Future Materials Requirements for the High-Energy-Intensity Production of Aluminum

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Like all metallurgical industries, aluminum smelting has been under pressure from two fronts—to give maximum return on investment to the shareholders and to comply with environmental regulations by reducing greenhouse emissions. The smelting process has advanced by improving efficiency and productivity while continuing to seek new ways to extend the cell life. Materials selection (particularly the use of more graphitized cathodic electrodes) has enabled lower energy consumption, while optimization of the process and controlling in a narrow band has enabled increases in productivity and operations at higher current densities. These changes have, in turn, severely stressed the materials used for cell construction, and new problems are emerging that are resulting in a reduction of cell life. The target for aluminum electro-winning has been to develop an oxygen-evolving electrode, rather than one that evolves substantial amounts of carbon dioxide. Such an electrode, when combined with suitable wettable cathode material developments, would reduce operating costs by eliminating the need for frequent electrode change and would enable more productive cell designs and reduce plant size. The materials specifications for developing these are, however, an extreme challenge. Those specifications include minimized corrosion rate of any electrode into the electrolyte, maintaining an electronically conducting oxidized surface that is of low electrical resistance, meeting the metal purity targets, and enabling variable operating current densities. Although the materials specifications can readily be written, the processing and production of the materials is the challenge.

INTRODUCTION

On June 23, 2000, Credit Suisse-First Boston released a report by Thomas M. Van Leeuwen titled *An Aluminium Revolution*.[1] The key points of this report were:

- Two new smelting technologies under development will substantially lower primary aluminium production costs.
- These advances in smelter technology should position aluminium for substantial market-share gains in the new millennium.

In particular, the report revolved around two areas: the development of a material that would serve as an inert anode, and the development of a composite that would serve as a wettable drained cathode. The industry quickly responded, with Alcoa issuing a press release admitting the company is in the advanced stages of developing a practical inert anode and, if successful, this technology would be more environmentally friendly.[2] Producers of carbon anodes reacted by either intensively trying to discredit the report or showing great concern about the future of their segment of the industry. Meanwhile, since this paper was intended to address the materials challenges that these new technologies presented, the authors wondered if their topic was still relevant. The answer was a resounding "Yes!"

If the new technology is as successful as claimed, three questions arise:

- How does it impact the existing technology?
- If applicable to the existing technology, how rapidly will it be applied?
- What are the materials challenges for further advancements?

To understand the answers to these questions, it is necessary to cross-reference against the existing technology.

DRIVING FORCES FOR TECHNOLOGICAL CHANGE

There have been four major driving forces for the improvement or replacement of the existing technology:[2]

- High heat loss from cells results in high electrical energy consumption. This heat loss is a consequence of the cell design and efficiency. Maintaining heat balance was less of a concern to the older, inefficient cells, where there was scope for performance improvements. However, modern technology limits the amount the voltage can be reduced.
- Capital cost are high. Because of the expensive automation and the large number of low-productivity cells, the capital cost per unit is high, typically between $3,500 and $4,000 per annual tonne for new capacity.
- Maintenance costs are high. Because of the mechanism of feeding the cells and also the degradation processes that occur between the electrolyte, metal, and cell materials, the reconstruction and repair costs are substantial. The cell life is an important and limiting factor, although in the last 25 years the average life has increased from 1,000 days to a peak of almost 3,000 days for some technologies. More recently, cell life has been decreasing again.
- Carbon-dioxide emissions must be reduced to conform to national or international greenhouse emissions requirements.

The primary practical action taken because of these driving forces is to increase the line current in existing smelters, increasing productivity per unit cell and reducing the capital-cost component. Where this increase can be done while maintaining cell life, it also reduces the maintenance costs. Increasing

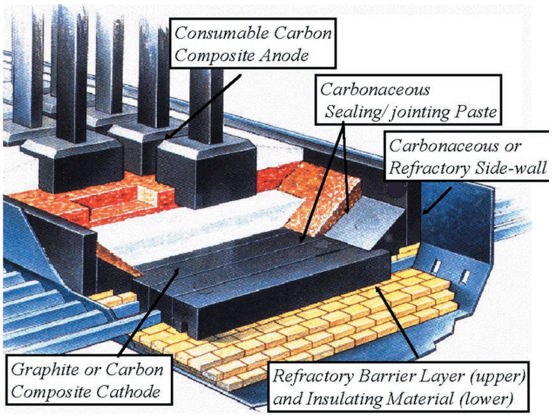

Figure 1. Key materials used in conventional aluminum smelting cells.

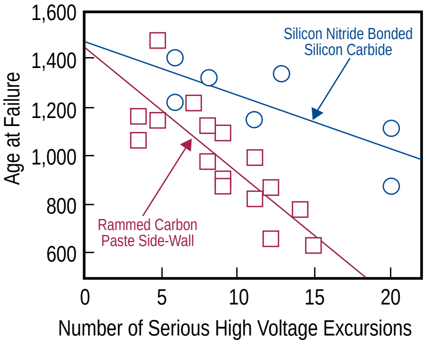

Figure 2. Illustrating the importance of both side-wall freeze protection and material on its performance life.

the line current has, however, resulted in an increase in heat generation because of the ohmic resistance of cell components. Consequently, heat dissipation in the existing technologies has become an issue for high-line currents, where an increased wear rate in the existing cell materials has been observed. This increased wear rate is contributing to the drive for better and new materials.

THE CONVENTIONAL CELL AND ITS MATERIALS CHALLENGES

Carbons, in various structural forms, have been the dominant materials used to contain both the electrolyte and molten metal. These liquids exhibit solvency, reduction, and oxidative properties, depending on the zone. This is evident from the schematic of a conventional aluminium smelting cell presented in Figure 1, which highlights six types of ceramic or composite materials used within the construction. Since it is not necessary or desirable to conduct current in the sidewall, silicon-nitride bonded silicon carbide has become an alternative to carbons in that region.

The jointing compounds (ramming pastes) are converted to carbon during the pre-heat of cells. The coal-tar-pitch based ramming paste initially swells while in a viscous state, but once carbonization occurs, the ram mix becomes rigid and steadily shrinks. Unless by the cathode blocks are expanded, the shrinkage results in potential cracks or leaks.

Sodium intercalation with the carbon occurs once the cathode material is under a cathodic potential. The resulting swelling can cause cracks to close.

Balancing these different expansion rates to ensure the hot operating cell is leak-proof presents the first design and materials selection challenge.

Anodes in cells are usually thermally insulated with an overlay of alumina or crushed solidified electrolyte, with that region of the cell typically accounting for 50% of the cell heat losses. Another 20% of the heat is lost through the bottom of the cell and collector bars. The remaining 30% of the heat is lost through the carbonaceous or refractory sidewalls, where it is transported from the electrolyte and molten metal by convective heat transfer (usually through a frozen layer of electrolyte).

It is well established that the different structural forms of carbon exhibit different resistances to the corrosive and degradation forces. Since the type of corrosive processes changes with zone in the cell, it follows that different properties are required in different zones.

The Jointing/Sealing Pastes

The most susceptible component is usually the ramming paste used to seal the container between the pre-formed components (such as the cathode blocks and the sidewalls). This material is usually made from coal-tar pitch combined with either a calcined anthracite or graphite powder. The paste is sufficiently plastic to enable forming and, when heated, it carbonizes to a solid mass. An alternative (albeit with limited use) has been condensation resins that give a high carbon yield on thermal decomposition.

Since the ramming paste is the most susceptible to degradation, a frozen protective layer of electrolyte has been used to protect the sidewall joints (the "big joint"). Because of the delicate heat balance, however, whenever the cells have excess voltage applied through operating disturbances, this protective layer tends to melt and expose the sidewall to the corrosive forces.[4,5] Because of poor process control, sidewall failure was the main cause of early failure.

Carbon Sidewall Wear

Traditionally, the more reactive carbon, when exposed to the electrolyte and at a cathodic potential, wears through four mechanisms:

- Swelling of the carbon through sodium inter-calation. This causes mechanical disruption through (differential) swelling and the effect is worst for less graphitized carbon structures.
- Particle detachment through preferential erosion and the (differential) swelling.
- Formation of aluminium carbide, especially at the metal/electrolyte interface, which dissolves in the more acidic electrolytes.
- Oxidation by air leaks between the steel shell and lining.[5]

Although the nitride-bonded silicon-carbide refractories are also corroded, these are deteriorated at a lower rate because they have an extremely high electrical resistance and, therefore, do not have the electrochemically initiated processes. The (heretofore unpublished) performance comparison in Figure 2 illustrates how the life of the cell was dependent on the sidewall material and the number of operating excursions with high extra voltage at that time. This diagram also emphasizes why the carbonaceous sidewall material has been replaced by silicon carbide.

Cell and Refractory Insulation

From the foregoing, it is evident that the best sidewall insulation is the freeze formed from the electrolyte because it reduces the sidewall corrosion reactions. Although some smelters have attempted to use sidewall insulation, this these days is not an issue.

The insulating refractory underneath the cell needs to be resistant to both the

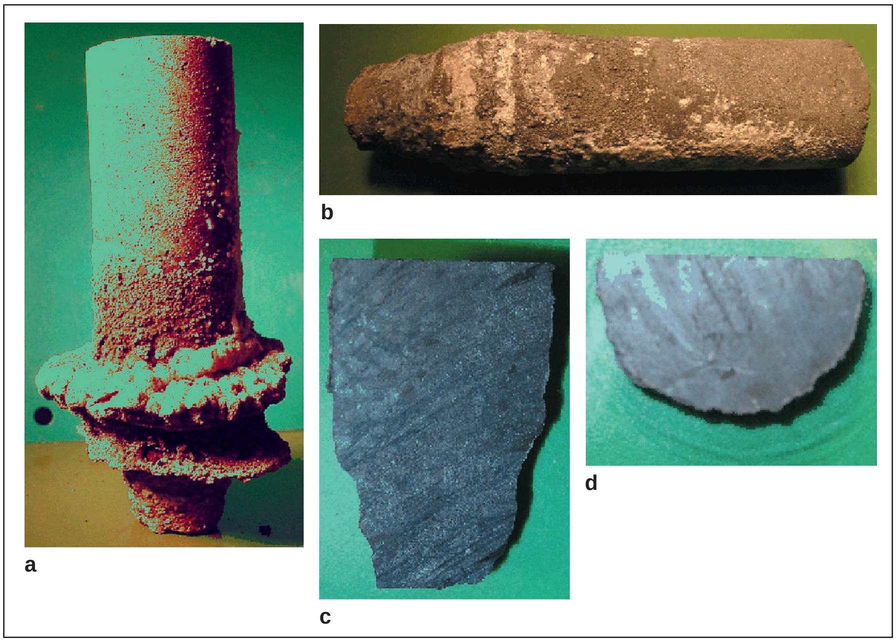

Figure 3. Carbonaceous-cathode test specimens subject to long-term electrolysis: (a) electrolysed specimen; (b) cleaned specimen showing roughened wear and sodium swelling; (c) vertical section; (d) horizontal disk. [10]

molten electrolyte and also molten aluminium, since leakage of both can occur. Typically, two types of materials are used, one with an emphasis on its corrosion-resistance properties against the electrolyte, and the other with an emphasis on thermal insulation. The latter is below the corrosion-resistant refractory. The corrosion-resistant refractory is usually selected for one that will form either a more viscous or a solid reaction product, thus sealing the insulation from further ingress. While they are normally alumina-silicate refractories, the silica content must be controlled because of the potential for thermite reactions between the silica and leaked aluminium.

Cathode Blocks and Their Deterioration

In the earlier era of cells (up to the 1980s), sodium swelling frequently caused heaving and arching of cathode blocks, thus contributing to the cell failure. The problems of cathode heave and sodium swelling have been minimized by the shift toward more graphitic cathode blocks, which take up less sodium.[6] This change has been combined with better designs that prevent the arching, and, thus, can maintain leak-proof cells. If, however, a highly graphitized block is used, and the design and shrinkage of the ramming paste do not match these properties, leakage around the ends of cathode blocks can occur. Thus, matching materials and design becomes a greater challenge.

For high-current intensities, wear is now important,[7] although considerable debate is continuing on the full mechanisms. Until the 1980s, wear was not considered a serious issue, although data established that cathode blocks typically would wear at about 10–15 mm per year. In that era, the electrolyte composition was relatively low in excess aluminium fluoride (less than 8 wt.%).

In more recent years, the following characteristics have been observed for cathode-carbon materials:[8]

- The wear rate accelerates for electrolytes with high aluminium fluoride (and these have exhibited high solvency for alumin-ium carbide, which is formed by a reaction between the aluminium and carbon).
- Cathode blocks high in the more amorphous anthracite carbon exhibit a lower wear rate than graphitic materials.
- The amorphous blocks wear by pitting mechanisms, where some larger particles are typically ejected, as well as general carbide wear.
- For cells with graphitic cathodes operating at high current densities, the rate of wear is accentuated significantly in the high-current density zones.
- All modern cathodes soon become filled with electrolyte, which is usually liquid through most of its depth.

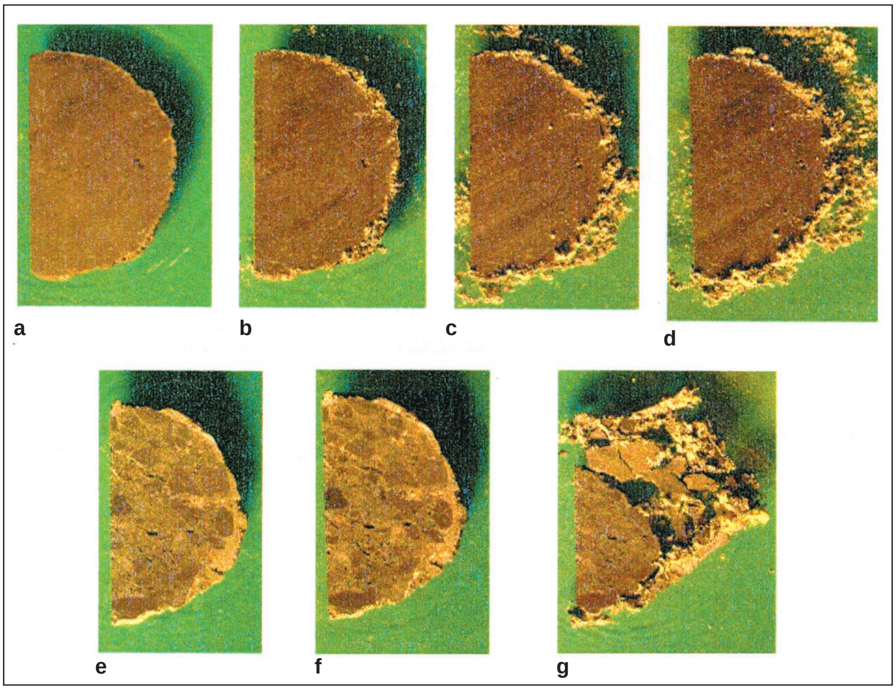

Figure 4. The zone and extent of carbidizing within sections of specimens by the subsequent hydrolysis graphitic specimen after hydrolysis of carbide after electrolysis for (a) 3 days; (b) 14 days; (c) 20 days; (d) 28 days. Antracitic specimen after hydrolysis of carbide after electrolysis for (e) 3 days; (f) 8 days; (g) 14 days.

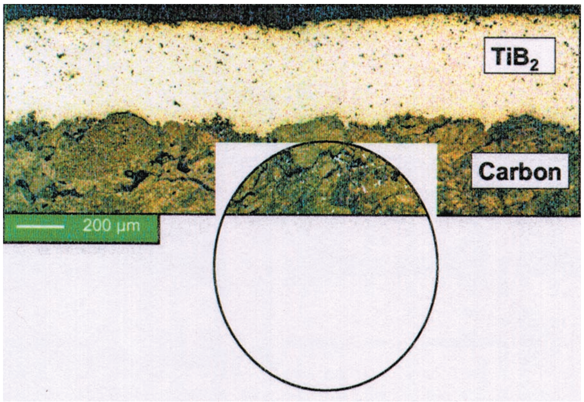

Figure 5. A plasma-coated TiB_2 on a carbon substrate.[12]

While aluminium carbide is accepted as one of the key wear mechanisms, it is inadequate to explain the full wear rate because of limited solubilities, and it does not explain the high-current density wear (if it is surface), or the accentuated tap-hole wear observed by others.

The Role of Carbide and Na(C) in Cathode Wear

Once electrolysis starts, sodium penetrates carbon cathodes rapidly, with the amount of sodium penetrating being greater for the more structurally disoriented carbons. The source of the sodium is from either direct electro-deposition from the electrolyte or, alternatively, co-deposition with aluminium. The phenomena associated with its penetration and uptake can be expressed by the following reaction:

$$\mathrm{Na(Al)} + x\mathrm{C} = \mathrm{NaC}_x \text{ (in C)} \qquad (1)$$

The sodium intercalation causes the carbon to swell, with the extent of the swelling dependent on the amount of sodium. Consistent with the general understanding of wetting phenomena, this penetrated sodium causes wetting of the carbon by the electrolyte, and the pores rapidly fill with molten electrolyte.

Chemical reactions subsequently occur within the carbon, as typified by the following reaction:

$$12\mathrm{NaC}_x + 4\mathrm{Na}_3\mathrm{AlF}_6 = 24\mathrm{NaF} + \mathrm{Al}_4\mathrm{C}_3 + (12x\text{-}3)\mathrm{C} \qquad (2)$$

Other reactions have been proposed and shown to occur, including the formation of cyanides, nitrides, and aluminum.[9] It should be noted that the AlF_3 component of the electrolyte (present as AlF_4^- ions) is the primary reactant in Equation 2, and, therefore, that equation is also variously represented by having AlF_3 or $NaAlF_4$ as reactants with the appropriate NaF-enriched product.

The combination of these reactions used to lead to formation of well-defined crystals of sodium fluoride and delamination or cracking forces through crystallization pressures in the cathode. With the operational shift toward more acidic electrolytes with higher aluminium-fluoride contents, the tendency to crystallize sodium fluoride has been reduced, but simultaneously, aluminum-carbide formation and dissolution becomes more predominant. These modern electrolytes have a lower solidus temperature and, therefore, ionically conducting electrolyte is present within the pores (typically >15% open porosity) at a cathodic potential. Electrochemical processes can occur within the electrified cathode specimen. For example, the electrode reaction:

$$4AlF_6^{3-} + 3C + 12e = 24F^- + Al_4C_3 \quad (3)$$

is energetically most favored and expected to proceed on the more active (thermodynamically) amorphous carbon. Based on the role of sodium, and the impact of carbon structure, one would therefore expect:

- More reaction to occur in porous segments of the cathode.
- The reaction to be more severe in less baked and more disoriented carbons.
- Aluminium carbide to be formed at the carbon interfaces.
- A weakening or delamination in the bonding if solid products, such as aluminium carbide, tended to grow, thus consuming the bonding carbon.
- The higher the current density, the greater the extent of such reactions would be and, hence, the greater the electrochemical potential gradient.

To understand whether these processes contribute to the accelerated cathode wear, Rafiei et al.[10] performed longer-term (>96 h) electrolyses in vertically oriented cathode specimens than were previously applied in laboratory tests. The classical short-term electrolysis tests are insensitive to processes that have either an initiation time or are extremely slow, and therefore do not give sufficiently accurate differences.

By having a vertically oriented electrode, any products within the cathode carbon would be either by the reactions given above or electrochemically formed because of the potential gradient. The non-wetting aluminium formed on the surface readily detaches.

The experimental arrangement gives a higher current density at the lower section and, therefore, would give a gradient in reaction intensities consistent with current density gradients.

As shown in Figure 4, a surface-pitting erosion occurs on the electrolyte specimens. Pitting/erosion increases with current density.

After sectioning the electrolyte specimens and examining them with conventional surface analytical techniques, such as scanning-electron micrography, energy-dispersive x-ray analysis, and x-ray photoelectron spectroscopy, the presence of aluminum carbide on the carbon interface of the bath-filled pores can also be detected. The extent of formation of this carbide and its formation zones can be semi-quantitatively followed by exposing sections to a controlled atmosphere of moist air.

Hydrolysis proceeds via the following reaction:

$$Al_4C_3 + 6H_2O = 3CH_4 + 2Al_2O_3 \quad (4)$$

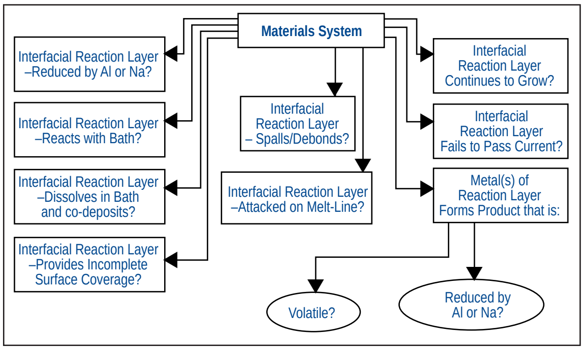

Figure 6. The potential limitations of materials being used as inert anodes.

The growth of the oxide product causes a yellowish powder to be evident, which also causes mechanical disruption of the weak interfaces. This gives a good identification of the zones of carbide formation, while the time for the sample to degrade is linked with the amount of carbide present. From these studies, it has been shown that:

- The carbide is preferentially formed on the bonding carbon.
- The more amorphous carbon shows a greater tendency to react and form carbide.
- The penetration of the electrolyte and material weakening occurs preferentially around the boundaries of the larger particulate material of the composite.
- The rate of formation increases with the applied surface current density.

These trends are also illustrated in various parts of Figure 3 and Figure 4.

Although graphite would be expected to be less susceptible to carbide formation, it is a more uniform product, and the data shows that carbide layers grow just below the surface. The weaker carbon structure can cause physical delamination if the carbide grows as a solid, potentially precipitating out of a mushy electrolyte.

These data emphasize that physical debonding of the grains, which is likely formed at higher current densities, can accelerate the wear of graphite electrodes at high current density.

The materials challenges presented by these degradation reactions are considerable: It is important to develop a long-life material, but it must be of constituents that are electronically conducting. One option might be to reduce the porosity, but this approach must not increase the reactivity of the carbon. Another option may be to use coating technology,[11] which faces the same challenges as those of the drained cathode.

THE DRAINED CATHODE

Because titanium diboride is wetted by aluminium and has extremely low solubility, it has been considered as an alternative material to carbonaceous composites for the cathode lining since the 1950s. Titanium diboride was introduced for its wetting properties in order to lower the cathode voltage drop. The emphasis then shifted to a drained-cell configuration that would avoid the loss of efficiency associated with the magnetic stirring of the metal pad. At that time, with the cells generating excessive heat, titanium diboride was expected to substantially reduce inter-electrode distance, thus lowering the energy requirements and increasing the efficiency.

Subsequently, high-current efficiencies have been obtained through magnetically compensated designs, process control, and optimized bath chemistry. Still, the desire to reduce the inter-electrode distance continued, even though such reductions would not maintain the necessary heat balance of the cell.

Interest in wetted and drained cathodes continued, however, as new designs became available.[11]

Because of the high cost of the titanium diboride and the refractory nature, the emphasis shifted to using composites. Four different approaches toward implementation of composites have been attempted:

- Plasma spraying of titanium diboride onto the carbon surface (Figure 5).[12]
- Use of a colloidal-alumina bonding for titanium-diboride particles.[13]
- Use of titanium diboride and titanium-diboride composite tiles, fixed to a carbon substrate.[14]
- Carbon-bonded titanium-diboride composites fixed to the carbon substrate.[11]

The colloidal-alumina bonded titanium-diboride matrix has been tested in a larger number of cells than any other coating composite, but has not been adopted widely at this point. This composite has the following advantages:

It can be applied in coatings to give layers of varying thickness to in excess of 2 mm; the thickness of the layer, combined with the solubility product of the titanium diboride in the aluminium, predict a long expected life of the coating; laboratory tests and plant performance tests have shown that the use of this material reduces the rate of sodium intercalation considerably.[15]

Whether the reduced sodium expansion is an advantage is yet to be established—with inadequate expansion to counter the shrinkage of the adjacent ramming paste, there would be potential for leakage of electrolyte. Its long-term performance is dependent on it being totally wetted and covered by aluminum, preventing access of the electrolyte to the bonding material, since the bonding aluminous material is porous and has a high solubility.

The difficulty with the tiling approach has been to maintain adherence of the tiles. Layers of aluminum carbide tend to grow between the tile and the carbon substrate, not only weakening the carbon but creating crystallization pressure which leads to debonding. Independent studies have shown that aluminum-carbide formation cannot be prevented if aluminum comes in contact with the carbon substrate (even though the reaction rate is low), and carbide formation can be accelerated with the presence of electrolyte. The latter is due to a galvanic growth mechanism. In the extreme case, large amounts of aluminum carbide can be formed underneath composites in just a few months and delamination processes are then evident.

An advantage of the carbon-bonded titanium-diboride composites is that the carbide corrosion reaction is at the surface. If the carbide forms and dissolves in the electrolyte at a slightly faster rate than the titanium diboride dissolves in the metal, an interfacial titanium diboride/aluminum slurry would form which has high viscosity and performs adequately.

The foregoing shows that several potential problems need to be addressed to develop wettable carbon cathodes suitable for long-term commercial applications. These are as follows:

- Aluminium-carbide formation either within the composite or beneath the composite layer will inevitably cause problems leading to delamination.
- Any porosity in the material must be filled with aluminium rather than electrolyte, since the electrolyte will accelerate growth of solid products.
- Bath penetration must be prevented at the interface between the composite and any carbon substrate. Alternatively, carbon substrate should be avoided.

Thus, serious material challenges remain.

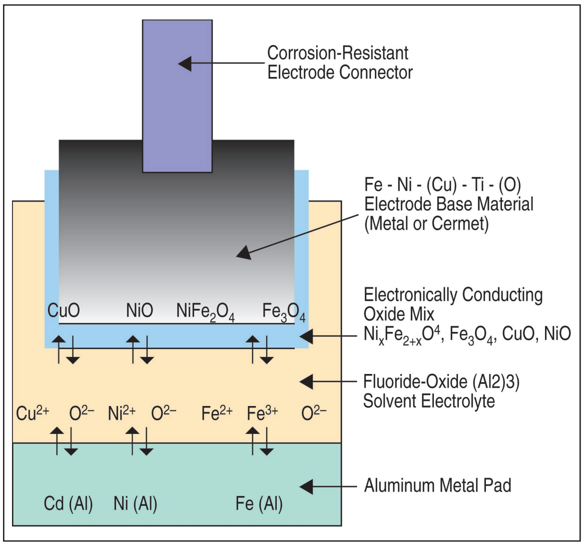

Figure 7. A schematic representation of the key elements of an inert-anode Hall-Héroult cell.

DEVELOPING INERT ANODES

Figure 6, which illustrates a materials systems selection approach, highlights criteria that can render a material to be unsuitable for production of an inert anode.[16]

The motivations for producing an inert anode are:

- To eliminate work practices associated with anode change.
- To eliminate all costs associated with the carbon anode.
- To eliminate carbon-dioxide emissions.

Thermodynamically, one volt more is required. Although some have argued that the oxygen-evolution reaction had lower polarization, and hence the voltage increase would be less, in fact, the anode polarization is manifest as heat and therefore, where cells are heat balance limited.[2]

Some opponents of inert anodes argue that carbon-dioxide emissions would increase by evolving oxygen, since the extra voltage would be generally supplied by carbo-thermally generated power, and that occurs at a lower efficiency than the carbon-anode reaction (which is more than 80% efficient).

For an inert anode to succeed, it must not only withstand the corrosive processes associated with the first column of properties listed in Figure 6, but it must also maintain electronic conductivity and not increase cell resistance too extensively.

Because of its high oxidation potential, the reaction layer for electrolysis will be some form of oxide. The range of oxides that are conducting is reduced to non-stoichiometric spinels and oxides of the metals that exhibit multiple valence.[17] Although cerium and tin oxides were favored earlier, mixed oxides involving iron, copper, nickel, and aluminum are now under investigation.[2,18,19]

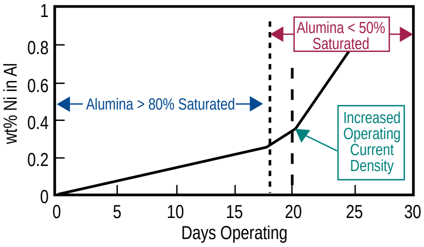

Figure 8. The pick-up of nickel by the aluminum product in an inert anode cell under various cell conditions.[19]

The following three approaches have been used in developing the latter group of mixed oxides:

- Applying an oxide coating to a metal substrate.
- Making a cermet of metal and oxides.
- Using a metal and chemically or electrochemically forming the oxide surface.

Until now, no interfacial oxide has been found that does not dissolve in the electrolyte. Other characteristics of mixed oxides include:

- No stable, electronically conducting oxide has been formed from a pure metal or pure oxide.
- The solubility of all oxides is determined by both temperature and the oxide concentration, buffered by the dissolved alumina.
- All dissolved oxides are reduced by aluminum.

Therefore, rather than developing an inert anode, interest is focused on developing a long-life anode.

Sadoway has been a strong proponent of alumina-based conducting oxide interfaces, especially using copper to give the interfacial electronic conductivity.[20] This is because the only contaminant that would then arise would be the secondary metal (presumably the copper). Others, such as the Cu-Fe-Ni systems, can have a complex mixture, and, therefore, balancing their rates of solubility to the rate of reformation of the surface film becomes a complication.

The structure of an inert anode based on Cu-Ni-Fe is illustrated in Figure 7.

Present Status of Inert Anodes

In 1986, Alcoa released several papers on its inert-anode development. The company's more recent patents, as well as other major developments, have varied slightly from the information disclosed at that time. Inert anodes under development have the following features in common:

- Nickel and iron are the main metallic elements in proportions of Ni:Fe :: 0.7 to 1.3
- A metallic phase is behind the oxide surface. This may be in the presence

of oxides, forming a cermet.

- Copper and titanium are sometimes present in the metal/cermet.
- The main active surface oxide phase is $Ni_xFe_{2+x}O_4$ and Fe_3O_4 with some $NiFe_2O_4$ and oxides of the pure metals present at the interface.
- While the oxides and the metals used have a low solubility in the electrolyte, their dissolved species are readily reduced by the aluminium that is present at the electrolyte/metal interface.
- All electrodes tested until now corrode at various rates.
- They have a tendency to passivate.

The most detailed testing[18,19] has shown that the corrosion rate of different metals differs from the proportions in which they are present in the cermet or metallic phase. These findings and Figure 7 show that the challenge is to replenish the surface at the same rate at which it is corroded.

Figure 8 illustrates the effect of the corrosion on the metal quality, demonstrating that the corrosion rate probably increases with time, causing selective dissolution of the iron. More importantly, the corrosion rates change with process conditions and the relative changes of different species are not the same. Operating challenges result since, as shown in Figure 8, the corrosion rate is sensitive to both current density and also the oxide concentration in the electrolyte. When the oxide concentration drops below saturation and the current density gets high, the anode reaction changes to formation of the metal fluorides.

The challenges of the materials development, therefore, are to maintain the corrosion rate, and therefore, metal contamination, at sufficiently low levels, and to allow the diffusion from the cermet/metal to the active surface at a rate that is equal to the rate of corrosion.

Fulfilling these challenges will be a major task. The selective depletion of metals behind the interface can lead to increased electrical resistance. Growth of the surface film through an imbalance can lead to an increased electrical resistance and an imbalance in the current distribution between electrodes.

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