples of 50 mm in diameter were cut into pieces of about 30 mm in height. The same protocol of impregnation, as described previously, was used to impregnate the samples with two different impregnation times of 1 and 15 minutes. A boron solution at 2 % and 50 °C was used for impregnation.

During the drying step of the impregnated sample, boron oxide is precipitated in the form of boron hydroxide. Depending on the drying temperature, boron hydroxide could be partially dehydrated to boron oxide. Thus, the evaluation of the exact boron quantity loaded on the sample becomes difficult. In order to overcome this difficulty, boron loading was calculated based on the weight of the impregnated solution. Knowing the concentration of the solution, it was possible to evaluate the exact boron quantity loaded on the sample during impregnation. To do so, the

samples were first dried in an oven at 140 °C for 4 hours in order to record their initial dry weight. Then, a solution of a known boron concentration was prepared for impregnation. A sample was dipped into the solution and the difference between the weight of the solution before and after dipping was recorded. Table 4 summarizes the experimental conditions of the impregnation process as well as the quantity of boron oxide loaded on each sample.

Two important observations were made at this step.

- a) The boron loading for a given impregnation time is different from one sample to another, ranging from 0.072 - 0.144 g for 10-min of impregnation and 0.074 - 0.157 g for 15 minutes of impregnation. The variation could be attributed to the different levels of porosity in the samples. This observation may explain the large variation in reactivity of the samples, as observed for samples 4 and 7 in figure 5, exhibiting different reactivity, in spite of the same impregnation time. Strictly speaking, this observation confirms that the boron loading could be different even if the impregnation conditions are the same.
- b) The average value of boron loading on two sets of samples (9 - 16 and 17 - 27) increased from 0.09 g to 0.13 g, respectively. This suggests that the average boron loading increases significantly by increasing the impregnation time.

Table 4. Boron loading on impregnated samples.

# Sample	Dry sample (g)	Beaker + solution (g)	Solution in sample (g)	B ₂ O ₃ loading (g)	Dipping Time (min)
-	-	701	-	-	-
9	74.2537	693.8	7.2	0.144	1
10	79.8949	689.4	4.4	0.088	1
11	76.9634	685	4.4	0.088	1
12	75.5964	679.9	5.1	0.102	1
13	75.3947	675.6	4.3	0.086	1
14	71.5214	671.2	4.4	0.088	1
15	74.0581	666.6	4.6	0.092	1
16	78.2129	663	3.6	0.072	1
-	-	682	-	-	-
17	78.3638	678.3	3.7	0.074	15
18	79.0604	670.5	7.8	0.156	15
19	62.7609	664	6.5	0.13	15
20	64.5848	657.4	6.6	0.132	15
21	59.4021	651.4	6	0.12	15
22	61.6083	643.8	7.6	0.152	15
23	61.829	637.8	6	0.12	15
24	61.5569	630.3	7.5	0.15	15
25	68.1607	623.3	7	0.14	15
26	75.3353	615.4	7.9	0.158	15
27	74.0279	609	6.4	0.128	15

Figure 5 shows the mass loss of the samples as a function of reaction time. The air reactivity tests were conducted in a muffle furnace with airflow of 3 L/min at a constant temperature of 500 °C. To generate each the point presented in this figure, several samples were placed in the furnace

and, at each target exposure time one sample was withdrawn from the furnace. Boron loading is indicated for each data point on the graph. The untreated samples showed the same reaction rate as observed previously in Figure 2. Once again, this series of experiment confirmed the positive effect of long impregnation time on air reactivity of anode samples.

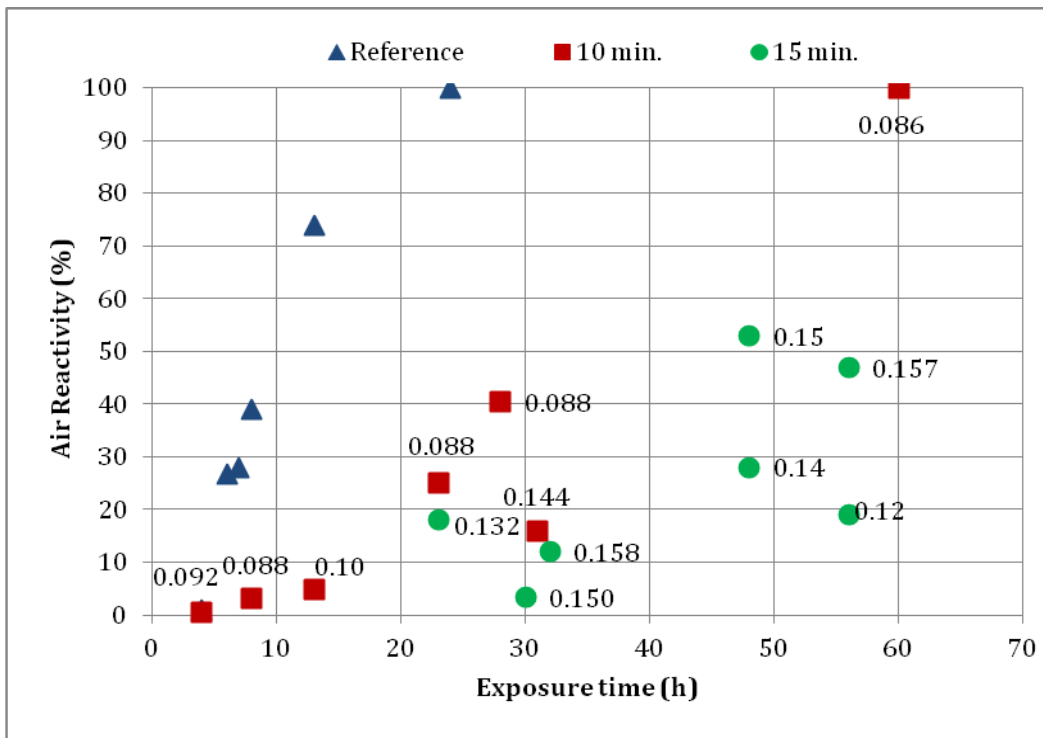


Figure 5. Air reactivity vs exposure time for a series of samples with different boron loading.

3.4. Effect of Boron-coating on anode reaction mode

X-ray tomography was used in this study to obtain the microstructural information of the samples before and after air reactivity tests. Two samples, impregnated and un-impregnated, were selected from those of the previous section (50 x 30 mm) and scanned before and after the air burning tests. This technique could show the evolution of the density by referring to the initial shape of the sample before and after air burning.

Figure 6a shows 16 images representing 16 equidistant scanned slices of an un-impregnated sample before the air reaction test, where the dark areas represent the pores. Scanning starts from the top of the sample (first image on the up-left), the bottom-right slice representing the bottom of the sample. Figure 6b shows the same sample after 6 h of exposure, representing 27 % of mass loss. The top of the sample burns faster than the middle because the fresh air was injected from the top of the furnace. The bottom of the sample did not react at the same rate as the top because the sample was placed on alumina wool in which the air was not freely circulated.

Comparing the images before and after air-burning test, it can be seen that the top surface of the sample (Figure 6b) was heavily attacked. Furthermore, the sample was shrunken, indicating that it was basically attacked from its external surface. In order to better visualize the surface attack of the sample, the patterns of the burnt slices are superimposed on that of the fresh sample in Figure

7, where the shrinkage of the sample is clearly revealed. The level of porosity inside the sample remained roughly the same, which could reveal important information regarding the gas concentration through the pores. These results suggest that oxygen reacts quickly with carbon and the CO_2/CO ratio falls rapidly inside the pores preventing further reaction of the sample core. Such data indicate the importance of diffusion inside the pores in anode reaction.

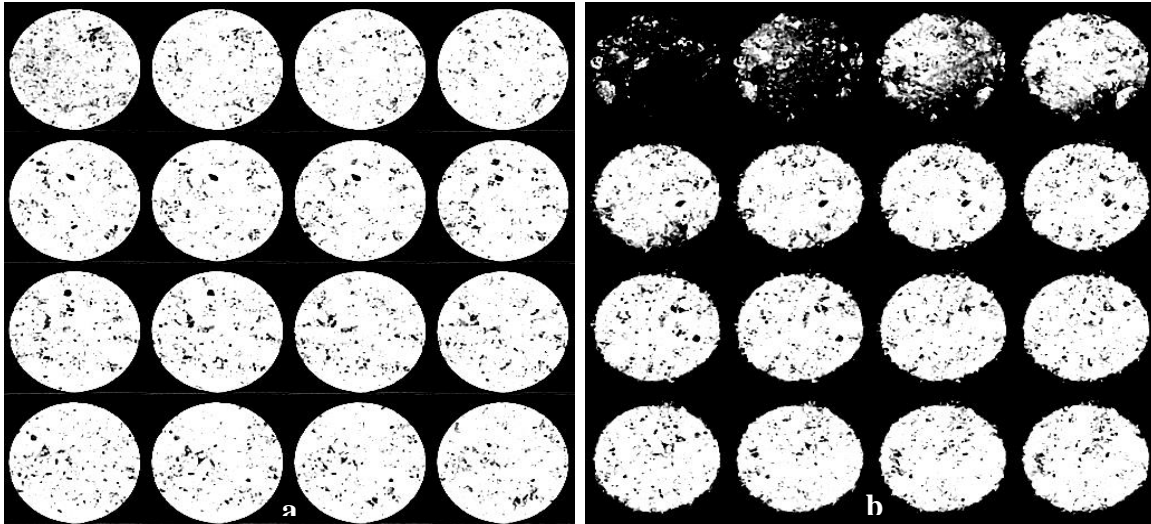


Figure 6. X-ray tomography images of uncoated samples; a) before air burning, b) after 6 h of exposure at 500 °C.

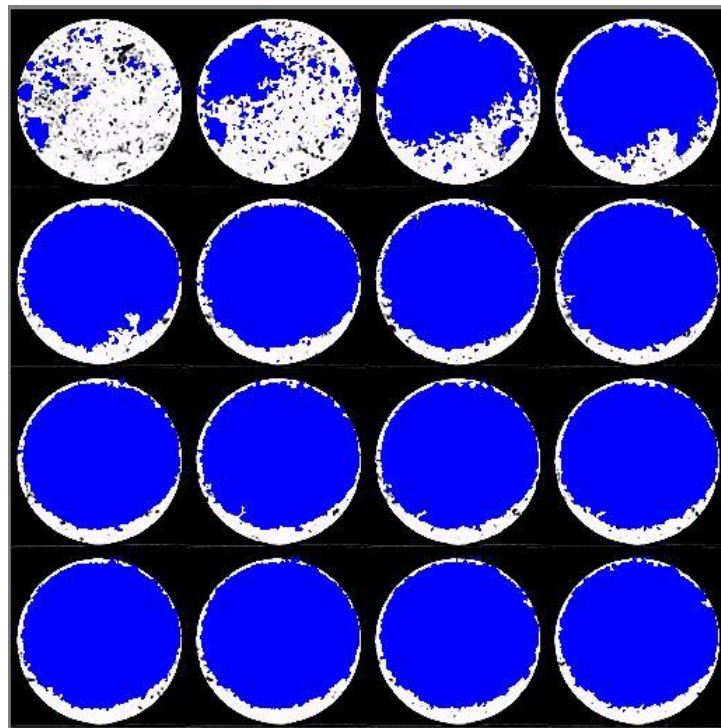


Figure 7. Superimposed patterns of fresh (white) and burnt (blue) sample reveal the shrinkage of the sample after 6 h exposure.

The impregnated sample was also scanned using X-ray tomography with the same parameters. Figure 8a shows the CT images taken from the sample before the air reactivity test. This sample was later impregnated for 15 minutes and exposed to air for 56 h in the furnace at 500 °C. A mass loss of 19.3 % was recorded after 56 h of exposure. The sample was again CT-scanned after air-burning test and the images are shown in Figure 8b. Comparing with the uncoated sample, the impregnated one did not shrink during the burning test and its diameter after burning remained the same as the fresh one. Another interesting observation in Figure 8b is that the reaction took place inside the sample and only the porosity increased during air-burning test.

It can be concluded from the reactivity tests and the CT scan results that the general oxidation resistance of anode increases by boron impregnation and its surface is well protected. The fact that air reaction takes place inside the sample leads us to believe that the diffusion of oxygen through the pores provides the reactant for oxidation of the sample core. In other words, due to the low intrinsic reactivity of the treated carbon, the CO_2/CO ratio does not decrease rapidly inside the sample and CO_2 (or oxygen) can reach the core of the sample. The low reaction rate of an impregnated sample could therefore be attributed to two facts;

- a) The impregnation solution reaches the entire pore network and provides a good protection even inside the sample.
- b) Oxygen diffusion through the pore network provides a kinetic barrier and reduces the reaction rate of the unprotected parts of the sample.

In addition, the fact that the reacted samples preserve their integrity suggests that an impregnated anode will generate far less dust during the oxidation reaction.

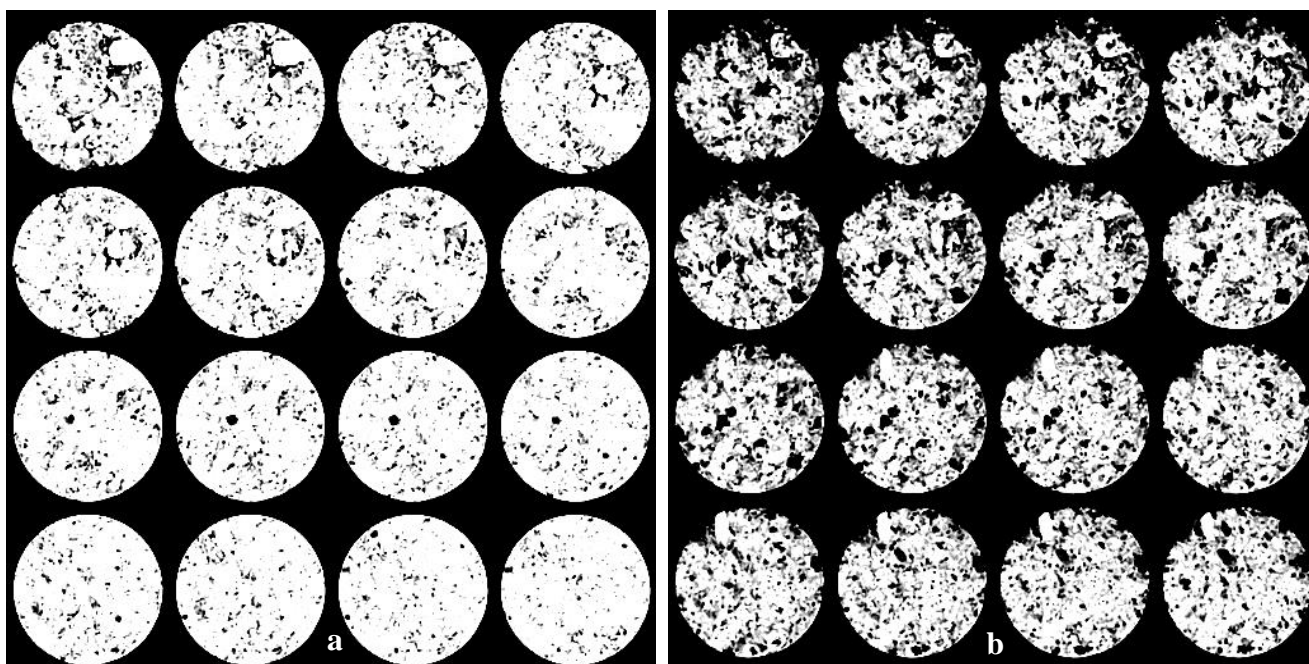


Figure 8. CT-scan images of a sample, a) fresh and b) impregnation for 15 min and exposure for 56 h at 500 °C.

4. Conclusions

In the present study, it was shown that a number of parameters affect the efficiency of the anode protection by boron impregnation. For instance, the level of the protection depends on the impregnation duration. Fifteen minutes of impregnation in warm solution (2 wt.% concentration) provides a significant protection level in small samples. Air reactivity results confirm that the protection of the anode surface using the impregnation method can decrease the oxidation reaction rate from 4 %/h to 0.2 %/h. CT-Scan results revealed that the inside of the impregnated samples seem to react with air, with much slower rate, and that the surface preserves its initial shape. The protected samples generate much less dust as compared to the unprotected ones.

Although this technique allows obtaining a very good anode protection and dust reduction, its implementation in industrial scale may be challenging. Indeed, a full impregnation can be obtained within a reasonable time for small samples. In an industrial context, a full impregnation of an anode with very large size would be practically impossible within a reasonable time. Accordingly, researchers and engineers will have to continue working in this avenue in order to find a practical way for in-depth impregnation of the large anode blocks.

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6. References

1. Fischer, W.K. and R.C. Perruchoud, Factors Influencing the Carboxy- and Air-Reactivity Behavior of Prebaked Anodes in Hall-Heroult Cells, *Light Metals 1986*, 575-580.
2. L.E. Jones, P.A. Thrower, P.L. Walker, Reactivity and related microstructure of 3d carbon/carbon composites. *Carbon*. Vol. 24, No. 1, (1986), 51-59.
3. G. J. Houston and H. A. Øye, Consumption of Anode Carbon During Aluminium Electrolysis, I-III, *Aluminium*, Vol. 61, (1985), 251-254.
4. Tordai, T., Anode dusting during the electrolytic production of aluminium. 2007, *École Polytechnique Fédérale de Lausanne*, p. 351.
5. F. Chevarin, F et al., Effects of Microstructural Characteristics on Anode Reactivity, *COM 2011, 40th Annual Conference of Metallurgists of CIM*, October 2–5, 2011, Montreal, Canada.
6. DW. McKee, CL. Spiro, EJ. Lamby, The inhibition of graphite oxidation by phosphorus additives, *Carbon*, Vol. 22, (1984), 285–90.
7. X. Wu, LR. Radovic, Inhibition of catalytic oxidation of carbon/carbon composites by phosphorus, *Carbon*, Vol. 44, (2006), 141–51.
8. X. Wu, LR. Radovic, Inhibition of catalytic oxidation of carbon/carbon composites by boron-doping. *Carbon*, Vol. 43, (2005), 1768–77.
9. DW. McKee, CL. Spiro, EJ. Lamby, The effects of boron additives on the oxidation behavior of carbons, *Carbon*, Vol. 22, (1984), 507–11.
10. D. Zhong, H. Sano, Y. Uchiyama, K. Kobayashi, Effect of low-level boron doping on oxidation behavior of polyimide-derived carbon films, *Carbon*, Vol. 38, (2000), 1199–206.

11. <http://www.csiro.au/en/Outcomes/Mineral-Resources/Minerals-Processing/Anode-coating-reduces-air-burn.aspx> (February 2009).
12. M. Jahedi et al., Anode coating to prevent airburn in aluminium smelters, *Light Metals 2009*, 951-955.
13. Y-J. Lee and L. R. Radovic, Oxidation inhibition effects of phosphorus and boron in different carbon fibrics, *Carbon*, Vol. 41, (2003), 1987-1997.
14. T. Durkic, A. Peric, M. Lausevic, A. Dekanski, O. Neskovic, M. Veljkovic, and Z. Lausevic, Boron and phosphorus doped glassy carbon: I. Surface properties, *Carbon*, Vol. 35, No. 10-11, (1997), 1567-1572.
15. W. Kowbel, Y. Huang, and H. Tsou, Effect of boron ion implantation on the oxidation behaviour of three-dimensional carbon-carbon composite, *Carbon*, Vol. 31, No. 2, (1993), 355-363.
16. L. R. Radovic, Murthy Karra, Kristina Skokova, and Peter A. Thrower, The role of substitutional boron in carbon oxidation, *Carbon*, Vol. 36, No. 12, (1998), 1841-1854.
17. J. Y. Howe and L. E. Jones, Influence of boron on structure and oxidation behaviour of graphite fiber, P120, *Carbon*, Vol. 42, (2004), 461-467.
18. D. H. Zhong, H. Sano, Y. Uchiyama, and K. Kobayashi, Effect of low-level boron doping on oxidation behaviour of polyimide-derived carbon films, *Carbon*, Vol. 38, (2000), 1199-1206.
19. T. Hagio, M. Nakamizo, K. Kobayashi, Studies on X-ray diffracton and Raman sectra of B-doped natural graphite, *Carbon*, Vol. 27, (1989), 259-263.
20. W. Xianxian, L. R. Radovic, Inhibition of catalytic oxidation of carbon/carbon composites by boron-doping, *Carbon*, Vol. 43, (2005), 1768-1777.
21. L. E. Jonse and P.A. Thrower, Influence of boron on carbon fiber microstructure, physical properties and oxidation behaviour, *Carbon*, Vol. 29, No. 2, (1991), 251-269.
22. L. E. Jonse and P.A. Thrower, The effect of boron on carbon-fiber microstructure and reactivity, *Journal de chimie physique et de physico-chimie biologique*, Vol. 84 No. 11-12, (1987), 1431-1438.
23. C. Courtois, J. Desmaison, and H. Tawil; Protection against oxidation of C/SiC composites: Oxidation behaviour of CVD TiB₂ coated substrates, *Journal de Physique IV, Colloque C9, supplement au Journal de Physique III*, Vol. 3, (1993), 843-853.
24. US, patent 5 486 278, Moltech (filing date 1994).
25. US, patent 5 753 382, Moltech (filing date 1996).
26. US patent 5 985 114, Moltech (filing date 1997).
27. Europeen patent, EP 0701635 B1, Moltech (filing date 1993).
28. US patent 6 475 358, Alcan (filing date 2001).
29. R. J. Tosta et al., Boron salt inhibitors of air reactivity of prebaked carbon anodes – Literature review and laboratory study, *Light Metals 2009*, 1173-1176.