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WETTABLE CATHODES: AN UPDATE

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Abstract

This overview covers the development of aluminium-wettable cathodes for the primary aluminium industry in the period 2000 to 2009. It continues a review of TiB_2/C composites, including their physical and mechanical properties. This overview also includes the development of binders, the manufacture of the composites, their application on the cathode surface, and their resistance to sodium penetration into the cathode lining. Mathematical modelling has been introduced for the drained slope, the cathode current distribution, the flow of anode gas bubbles, and the heat balance. Practical tests involved not only laboratory and bench scales but also use in big electrolysis cells operated at more than 160 kA. Although they can prolong cell life, the main advantage of aluminium-wettable cathode coatings appears to be for future multi-cell designs and for new electrolysis pot designs rather than for revamping existing Hall-Héroult aluminium electrolysis cells.

Introduction

The development of titanium diboride (TiB_2) coated cathodes has been reviewed in several earlier publications [1-14]. Therefore this overview considers only literature which has not been mentioned already in previous updates and it forms a continuation of [7]. The most promising candidate as aluminium wettable cathode has proved to be titanium diboride. This material has attractive features, which include:

- very low solubility in aluminium
- resistance to corrosion by molten electrolyte
- good electrical conductivity

As it is difficult to make a cathode from TiB_2 tiles alone, attention has focussed on using TiB_2 as a composite or coating material on a carbon base.

Manufacture of TiB_2 cathodes and coatings

According to de Nora [15], the material to be used as an aluminium-wettable electrode in aluminium reduction cells comprises an openly porous ceramic structure whose surface during operation is exposed to and wetted by molten aluminium. TiB_2 is a promising electrode material for electrolysis of high temperature molten salt, but it is difficult to make TiB_2 with a high density structure. The preparation routes were reviewed by [16]. Rapp [17] proposes to manufacture TiB_2 by compaction and at least partial sintering of titanium powder and/or titanium hydride powder into the desired shape, followed by boriding the porous powder at about 1100 – 1200°C .Then, Luo et al.[18] tried to improve the densification of hot-pressed TiB_2 powder by adding metals such as Ni, Co, Mo and Ti. Adding liquid titanium can produce high compact samples and it avoids the growth of abnormal grains. Tungsten silicide was also used [19] to help compact TiB_2 powder and to improve corrosion resistance against aluminium. Unfortunately corrosion resistance of such composites suffers in other ways: TiB_2 reacts with aluminium to form TiAl, and WSi_2 dissolves in the cryolite electrolyte.
A limiting factor in the industrial use of conventional titanium diboride was found to be its low resistance to cryolite bath, which attacks the grain boundary layer phase. In order to avoid grain boundary attack Elektro Schmelzwerke Kempten (ESK) [20] developed a special sintering technique eliminating the grain boundary.

TiB_2-coating by electrodeposition

Simakov et al.[21] proposed the deposition of wettable titanium diboride containing coatings in situ from temporary, Al_2O_3-free industrial baths. Diboride coatings can be electrodeposited in a wide cryolite ratio range (2.3-3.0). The total concentration of boron and titanium oxide should not exceed 1.2 wt.%, and the proposed current density should be in the 0.35-0.55 A/cm^2 range.
Generally the electrolyte to deposit a TiB_2-layer in situ had the following composition [22-24]: KCl-KF-K_2TiF_6-KBF_4, with varying amounts of the constituents. Molten salt electrolysis is carried out at 820°C for about 4 hours with a current density of 0.3-0.8 A/cm^2. The 0.2 mm - thick coating bonds very firmly to the cathode substrate. Ban [25] improved the electrical conductivity of the bath by adding LiF.
In laboratory tests Devyatkin [26] deposited zirconium diboride, another aluminium wettable diboride, from cryolite alumina melts containing zirconium and boron oxides.

Plasma spraying and micropyretic reaction

Lu et al.[27] used self-propagating high temperature synthesis with reduction process to prepare TiB_2 powder from the TiO_2-B_2O_3-Mg system, and then added $MoSi_2$ to

the TiB_2 powder. The mixture was then applied to the carbon cathode surface by atmospheric plasma spraying. They observed that the porosity of TiB_2-$MoSi_2$ composite coating decreases with increasing $MoSi_2$ content, and the microstructure showed a crack-free interface between the coating and the substrate. Using such a coating in industrial cells should achieve estimated life spans of up to 8 years.
Another method was proposed by Sekhar and de Nora [28]: an adherent TiB_2 coating on the surface of a cathode carbon is produced by applying a well-chosen micropyretic reaction layer from a slurry. When dried and ignited, this layer propagates a self-sustaining micropyretic reaction across the combustion front, to produce a protective, crack free, adherent coating. Normally, the TiB_2 containing slurry is applied in several layers before ignition.

TiB_2 suspension in liquids

A method for providing a protective coating against cathode deterioration during operation was proposed by Mirchi and Bergeron [29]. A liquid suspension is prepared containing TiB_2 powder, lignosulfate binder and a phenolic resin binder. This coating is preferably applied up to a thickness of about 1-3 mm and the coated cathode is air dried at room temperature. The coating thickness can be increased by applying and drying many layers of the suspension. Huni et al. [30] proposed to use aluminium oxalate as binder instead of the phenolic resin.
A colloidal alumina-based TiB_2 slurry was used by Sekhar et al.[31], de Nora and Duruz [32] and Wang [33] with an organic additive selected from polyvinyl alcohol, polyacryl acid methyl cellulose, glycol, benzyl phthalate, and combinations thereof.

TiB_2/C composite manufacture and application as slurry

Literature [34 -51] shows that TiB_2/C composites were often used in laboratory and industrial tests. The manufacture of TiB_2/C composites was especially investigated in the laboratory scale. Li [37] manufactured TiB_2/C composites with a mass fraction of less than 70% TiB_2, because the resistance to sodium and bath penetration has a maximum at 70% TiB_2 content.
The effects of modified pitch used as binder on properties of TiB_2/C composite cathodes were investigated by Lü et al. [50]. When the treatment temperature increased from 220°C to 420°C the viscosity increased and the coke yield increased from 47% to 70%.
Ibrahiem et al. [40] examined several recipes of pitch-bonded TiB_2 with respect to adherence, cracking and stability during electrolysis. They found a successful recipe for crack-free coating: 70% TiB_2 + 20% pitch + 7.5% ECA + 2.5% carbon fiber (ECA = electrical calcined anthracite). The authors [47] found that the open porosity of pitch and furan-based TiB_2/C bulk materials was 13.3% and 34.6% respectively. They also found [40] that aluminium did not wet furan resin-based TiB_2 coatings during electrolysis because a carbon layer covers the coating surface.
Ren and coworkers [43] coated some carbon cathode block surfaces with TiB_2/C compound layer by vibration moulding. This method was also used by Wang et al. [62].

Sodium penetration barrier

A primary interest for many scientists was to investigate the resistance of TiB_2/C composites against sodium and bath penetration. Xue et al. [45, 51] found that the sodium expansion increased with increasing current density and cryolite ratio, but decreased with increased TiB_2 content. Decreasing sodium expansion with increasing TiB_2-content was confirmed by Li [37] and Li [52]. Xue [51 reports that the rate of sodium penetration into carbon-based cathodes follows Fick's second law when the sodium concentration is about or below 0.34%. Then a sodium profile develops in the cathode along the penetration direction and it peaks at 3.5%. But the peak concentrations of NaF and Na_3AlF_6 are much higher in carbon than in TiB_2/C materials. According to Wang et al. [46], sodium penetrated TiB_2/C composites by the same mechanism as in a normal carbon cathode. Sodium not only penetrated into TiB_2/C through pores but also through carbon grains inside the TiB_2/C cathode. Sodium penetrates by vapour diffusion through cathode pores and cracks as well as by solid phase diffusion in the crystal lattice of cathode. New reaction products with sodium expand and weaken the carbon lattice in TiB_2/C.
Experimental investigations of sodium penetration and expansion of carbon cathodes during aluminium electrolysis were carried out by Liu [53] and Xue et al. [54]. They observed that adding B_2O_3 to the binder phase slows sodium penetration but speeds up sodium expansion, while adding of TiB_2 slows both sodium penetration and sodium expansion.
The unpolarised exposure of TiB_2/C to liquid aluminium caused aluminium to penetrate the TiB_2/C samples through open pores, forming a coating of Al_4C_3 and Al_2O_3 at the interface with the aluminium pool. Ibrahiem et al. [42] believe that this is due to the direct reaction between aluminium and carbon, or possibly between aluminium and other phases formed during cathode baking. Furthermore, TiB_2 is known to be very sensitive to oxidation in the presence of oxygen.

Modelling drained cell

In order to take advantage of aluminium wettable cathodes to improve the energy balance in conventional Hall-Héroult cells, we need to reduce the interpolar distance significantly, so as to reduce the cell voltage and the heat produced. This requires major re-design for the magnetic effects and heat balance, which is only possible via computer modelling. The collector bar installation on the current distribution of drained electrolysis cells was modelled by Lai et al. [55], who demonstrated that the

current distribution will be more even when the collector bars are installed horizontally. Based on the principal of energy conservation, Lai et al. [56] and Liu [57] adapted the heat balance of conventional electrolysis cells by modelling the freeze profile, heat dissipation from the cell surfaces, and the technical parameters. When retrofitting a 150 kA conventional cell to a drained electrolysis cell [57], the simulation showed that the retrofitted cell could keep the thermal balance with a line current of 190 kA, an anodic current density of 0.96 A/cm^2, an anode cathode distance of 2.5 cm, a 16 cm thick alumina cover, and an electrolyte bath temperature of 946°C.

Li [58] simulated the gas-induced bath flow of drained reduction cells, while Jiang et al. [59] used a model to design the slope of a drained cathode.

Tests in industrial cells and start-up

Besides using a small laboratory cell [60] Chinese scientists reported industrial scale tests in smelters with 75 kA, 160 kA cells [8], and 300 kA cells [43, 44] with good results. Li et al. [8] reported that the bottom voltage drop decreased by 10 mV and the average current efficiency increased by 2%.

Ren et al. [43] reported that when using TiB_2 coating on the carbon cathode surface, the voltage drop can be up to 50 mV less than with conventional cells. This means saving about 400 kWh/t Al and improving current efficiency by 1 - 2.5%. The titanium content in the primary metal will be about 0.0025 wt. %. It also economises about 1.7 tonnes of Na_2CO_3 during start-up of the pot.

In the small electrolysis cell described in [60], the cathode slope was 10°, and the dissolution speed of TiB_2 into the electrolyte was about 1.0 gh^{-}1m^{-2}.

Andrews, Hardie and Taylor [61] reported excellent cell life and reduced energy consumption. RioTinto Alcan, then Comalco tested TiB_2 coatings in all electrolysis pot types in Australia and New Zealand. These ranged from current loads of 100 kA in the Bell Bay, Tasmania, smelter over 150 kA cells in the New Zealand smelter to the Boyne Smelter 300 kA potline. Autopsy and cathode wear monitoring data have shown that cathode erosion is reduced to typically less than 4 mm/y with application of a TiB_2/composite coating.

Lai, Li and Chen [63] propose the ideal preheating and start-up procedure should ensure low thermal shock, low temperature gradient and low expansion stress. They recommend flame-heating and optimised start-up procedure. Careful start-up is also recommended by de Nora et al. [64]. This involves protecting the coated cathode surface temporarily with one or several thin aluminium sheet(s), laid on the cathode surface for example with a boron-containing solution. The aluminium sheet is covered with resistor coke up to the bottom of the anode facing the cathode. When current passes from the anode to the cathode via the resistor coke and the thin aluminium sheet it generates heat mainly in the resistor coke.

Cells design and further development

De Nora patented some futuristic conventional cell designs. These include: anode and cathodes to be sloped up to about 60° [65]; V-shaped surfaces and recessed grooves with a sloping bottom [66]; aluminium-wettable foams pre-filled with aluminium and placed flat on the wettable cathode surface [67]; the use of a metal anode in combination with wettable cathode [68]; an outer cathode shell housing inner electrical conductive cathode holder shells connected to a busbar [69]; and a multi-cell aluminium electrolysis pot with vertically inclined electrodes [70].

Northwest Aluminum Technologies is developing another approach which differs significantly from the Hall-Héroult process. According to Brown [71] and [72], the low temperature process employs a more acidic electrolyte than cryolite, an alumina slurry, oxygen-generating metal anodes, and vertically suspended electrodes. Wetted and drained vertical cathodes are crucial to the new process, which is under way. Its progress can be followed up by the patent applications of Northwest Aluminum Technologies. These include: a multi-electrode electrolytic cell design with hollow cathode [73]; a design to collect the produced aluminium in a reservoir [74]; a cathode connector to a bus bar outside the electrolysis cell [75]; the cathode base materials selected from boron carbide and zirconium oxide [76]; and a cathode bar extended from a reaction layer through a poorly conducting base material [77].

Conclusion

Wettable cathodes appear to be closer to industrial use than are inert anodes.

Recent years have seen much progress in laboratory and industrial scale tests using wettable cathodes, as well as in understanding how sodium penetrates into the carbon cathode of aluminium electrolysis cells.

So far, the retrofit of conventional cells does not seem to offer conclusive advantages. To achieve the full potential saving in energy will require radically new cell designs.

However, TiB_2-based composites do help to protect against sodium and bath infiltration into the carbon cathode, and can thus increase potlife considerably.

Computer modelling must be used to explore new cell designs of more or less conventional cells, which may employ inert anodes and/or wettable cathodes.

As Welch [6] remarked, there are many obstacles. However, the likelyhood of successfully developing and implementing wettable cathodes industrially has increased in recent years. The obstacles are high. To overcome them will require a change in attitude, better planning and analysis, dedication, time, and many millions of dollars.

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References

[1] J. Keniry, "Future directions for aluminium reduction cell technology", 7th Australasian Aluminium Smelting Technology conference, Melbourne, Australia 11-16 November 2001, 14 pp.
[2] J. Keniry, "Strategic issues for aluminium smelting defined needs and opportunities for technology developments", Aluminium International Today 14 (2002) 6, pp. 20,24,26,28,30
[3] W. Haupin and W. Frank, "Current and energy efficiency of Hall-Héroult cells – past, present and future", Light Metal Age 60 (2002) 5-6, pp 6-8, 10-13
[4]W. Choate and J. Green, "Techno-economic assessment of the carbothermic reduction process for aluminium production", Light Metals 2006, ed. T. J. Galloway (TMS, Warrendale, Pa), pp. 445-450
[5] J. W. Evans, "The evolution of technology for light metals over the last 50 years: Al, Mg, and Li", JOM 59 (2007) 2, pp. 30-38
[6] B. Welch, "Inert anodes – the status of the materials science, the opportunities they present and the challenges that need resolving before commercial implementation", Light Metals 2009, ed. G. Bearne (TMS, Warrendale, Pa), pp. 971-978
[7]R. P. Pawlek, "Aluminum wettable cathodes: an update", Aluminum Transactions 3 (2000) 1, pp. 139-146
[8] J. Li et al., "Research progress in TiB_2 wettable cathode for aluminium reduction", JOM 60 (2008) 8, pp. 32-37
[9] R. J. Batterham and M. J. Hollitt, "Production of primary metals – towards improved sustainability". Erzmetall 56 (2003) 9, pp. 519-528
[10] D. A. Simakov et al., "The pilot tests of wettable cathode coating", XI Int. Conf. on Aluminium Siberia 2005, Krasnoyarsk 13 Sept. 2005
[11] M. Scherkl and A. Bischoff, "Stabile Elektroden für die Aluminiumschmelzflusselektrolyse", Metall 56 (2002) 4, pp. 208-213
[12] T. Nguyen and C. McMinn, „The Moltech metallic anode and wettable cathode coating", Aluminium World 2 (2002) 1, pp. 30-33
[13] V. de Nora, "Veronica and Tinor 2000: new technologies for aluminium production", Interface 11 (2002) 4, pp. 20-24
[14] B. H. Boost, "Wettable cathodes and inert anodes", IX Int. Conf., Sept. 9-11, 2003, Proc. Aluminium of Siberia 2003, Krasnoyarsk, pp. 153-159
[15] V. de Nora, "Aluminium-wettable porous ceramic material", WO patent 02/070783 (7 March 2001)
[16] Anonymous, "Titanium diboride", Am. Ceram. Soc. Bull. 80 (2001) 8, pp. 102-104
[17] R. A. Rapp, "Cathode for aluminium production and electrolytic cell", US patent application 2002/0125125 (6 March 2001)
[18] X. Luo et al., "Influence of metallic additives on densification behaviour of hot-pressed TiB_2", Light Metals 2009, ed. G. Bearne (TMS, Warrendale, Pa), pp. 1151-1155
[19] H. Lu et al.,"Titanium diboride and tungsten silicide composite used as aluminium electrolysis inert cathode material", Light Metals 2006, ed. T. J. Galloway (TMS, Warrendale. Pa), pp. 687-690
[20] Anonymous, "Advanced technical ceramics for metallurgy", APT Aluminium News 5 (2009) 1, p. 3
[21] D. Simakov et al., "Electrodeposition of TiB_2 from cryolite alumina melts", Light Metals 2008, ed. D. H. de Young (TMS, Warrendale, Pa), pp. 1019-1022
[22] J.-L. Xu, "Preparation of TiB_2 inert cathode by electrodeposition process for aluminium electrolysis", J. Northeast Univ. Nat. Sci. 25 (2005) 9, pp. 873-875
[23] J. Li, "Preparation of TiB_2 coatings by electroplating in molten salt", Rare Metals 24 (2005) 3, pp. 261-266
[24] Y. Ban et al., "Preparation of TiB_2 inert cathode on graphite by electrodeposition process for aluminium electrolysis", Light Metals 2007, ed. M. Sørlie (TMS, Warrendale, Pa.), pp. 1055-1059
[25] Y. G. Ban, "Preparation of TiB_2 coating and its corrosion resistance to electrolyte", J. Northeast. Univ. 28 (2007) 12, pp. 1729-1732
[26] S. V. Devyatkin, "Electrosynthesis of zirconium boride from cryolite-alumina melts containing zirconium and boron oxides", Russian Journal of Electrochemistry 37 (2001) 12, pp. 1308-1311
[27] H. Lu et al., "Titanium diboride and molybdenum silicide composite coating on cathode carbon blocks in aluminium electrolysis cells by atmospheric plasma spraying", Light Metals 2005, ed. H. Kvande (TMS, Warrendale, Pa), pp. 785-788
[28] J. A. Sekhar and V. de Nora, "application of refractory protective coatings on the surface of electrolytic cell components", US patent 6,402,926 (17 June 1996)
[29] A. A. Mirchi and J. Bergeron, "A method for providing a protective coating for carbonaceous components of an electrolysis cell", US patent 6,475,358 (16 February 2000)
[30] J.-P. Huni et al.,"Titanium diboride – aluminium oxalate slurry for refractory coatings on components of an aluminium electrolysis cell", WO patent 01/061,077 (16 February 2000)
[31] J. A. Sekhar, J.-J. duruz and J. J. Liu, "Slurry and method for producing refractory boride bodies and coatings for aluminium electrowinning cell apparatus", US patent 6,436,250 (20 October 1997)
[32] V. de Nora and J.-J. Duruz, "Aluminium wettable protective coatings for carbon components used in metallurgical processes", EP patent 1,240,118 (9 December 1999)
[33] X.-X. Wang, "Processing and characterization of titanium boride – colloidal alumina coating on carbon

cathode in Hall-Héroult cell", University of Cincinnati, Cincinnati, Ohio, USA, Ph.D. Thesis 2000, 128 pp.
[34] M. Dionne, "Characterization of the titanium diboride-carbon composite with liquid aluminium and the cryolite bath of the aluminium electrolysis cell", Ecole polytechnique, Montreal, Quebec, Canada, Thesis 2001, 382 pp.
[35] J. Fang et al., "The TiB_2-carbon composites sintered at moderate low temperature used as wettable cathode for aluminium electrolysis", J. Cent. South Univ. Technol. 34 (2003) 1, pp. 24-27
[36] X.-L. Duan, "Study on expansibility of TiB_2-C compound and Na penetration in electrolysation", J. Mater. Metall. 4 (2004) 1, pp. 30-33
[37] J. Lie, "Effect of TiB_2-content on resistance to sodium penetration of TiB_2/C cathode composites for aluminium electrolysis", J. Cent. S. Univ. Technol. 11 (2004) 4, pp. 400-404
[38] Q. Li et al., "The effect of sodium-containing additives on the sodium-penetration resistance of TiB_2/C composite cathode in aluminium electrolysis", Light Metals 2005, ed. H. Kvande (TMS, Warrendale, Pa.), pp. 789-791
[39] J. Li, "Technological progress in Chinese primary aluminium industry and the characteristics of Chinese technologies", Proc. Int. Forum on Aluminium, Shanghai Future Exchange, May 2005, pp. 111-127
[40] M. O. Ibrahiem, T. Fosnæs and H. A. Øye, "Stability of TiB_2-C composite coatings", Light Metals 2006, ed. T. J. Galloway (TMS, Warrendale, Pa.), pp. 691-696
[41] J. Lie, "Electrical resistivity of TiB_2/C composite cathode coating for aluminium electrolysis", J. Centr. South Univ. Technol. 13 (2006) 3, pp. 209-213
[42] M. O. Ibrahiem, T. Fosnæs and H. A. Øye, "Chemical stability of pitch-based TiB_2-C coatings on carbon cathodes", Light Metals 2007, ed. M. Sørlie (TMS, Warrendale, Pa.), pp. 1041-1046
[43] B. Ren et al., "Application of TiB_2 coating cathode blocks made by vibration moulding for 300 kA aluminium reduction cells", Light Metals 2007, ed. M. Sørlie (TMS, Warrendale, Pa.), pp. 1047-1050
[44] Y. Ban et al., "Application of TiB_2/C composite cathode coating solidified at ambient temperature in 300 kA prebaked aluminium reduction cells", ed. M. Sørlie (TMS, Warrendale, Pa.), pp.1051-1054
[45] J. Xue, Q. Liu and W. Ou, "Sodium expansion in carbon/TiB_2 cathodes during aluminium electrolysis", Light Metals 2007, ed. M. Sørlie (TMS, Warrendale, Pa.), pp. 1061-1065
[46] Y. Wang et al., "Study on expansion of TiB_2/C compound cathode and sodium penetration during electrolysis", Light Metals 2007, ed. M. Sørlie (TMS, Warrendale, Pa.), pp. 1067-1070
[47] M. O. Ibrahiem, T. Fosnæs and H.A. Øye, "Properties of pitch and furan-based TiB_2-C cathodes", Light Metals 2008, ed. D. H. de Young (TMS, Warrendale, Pa.) pp. 1013.1018
[48] J. Xue, Q. Liu and B. Li, "Creep deformation in TiB_2/C composite cathode materials for aluminium electrolysis", Light Metals 2008, ed. D. H. de Young (TMS, Warrendale, Pa.) pp.1023-1027
[49] X.-J. Lü et al., "Effects of grain graduation on tapped packing efficiency in preparing TiB_2/C composite material for aluminium electrolysis", Light Metals 2008, ed. D. H. de Young (TMS, Warrendale, Pa.) pp. 1033-1036
[50] X.-L. Lü et al., "Effects of pitches modification on properties of TiB_2/C composite cathodes", Light Metals 2009, ed. G. Bearne (TMS, Warrendale, Pa.), pp. 1145-1149
[51] J. Xue et al., "Analysis of sodium and cryolite bath penetration in the cathodes used for aluminium electrolysis", Light Metals 2009, ed. G. Bearne (TMS, Warrendale, Pa.), pp. 1177-1181
[52] Q. Y. Li, "Effect of TiB_2 coating on evolution of cathode lining during the process of primary aluminium production", Metallurgical and Materials Transactions A38(2007)13, pp. 2358-2361
[53] Q. S. Liu, "Effects of additives on the sodium penetration and expansion of carbon-based cathodes during aluminium electrolysis", J. Univ. of Scienc. Technol. Beijing 30 (2008) 4, pp. 403-407
[54] J. Xue, et al., "Sodium penetration into carbon-based cathodes during aluminium electrolysis", Light Metals 2006, ed. T. J. Galloway (TMS, Warrendale, Pa.), pp. 651-654
[55] Y.-Q. Lai et al, "Influences of different collector bar installations on cathode current distribution of drained cell", Chin. J. Nonferrous Met. 13 (2003) 4, pp. 1017-1020
[56] Y.-Q. Lai et al., "Heat balance simulation of drained aluminium reduction cell", Trans. Nonferrous Met. Soc. China 13 (2003) 5, pp. 1199-1202
[57] W. Liu, "2D finite element analysis of thermal balance for drained aluminium reduction cells", J. Central South Univ. of Technology 14 (2007) 6, pp. 783-787
[58] X.-P. Li, "Mathematical simulation of gas induced bath flow in drained aluminium reduction cell", Trans. Nonferrous Metals Soc. China 14 (2004) 6, pp. 1221-1226
[59] C.-W. Jiang et al., "A method of determining and designing the drained slope in drained aluminium reduction cells", J. Cent. S. Univ. Technol. 10 (2003) 1, pp. 74-77
[60] N. Feng et al, "Electrolysis test of a 1350 A drained cathode reduction cell with TiB_2-coated cathode", Light Metals 2006, ed. T. J. Galloway (TMS, Warrendale, Pa.), pp. 505-509
[61] E. W. Andrews, G. J. Hardie and M. J. Taylor, "Implementation of TiB_2 composite coated cathode technology in aluminium reduction cells", Proc. VII Australasian aluminium Smelting Technology Conference and workshop, Melbourne, Australia, 11-16 November 2001, 1 p.
[62] Z. Wang et al., " Penetration of sodium and electrolyte to vibratory compaction TiB_2 cathode", Light Metals 2008, ed. D. H. de Young (TMS, Warrendale, Pa.), pp. 1029-1032

[63] Y.-Q. Lai, Q.-Y. Li and Z. chen, "Effects of preheating and start-up procedure on pot life of prebaked anode aluminium reduction cells", Min. Metall. Eng. 22 (2002) 4, pp. 76-78
[64] V. de Nora et al., "Start-up of eletrowinning cells", US patent 6,338,785 (17 October 1997)
[65] V. de Nora and J.-J. Duruz, "A drained cathode cell for the production of aluminium", EP patent 0,996,773 (7 July 1997)
[66] V. de Nora and J.-J. Duruz, "Drained cathode aluminium electrowinning cell with alumina distribution", US patent 6,436,273 (11 August 2000)
[67] V. de Nora, "Cell for the electrowinning of aluminium operating with metal based anodes", WO patent 02/070,785 (7 March 2001)
[68] T. T. Nguyen and V. de Nora, "Metal-based anodes for aluminium production cells", WO patent 02/070,786 (7 March 2001)
[69] G. Berclaz and V. de Nora, "Aluminium production cell and cathode", US patent 6,358,393 (23 May 1997)
[70] V. de Nora, "Aluminium electrowinning cells with inclined cathodes", WO patent 03/023,091 (7 September 2001)
[71] C. W. Brown, "Wetted cathodes for low-temperature aluminium smelting: final report", STAR 41 (2003) 6.
[72] Anonymous, "Aluminum: revolutionizing the way aluminium is made", OIT Times Turning Ind. Visions into Real. 4 (2001) 3, p. 3
[73] C. W. Brown and P. B. Frizzle, "Low temperature aluminium reduction cell using hollow cathode", US patent 6,436,272 (4 October 2000)
[74] T. R. Beck and C. W. Brown, "Aluminum low temperature smelting cell metal collection", US patent 6,419,812 (27 November 2000)

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Recommended Reading

Antille, J., et al. Modeling of a 25 kA de Nora inert metallic anode test cell (2006, pp. 391–396).

Antipov, E.V., et al. Electrochemical behavior of metals and binary alloys in cryolite-alumina melts (2006, pp. 403–408).

Assouli, B., et al. Mechanically alloyed Cu-Ni-Fe based materials as inert anode for aluminium production (2009, pp. 1141–1144).

Ban, Y., et al. Application of TiB_2/C composite cathode coating solidified at ambient temperature in 300kA prebaking aluminium reduction cells (2007, pp. 1051–1054).

Brown, C.W. Laboratory experiments with low-temperature slurry-electrolyte alumina reduction cells (2000, pp. 391–396).

Cassayre, L., et al. Gas evolution on graphite and oxygen-evolving anodes during aluminium electrolysis (2006, pp. 379–383).

De Nora, V., et al. Semi-vertical de Nora inert metallic anode (2007, pp. 501–505).

De Nora, V., and T. Nguyen. Inert anode: Challenges from Fundamental research to industrial application (2009, pp. 417–421).

Glucina, M., and M. Hyland. Laboratory scale testing of aluminum bronze as an inert anode for aluminum electrolysis (2005, pp. 523–528).

Haupin, W. Cathodes wetted by aluminum improve current efficiency (1999, pp. 395–398).

Hryn, J.N., and M.J. Pellin. A dynamic inert metal anode (1999, pp. 377–381).

Hryn, J.N., and D.R. Sadoway. Cell testing of metal anodes for aluminium electrolysis (1993, pp. 475–483).

Huazhang, W., et al. Laboratory study on TiB_2-based ceramic cathode for aluminium reduction cell (1994, pp. 505–511).

Ibrahiem, M., T. Foosnæs, and H.A. Øye. Chemical stability of pitch-based Tib_2–C coatings on carbon cathodes (2007, pp. 1041–1046).

Ibrahiem, M.O., T. Foosnæs, and H.A. Øye. Properties of pitch and furan-based TiB_2-C cathodes (2008, pp. 1013–1018).

Ibrahiem, M.O., T. Foosnæs, and H.A. Øye. Stability of TiB_2-C composite coatings (2006, pp. 691–696).

Jianhong, Y., L. Yexiang, and W. Huazhang. The behavior and improvement of SnO_2-based inert anodes in aluminium electrolysis (1993, pp. 493–495).

Kiss, L., et al. The bubble laden layer around inert anodes (2007, pp. 495–500).

Kvande, H. Inert electrodes in aluminum electrolysis cells (1999, pp. 369–376).

Li, Q.-Y., et al. Laboratory test and industrial application of an ambient temperature cured TiB_2 cathode coating for aluminum electrolysis cells (2004, pp. 327–331).

Lorentsen, O-A., and J. Thonstad. Electrolysis and post-testing of inert cermet anodes (2002, pp. 457–462).

Nguyen, T., and V. de Nora. De Nora oxygen evolving inert metallic anode (2006, pp. 385–390).

Pawlek, R.P. Aluminum wettable cathodes: An update (2000, pp. 449–454).

Ren, B., et al. Application of TiB_2-coating cathode blocks made by vibration molding for 300 kA aluminum reduction cells (2007, pp. 1047–1050).

Sekhar, J.A., et al. Cathodic coating for improved cell performance (1995, pp. 507–513).

Sekhar, J.A., et al. Graded non-consumable anode materials (1998, pp. 597–603).

Sekhar, J.A., et al. TiB_2/colloidal alumina carbon cathode coatings in Hall-Heroult and drained cells (1998, pp. 605–615).

Shi, Z.-n., J.-l. Xu, and Z.-x. Qiu. An iron-nickel metal anode for aluminum electrolysis (2004, pp. 333–337).

Tabereaux, A., et al. The operational performance of 70 kA prebake cells retrofitted with TiBz-G cathode elements (1998, pp. 257–264).

Thonstad, J., A. Kisza, and J. Hives. Anode overvoltage on metallic inert anodes in low-melting bath (2006, pp. 373–377).

Vassiliev, S., et al. Electrochemistry of tin-species in mid temperature cryolite-alumina melt (2009, pp. 1135–1140).

Welch, B.J. Inert anodes – the status of the materials science, the opportunities they present and the challenges that need resolving before commercial implementation (2009, pp. 971–978).

Xu, J., et al. Aluminum electrolysis in a low temperature heavy electrolyte system with Fe-Ni-Al_2O_3 composite anodes (2007, pp. 507–511).

Xu, J., et al. Effects of the NaF to AlF_3 ratio on Fe-Ni-Al_2O_3 anode properties for aluminum electrolysis (2008, pp. 1047–1050).

Yang, J., et al. New opportunities for aluminum electrolysis with metal anodes in a low temperature electrolyte system (2004, pp. 321–326).

Yang, J., J.N. Hryn, and G.K. Krumdick. Aluminum electrolysis tests with inert anodes in KF-AlF_3-based electrolytes (2006, pp. 421–424).