SIDEWALL MATERIALS FOR HALL-HÉROULT PROCESS

Reiza Mukhlis, M. Akbar Rhamdhani, Geoffrey Brooks
Swinburne University of Technology, Hawthorn, VIC 3122, Australia
Keywords: Aluminium, Sidewall, Hall-Héroult

ABSTRACT

The performance of current sidewalls made of carbon and silicon based materials relies on the existence of a frozen electrolyte layer. The development of the Hall-Héroult cell technologies such as inert anodes and wettable cathodes, call for new sidewall materials since the frozen ledge may no longer be applicable. Nickel ferrite has been identified as a possible sidewall material, particularly in relation to its resistance to cryolite and air attack. The presentation proposes some strategies to tackle the combined corrosive action of cryolite, molten aluminium and oxygen upon sidewalls. A multi-layer approach is proposed that optimizes both the chemical and heat flux requirements of a sidewall. Issues relating to joining of materials, process control, manufacturing, maintenance and cost need to be addressed before new sidewall designs can be implemented.

INTRODUCTION

The Hall-Héroult process is the only industrially viable method used to produce aluminium. The process is based on electrolysis of high purity alumina, which is dissolved into molten cryolite, and reduced to aluminium at 965 °C using carbon anodes. The overall chemical reaction in the carbon anode cell is as follows:

\[ 2\text{Al}_2\text{O}_3 \text{(dis)} + 3\text{C (s)} = 4\text{Al (l)} + 3\text{CO}_2 \text{(g)} \]

Recently, the process consumes about 13 kWh of electric energy to produce 1 kg of aluminium at a current efficiency of 100% [1]. It is estimated that more than half of the total energy requirement is lost as low grade heat, in which almost 35 % of the total heat loss is transferred through sidewalls [2].

The heat needs to be dissipated through the sidewalls in order to form a frozen layer of electrolyte to protect the sidewall materials from the attack of cryolite [3]. The heat dissipation to the side is also needed to prevent excess heat going up through the anode which can increase the chance of anode air-burning [4].

With the application of inert anodes, which is intended to reduce the greenhouse gas emission and process disturbances due to anode changing, the energy needed to produce aluminium is increased due to the absence of the carbon-oxygen reaction that provides energy [3]. The overall reaction would be:

\[ 2\text{Al}_2\text{O}_3 \text{(diss)} = 4\text{Al (l)} + 3\text{O}_2 \text{(g)} \]
In combination with wettable cathode or drained cell technology, it is possible to implement inert anode with the same energy consumption as carbon anode or even further reduce it by reducing the inter electrode distance [5]. However, the amount of heat needed to dissipate is also reduced, which make it difficult to form the electrolyte frozen layer [6].

In this case, the protective frozen ledge will be difficult to maintain and the sidewall materials will be exposed directly to the cryolite bath, which is likely to cause significant reduction on the life of the sidewall based on the current materials and design.

This condition calls for new sidewall materials that have high resistance against corrosion in the range of environments that exist within the cell. The materials should also have high thermal insulation, opposed to the current required sidewall material properties, in order to keep the heat inside the cell and maintain the heat balance of the cell.

Since the sidewall materials likely to be exposed to three different environments, namely reducing gas zone, corrosive bath zone and reducing molten aluminium, it would be difficult to develop a single material that can satisfy all required properties of the ideal sidewall materials.

NICKEL FERRITE AS SIDEWALL MATERIAL ALTERNATIVE

The desirable properties of sidewall materials are quite similar to that proposed for inert anodes and therefore, some of the inert anodes materials can be proposed as sidewall materials [7]. Both inert anode and sidewall material candidates should have low solubility in cryolite and aluminium; low porosity, not wetted by bath or metal, and high oxidation resistance. They also have to be mechanically robust to survive plant conditions, thermally stable, have adequate thermal shock resistance, and be easy to fabricate and join. The only significant difference on the required properties of sidewall materials and inert anode materials is on their electrical resistivity. With a modification in that property, i.e. doping, we proposed that inert anodes material may also be suitable as part of a sidewall design.

Among inert anode materials, nickel ferrite (NiFe₂O₄) based materials are of interest as sidewall material [7]. It has high thermodynamic stability [8] and corrosion resistance toward cryolite and alumina bath [9]. Study by Yan et al. [9] showed that the extent of corrosion of the nickel ferrite could be lowered by using high alumina content, close to alumina saturation. Yan et al. suggested that the corrosion of nickel ferrite due to dissolution in bath could be lowered by using low bath ratio. Their study showed that the solubility of the nickel ferrite was reduced when lowering bath ratio from 1.43 to 1.38. Laboratory test conducted by Olsen and Thonstad [10] on the nickel ferrite material showed that a dense oxide layer formed on the outer surface and it protects the material from further oxidation.

Hall-Héroult electrolysis cell can be divided into three different zones, namely the gas zone, the electrolyte (bath) zone, and the aluminium (metal) zone [11]. Each zone contains different chemical species and therefore has different characteristic. In the gas zone, the presence of air contributes to the oxidising condition in the zone. The cryolite
content in the bath zone provides a very aggressive corrosive environment. In the metal zone, molten aluminium creates a highly reducing condition.

Due to its high oxidation resistance and high stability toward molten bath, nickel ferrite could be suitable to be applied in the gas zone and bath zone. However, nickel ferrite may not be suitable to be applied in the aluminium zone since it is likely to react with aluminium that will lead to the degradation of the nickel ferrite and contamination to molten aluminium. Equilibrium calculations with 1 mol nickel ferrite and 10 mol liquid aluminium at 860 °C to 1200 °C show the dissolution of iron and nickel to aluminium as shown in Figure 2 [12]. At 965 °C, the composition of liquid phase is 62.1 % Al, 29.1 % Ni and 7.8 % Fe (Figure 1). This analysis indicate that exposure of nickel ferrite to aluminium is likely to result in severe degradation of that material, illustrating that it will difficult to find one material that can satisfy the range of chemical conditions inside the cell.

![Figure 1 - Equilibrium calculations of 1 mol nickel ferrite and 10 mol aluminium showing dissolution of nickel and iron to aluminium](image)

**PROPOSED APPROACH**

In this paper, author proposed multi-layer strategy and heat flux strategy to tackle the combine corrosive action of the different environments within the cell as illustrated in Figure 2. With multi-layer strategy, two or three different materials are combined. Multi-layer strategy can be applied horizontally, using three different materials in which each of the material can withstand each zone mentioned above. It can also be applied vertically, using two different materials in which one of them have high corrosion resistance while the other has low heat conductivity to maintain the heat balance of the cell.

In heat flux strategy, the amount of heat transferred through each zone of the sidewall is varied, making it possible to maintain frozen ledge in particular zone while maintaining the cell heat balance. As for example is to control heat flux through sidewall bath zone to allow ledge formation on this zone and incorporate air gaps or inserting low heat conductivity material into sidewall at the air and molten aluminium zone to minimize heat flux through this area. This strategy would reduce the material properties constrain since the sidewall does not have to withstand all the zones within the cell.
At this stage, these proposals are highly speculative and the authors acknowledge that there are very significant materials science, process control, maintenance and cost issues associated these ideas that are yet to be explored. It is the intention of this paper to raise awareness of these issues and stimulate further study on these exciting and challenging problems.

REFERENCES

7. K. Downie, NiFe₂O₄ as a sidewall materials in Hall-Heroult cells, in Faculty of Engineering. 2007, University of Wollongong: New-South Wales.