

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

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## Abstract

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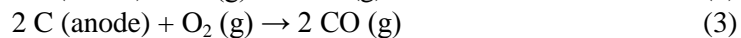
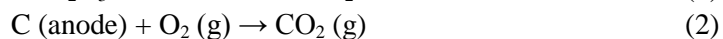
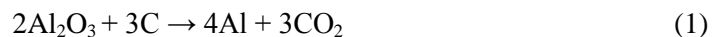


Oxidation of carbon anode with air and CO<sub>2</sub> occurs during the electrolysis of alumina in Hall-Héroult cells, resulting in a significant overconsumption of carbon and dusting. Boron is well known to decrease the rate of this reaction for graphite. In this work, the application of boron oxide 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 CO<sub>2</sub> 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.

#### 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 TiB<sub>2</sub> 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.