Sludge Formation in Hall Héroult Process: An Existing Problem

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Abstract

A concise literature review is done on the industrial and laboratory scale investigations of sludge formation in the Hall Héroult Process. Formation of sludge and consequently its transformation into resistive cathodic deposits has been one of the focal concerns of the aluminum producers. However, nowadays due to the profusion of production, especially by China, all the major producers of aluminum have increased their efforts towards sludge minimization and better understanding of the phenomena that lead to formation of such deposits. In this review article, first the sludge formation phenomenon and its detrimental effect in Hall-Héroult process is introduced. Later, the thermochemistry of the sludge is presented. Furthermore, four of the most important factors in sludge formation namely hydrodynamics, operational temperature (i.e. superheat level), alumina feeding and bath chemistry are reviewed.

Keywords: Hall Héroult process, hydrodynamics, sludge formation, alumina feeding strategy, bath chemistry and operational temperature.

1. Introduction

Aluminum is a strategic metal in transportation, packaging, construction, electrical industry, consumer durables and machinery [1]. Furthermore, recent developments in the production of aluminum batteries has created yet another potential market for the consumption of aluminum in the future [2]. According to the world's annual production of aluminum and its trend in recent years, China has become a formidable producer of aluminum in the last 6 years [3] and this has forced other producers of aluminum to try to reduce their production cost more and more by investing in research and development (R&D).

In an ideal aluminum electrolysis process, according to Faraday's law, 0.335573 kg of aluminum is produced with 1 kAh of electrical charge. However, in reality, a current efficiency of ≈ 95 – 96 % is observed [4]. Two major phenomena account for such a loss of current efficiency. The first reason is the back reaction of solubilized aluminum ions with CO_2 gas and production of CO gas and dissolved Al_2O_3. The second major phenomenon is the formation of resistive deposits on the surface of the cathode. Such deposits not only create more resistivity against the electrical current and increase the required electrical energy, but also as it is mentioned in the following paragraphs (Section 2.), contributes to the four significant factors reducing the current efficiency.

2. Sludge Formation and Its Drawbacks

In an ideal scenario, upon the introduction of alumina onto the cryolitic bath surface, alumina particles easily dissolve and disperse evenly at interelectrode space (i.e. distance between anode and upper surface of metal pad). Unfortunately, just like most of engineering cases, such ideal situation is hardly possible and when undissolved clumps of alumina sink to the bottom of the cell, beneath the metal pad, a dense and viscous phase called sludge is formed. According to Tabereaux and Peterson [4], the following steps are followed upon addition of 1 – 2 kg of alumina particles onto the surface of bath by point feeders. At first, the particles get wetted by the bath. Later the alumina particles absorb the sensible heat and their temperature increases from 100 °C to 960 °C. At this stage, the wetted undissolved particles form agglomerates and subsequent dissolution occurs around the alumina particles creating a supersaturated local bath. Gradually most of the alumina particles dissolve into the bath and distribute in the cell by the turbulence flow. Sludge is a paste-like viscous combination of alumina particles and alumina-saturated bath. The average properties of a typical sludge sample is as follows: density of ~ 2 400 kg/m^3, alumina content of 20 - 50 %, AlF_3 of 2 - 10 %, $CaF_2$of 2 - 5 % [5, 6: p. 77].

Formation of sludge is not a favorable phenomenon due to the fact that, it contributes to the four significant factors reducing the current efficiency, namely operational temperature, bath chemistry, current density and the stability of the metal-bath interface. A typical sludge phase with the aforementioned characteristics has an electrical resistivity of 0.01 Ωm [7, 8], which is about twice the resistivity of bath and about 35 000 times greater than molten aluminum. Such electrical resistivity diverts the local current density and creates areas with higher current density and consequently higher cathode wear [9]. The sludge formation also consequently influences the carbide content, carbon particles dispersion, bath superheat and loss of current efficiency. Extensive sludge formation increases the occurrence of anode effect, during which the anode is poorly wetted by the electrolyte resulting in extensive carbon dusting. Presence of dispersed carbon particles in the bath not only increases the electrical resistivity of the bath (i.e. higher energy consumption) [10], but also by reaction with dissolved aluminum and formation of aluminum carbide, causes higher solubility of aluminum and loss of current efficiency [11, 12].

Besides, the sludge also tampers with the hydrodynamics of the cell. The higher electrical resistivity of the sludge-covered cathode area diverts the local current to flow horizontally towards the edges of the sludge. Such horizontal current flows perturb the dominant vertical current flows leading to additional instability of the metal-bath interface. The oscillation of metal-bath interface has a dramatic effect on the optimum operation of the cell considering the large aspect ratio of the cell and higher resistivity of the bath compared to metal pad [13]. Moreover, the shear amount of metal-bath interfacial stress leads to higher aluminum solubility (i.e. fogging effect), which consecutively accounts for higher back reaction and loss of current efficiency [14: p. 216-226]. In addition, such metal/bath instabilities results in an increase of anode-cathode distance (ACD), cathode voltage drop (CVD) and disturb heat balance which dramatically affect the current efficiency and energy consumption [15].

3. Thermochemistry of Sludge Phase

Thermodynamics of the metallurgical systems is of great importance since it can guide the scientists to not only find the optimum pressure, temperature and compositions but also it provides an in depth study of the interactions that happen between the cell's fluids, linings, cathode materials and impurities. The review of such systems is way out of the scope of this concise review article but avid readers are referred to references such as Thonstad et al. [14] and Sorlie and Øye [16]. To our best of knowledge, the most exhaustive and specific thermodynamic study of the sludge in the aluminum electrolysis cells has been done partially by Liu [17] and more comprehensively by Allard et al. [5].

chemistry, current density and stability of the metal-bath interface. This concise review article tries to provide a reminder on the existing problem of sludge formation (also known as muck) and hopes to motivate young scientists and engineers to pull the aluminum industry out of sludge!

5. References

1. E.L. Bray, Aluminum, *U.S. Geological Survey, Mineral Commodity Summaries*. (2016).
2. X. Zhang, et al., A Novel Aluminum–Graphite Dual-Ion Battery, *Advanced Energy Materials*. Vol. 6, No. 11, (2016), 1502588-n/a.
3. E.L. Bray, *U.S. Geological Survey, Minerals Yearbook*. 2017.
4. A.T. Tabereaux and R.D. Peterson, Aluminum Production, in *Treatise on Process Metallurgy,* Vol. 3, S. Seetharaman, Editor. 2014, Elsevier: Boston, MA, USA. 839-917.
5. F. Allard, et al., Thermodynamic and thermochemical investigation of the deposits formed on the cathode surface of aluminum electrolysis cells, *Journal of Thermal Analysis and Calorimetry*. Vol. 119, No. 2, (2015), 1303-1314.
6. K. Grjotheim and H. Kvande, Introduction to Aluminium Electrolysis: Understanding the Hall-Héroult Process. 1993, Düsseldorf, Germany: Aluminium-Verlag GmbH. 260.
7. R. Keller, Alumina dissolution and sludge formation revisited, in *Light Metals* 2005, 147-150.
8. P.-Y. Geay, B.J. Welch and P. Homsi, Sludge in operating aluminum smelting cells, *Light Metals* 2001, 541-547.
9. X. Liao and H.A. Øye, Carbon Cathode Corrosion by Aluminium Carbide Formation in Cryolitic Melts, in *Essential Readings in Light Metals,* Vol. 4, A. Tomsett and J. Johnson, Editors. 2013, John Wiley & Sons, Inc. 992-998, also in *Light Metals* 1999, 621-627.
10. L. Bugnion and J.C. Fischer, Effect of Carbon Dust on the Electrical Resistivity of Cryolite Bath, in *Light Metals* 2016, 587-591.
11. R. Odegård, A. Sterten, and J. Thonstad, On the Solubility of Aluminium Carbide in Cryolitic Melts - Influence on Cell Performance, in *Essential Readings in Light Metals,* Vol. 2, G. Bearne, M. Dupuis, and G. Tarcy, Editors. 2013, John Wiley and Sons Inc. 25-32, also in *Light Metals* 1987, 295-302.
12. L. Wang, A.T. Tabereaux, and N.E. Richards, Electrical conductivity of cryolitic melts containing aluminum carbide, in *Light metals* 1994, 177-185.
13. P.A. Davidson and R.I. Lindsay, Stability of interfacial waves in aluminium reduction cells, *Journal of Fluid Mechanics*. Vol. 362, (1998), 273-295.
14. J. Thonstad, et al., Aluminium electrolysis: fundamentals of the Hall-Héroult process. 3rd ed. 2001, Düsseldorf, Germany: Aluminium-Verlag. 359.
15. B.J. Welch and G.I. Kuschel, Crust and alumina powder dissolution in aluminum smelting electrolytes, *JOM*. Vol. 59, No. 5, (2007), 50-54.
16. M. Sorlie and H.A. Oye, Cathodes in Aluminium Electrolysis. 3rd ed. 2010, Düsseldorf, Germany: Aluminium Verlag GmbH. 662.
17. X. Liu, Thermochemistry of Electrolyte, Sludge/Ridge, Ledge and Cell Cover, in *Proceedings of the 5th Australasian Aluminum Smelter Technology Workshop*. 1995: Queenstown, New Zealand. 619-627.
18. J. Thonstad, P. Johansen, and E.W. Kristensen, Some properties of alumina sludge, in *Light Metals* 1980, 227-239.
19. S.J. Hove and H. Kvande, Center-break alumina feeding and sludge control of prebaked cells, in *Light Metals* 1982, 513-529.
20. O. Kobbeltvedt, Dissolution kinetics for alumina in cryolite melts. Distribution of alumina in the electrolyte of industrial aluminium cells. Thesis (Dr.ing.), Norwegian

University of Science and Technology, Department of Electrochemistry, Trondheim, Norway, 1997, p191.
21. G.I. Kuschel and B.J. Welch, Further Studies of Alumina Dissolution Under Conditions Similar to Cell Operation, in *Essential Readings in Light Metals*, Vol. 2, G. Bearne, M. Dupuis, and G. Tarcy, Editors. 2013, John Wiley & Sons, Inc.: Hoboken, NJ, USA. 112-118.
22. M.P. Taylor and B.J. Welch, The future outlook and challenges for smelting aluminium, *Aluminium International Today*. Vol. 16, No. 2, (2004), 20-24.
23. M.-A. Coulombe, et al., Factors Leading to the Formation of a Resistive Thin Film at the Bottom of Aluminum Electrolysis Cells, *Metallurgical and Materials Transactions B*. Vol. 47, No. 2, (2016), 1280-1295.
24. J. Gerlach and G. Winkhaus, Interactions of alumina with cryolite-based melts, in *Light Metals* 1985, 301-313.
25. L.A. Isaeva, A.B. Braslavskii, and P.V. Polyakov, Effect of the content of the α-phase and granulometric composition on the dissolution rate of alumina in cryolite-alumina melts, *Russian Journal of Non-Ferrous Metals*. Vol. 50, No. 6, (2009), 600-605.
26. J.B. Metson, M.M. Hyland, and T. Groutso, Alumina phase distribution, structural hydroxyl and performance of smelter grade aluminas in the reduction cell, in *Light Metals* 2005, 127-131.
27. A.N. Bagshaw and B.J. Welch, The Influence of Alumina Properties on Its Dissolution in Smelting Electrolyte, in *Essential Readings in Light Metals*, Vol. 1, D. Donaldson and B.E. Raahauge, Editors. 2013, John Wiley & Sons, Inc.: Hoboken, NJ, USA. 783-787.
28. H. Maeda, S. Matsui, and A. Era, Measurement of dissolution rate of alumina in cryolite melt, in *Light Metals* 1985, 763-780.
29. X. Wang, Alumina dissolution in aluminum smelting electrolyte, in *Light Metals* 2009, 383-388.
30. R.K. Jain, et al., Interaction of aluminas with aluminium smelting electrolytes, in *Light Metals* 1983, 609-622.
31. J.P. McGeer and J.D. Zwicker, Alumina: Calcination Control and Smelting Use, *JOM*. Vol. 34, No. 5, (1982), 50-54.
32. I.S. Kachanovskaya and O.I. Arakelyan, Behavior of alumina in the deposits and crust of an aluminum electrolytic cell, *Tsvetnye Metally*. No. 4, (1976), 37-40.
33. G.P. Tarcy, H. Kvande, and A. Tabereaux, Advancing the industrial aluminum process: 20^{th} century breakthrough inventions and developments, *JOM*. Vol. 63, No. 8, (2011), 101-108.
34. P. Lavoie, M.P. Taylor, and J.B. Metson, A Review of Alumina Feeding and Dissolution Factors in Aluminum Reduction Cells, *Metallurgical and Materials Transactions B*. Vol. 47, No. 4, (2016), 2690-2696.
35. B.P. Moxnes, B.E. Aga, and J.H. Skaar, How to obtain open feeder holes by installing anodes with tracks, in *Light Metals* 1998, 247-255.
36. J. Tessier, et al., Improvement of Alumina Dissolution Rate through Alumina Feeder Pipe Modification, in *Light Metals* 2013, 711-717.
37. A.N. Bagshaw, et al., Effect of operating conditions in the dissolution of primary and secondary (reacted) alumina powders in electrolytes, in *Light Metals* 1985, 649-659.
38. B.J. Welch, Gaining That Extra 2 Percent Current Efficiency, in *Hall-Héroult Centennial*, W.S. Peterson and R.E. Miller, Editors. 2007, John Wiley & Sons, Inc.: Hoboken, NJ, USA. 120-129.
39. G.T. Holmes, Hall cell ampere efficiency up 12% in 3 decades, in *Light Metals* 1995, 371-373.
40. E. Rosshard, et al., EPT 18: the new 180-kA-pot of Alusuisse, in *Light Metals* 1983, 595-605.

41. J. Thonstad, S. Roenning, and P. Entner, Formation of bottom crusts in aluminum pots. A laboratory study, in *Light Metals* 1982, 485-97.
42. F. Habashi, Extractive Metallurgy of Aluminum, in *Handbook of Aluminum,* Vol. 2, G.E. Totten and D.S. MacKenzie, Editors. 2003, Marcel Dekker: NY, USA. 1-79.
43. K. Grjotheim, et al., Aluminium electrolysis: fundamentals of the Hall-Héroult process. 2nd ed. 1982, Düsseldorf, Germany: Aluminium-Verlag. 443.
44. W. Haupin, The influence of additives on Hall-Héroult bath properties, *JOM*. Vol. 43, No. 11, (1991), 28-34.
45. K. Grjotheim, W.E. Haupin, and B.J. Welch, Current efficiency - relating fundamental studies to practice, in *Light Metals* 1985, 679-694.
46. R. Keller, Alumina dissolution and sludge formation, in *Light Metals* 1984, 513-518.
47. P. Coursol, et al., Application of Thermodynamic Models for Better Understanding and Optimizing the Hall-Heroult Process, *JOM*. Vol. 64, No. 11, (2012), 1326-1333.
48. C. Robelin and P. Chartrand, A viscosity model for the (NaF + AlF3 + CaF2 + Al2O3) electrolyte, *The Journal of Chemical Thermodynamics*. Vol. 43, No. 5, (2011), 764-774.
49. F. Allard, et al., Cartography and chemical composition of the different deposits in the hall-heroult process, in *Light Metals* 2014, 1233-1238.
50. H. Kvande, Production of primary aluminium, in *Fundamentals of Aluminium Metallurgy: Production, processing and applications*, R. Lumley, Editor. 2011, Woodhead Publishing: Cambridge, UK. 49-69.