INERT ANODES: AN UPDATE

R. P. Pawlek
TS+C
Avenue du Rothorn 14
CH – 3960 Sierre

Abstract

During the last few years the development of inert anodes for the primary aluminium industry has advanced considerably. This update reviews results of tests on (1) anodes made of ferrites (Ni, Co and Zn) alone or in combination with nickel oxide and copper leading to the final composition $Ni_{1-x-y}Fe_{2-x}M_yO_4$, where M is zinc and/or cobalt, x is from 0 to 0.5 and y is from 0 to 0.6; (2) anodes made of oxides (Ni, Li, Sn, Sb, Cu) alone or in combinations; and finally (3) anodes made of combinations of metal powders including Ni, Al, Fe, Cu and Zn. The studies examined the solubility in cryolite alumina melts, but also performance in electrolysis tests from which the results are discussed. Laboratory solubility tests revealed that compositions with limited corrosion (1-2 cm/y) exist and could be successful not only in laboratory but also in industrial cells.

Introduction

The development of inert anodes for the primary aluminium industry has been reviewed several times[1-15] during recent years. The primary reason is that inert anodes eliminate production of greenhouse gases during the electrolysis process and evolve oxygen instead. Benedyk [11] and de Nora [15] have proposed the following criteria, which inert (or non-consumable) anodes should fulfil:

- an erosion rate of less than 10mm per year at a normal current density of 0.8 Acm^{-2}
- polarization voltage of less than 0.5V at $0.8Acm^{-2}$
- continuous voltage drop no worse than carbon anodes
- robust properties to survive in normal plant conditions
- stability in oxygen at 1,000°C
- resistance to fluoridation
- thermal stability with adequate thermal shock resistance
- adequate mechanical strength
- low electrical resistivity
- low overvoltage for oxygen evolution
- electronically conductive
- no lowering of metal quality standards
- easy, stable electrical connections
- environmentally safe
- improved health and safety
- lower cell capital cost
- retrofit potential
- improved cathode life
- low cost and easy fabrication into large shapes

All these criteria are very difficult to fulfil. However, according to Welch et al [12] the reasons for developing an inert anode are to eliminate work practices associated with anode changes, namely;

- elimination of all costs associated with carbon anodes and
- elimination of carbon dioxide emissions

Of special interest recently has been the compilation of a series of papers dealing with the material challenge [14], the energy balance of electrolysis cells [13], metal purity [16], and the economic aspects [17] of producing inert anodes. The following update is a continuation of a previous review [1] and reviews of previously un-referenced literature.

Oxides

Oxygen-evolving, non-consumable anodes are being developed for use in industrial aluminium production. Ceramic type electrodes dissolve slowly into the electrolyte, a process governed by mass transport conditions. According to Keller et al [18], the life of all-oxide or cermet anodes used in practical aluminium electrolysis will depend largely on the rate of dissolution of the electrode constituents into the electrolyte. This depends mainly on the reduction rates for the anode components at the cathode.

CeO_2

The solubility reaction of cerium oxide into cryolite melts was studiedby Dewing et al [19], who investigated solubility as a function of the oxygen pressure, alumina content of the melt and the aluminium fluoride content of the melt. They found that the cerium in solution is exclusively Ce^{3+}. The dominant species is CeF_3, where the CeF_3 is probably complexed as Na_2CeF_5. There is no evidence for the existence of CeOF [20]. The control of oxygen pressure is important in measuring the solubility of an oxide which has more than one oxidation state. Practical experience when using CeO_2-coated anodes as oxygen-liberating electrodes, has shown that the solubility varies less with alumina concentration than expected. The absence of Ce^{4+} in solution is also favourable; however if Ce^{3+} and Ce^{4+} coexisted, then an oxidation-reduction cycle could lead to poor current efficiency.

Cr_2O_3 – NiO – CuO

On a laboratory scale, Pietrzyk and Oblakowsky [21]examined an inert anode with the composition 62.3 wt% Cr_2O_3, 35.7wt% NiO and 2wt% CuO, which had a bulk density of 3.66 gcm^{-3}. The electrolyte contamination was found to be 0.0008 wt% Cr, 0.0005 wt% Ni and 0.0222wt% Cu. The rate of dissolution was lower than one centimetre per year and metal contamination was 0.3wt%. A mass transfer anode dissolution mechanism was experimentally confirmed. The Ni in the electrolyte reaches a stable value and does not contribute to the time-dependent corrosion. The concentration in the metal becomes linear with

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time provided that the concentration in the electrolyte remains constant. The dissolution of Cr does not depend on the concentration already found in the bath. A saturation solubility was not reached after 10 hours.

$NiFe_2O_4$ and $CoFe_2O_4$

Metal oxides, due to their high thermodynamic stability and favourable electro-catalytic activity for oxygen evolution, are tested as anodes for the electrolysis of alumina. Oxygen is liberated at the anode and is environmentally friendly. In this respect, Augustin et al [22, 23] investigated the behaviour of nickel and cobalt ferrites. Laboratory tests were run, and the corrosion stability in molten cryolite electrolyte was found to be satisfactory.

NiO-Li_2O

The rate of corrosion of electrodes based on NiO-(2.5wt%)Li_2O was determined by Zaikov et al [24] by weighing the sample during the experiment after placing it in the melt. The rate of corrosion of oxide electrodes depends on the preparation parameters. Increasing sintering time and temperature decreased the corrosion rate. The main focus of attention must be the physical and structural properties of the formed oxide bodies. Samples had been tested in alumina-saturated electrolyte for 4.5 hours under electrolysis conditions [25]. After the test, the anode was in good shape without any visible changes.

Ni_2O_3, NiO

Research on nickel oxide electrodes was performed by Wu and Mao [26]. They prepared five kinds of Ni_2O_3-based and NiO-based cermet materials which they used in aluminium electrolysis tests. They found that during sintering, Ni_2O_3 was transformed into NiO, thus resulting in anode cracking. In corrosion and electrolysis tests, Du [27] determined the thermal shock and corrosion resistance of the test anodes. The measured corrosion rate was less than 3 cm per year, which completely met their requirements.

SnO_2

The solubility of SnO_2 in cryolite melts and its dissolution mechanism have been examined several times. Haarberg et al [28] found the SnO_2-solubility to be 0.08wt% in pure cryolite at 1,035°C. It will be higher under reducing conditions. They expected increased solubility due to the presence of divalent or even mono-valent tin. The dissolved species can be reduced to metallic tin at the aluminium cathode. However, the electrochemical behaviour was examined more intensively by Issaeva et al [29] and Yang and Thonstad [30]. Cyclic voltammetry and potential step measurements were performed on platinum, gold and glassy carbon electrodes. The voltammograms showed peaks associated with the presence of two oxidation states in the melt i.e. Sn^{2+} and Sn^{4+}. In melts without oxides, volatile species such as SnF_2 and SnF_4 were formed anodically. The presence of dissolved alumina was found to stabilize the dissolved tin species. The anodic dissolution of tin demonstrated the co-formation of divalent and tetravalent tin in cryolite-alumina melts.

The preparation of tin oxide doped with copper oxide was examined by Dolet et al [31]. They observed fast and high densification rates in air at 1,150°C. Copper dissolved into the SnO_2 structure. They prepared highly densified 0.99 SnO_2-0.01CuO-based ceramics with additions of antimony, tantalum or niobium oxides. Las et al [32] observed that the electrical properties of tantalum and niobium-doped ceramics are grain-boundary controlled at least at low temperatures. Antimony-doped materials have a different electrical behaviour due to the presence of a segregation layer of antimony which inhibits grain boundary effects.

Of greatest interest, has been the composition: 96 wt% SnO_2 + 2 wt% Sb_2O_3 + 2 wt% CuO. First of all, Galasiu et al [33] developed a method to increase the thermal shock resistance by adding pre-sintered, ground material to the bulk composition. They also found [34] that the higher the sintering temperature, the better the mechanical properties. Then they varied the amount of the Sb_2O_3 and CuO-dopants [35].At dopant concentrations of more than 2 wt% the sintering behavior and electronic conductivity decreases while the activation energy for the conductivity increases.

Popescu and Constantin [36] developed a method to fix tin oxide bodies to a metallic conductor, before Galasiu et al [37] performed electrolysis tests in 200 A laboratory test cells for a maximum duration of 100 hours. During this time the test electrodes were completely destroyed. They observed migration of copper to the surface of the inert anode and dissolution of copper into the electrolyte during electrolysis causing anode corrosion. This phenomenon was confirmed by Vecchio-Sadus and co-workers [38], who examined the corrosion behaviour in detail. They electrolysed anodes for 90 minutes at an anodic current density of 1 Acm^{-2} and selected electrolyte compositions so as to keep the bath temperature between 830-975°C. The anodic corrosion rate at a bath ratio of 1.5 and at 975°C was 12.5 $mgAh^{-1}$, while the anodic corrosion rate at a bath ratio of 0.74 and at 830°C was 6.5 $mgAh^{-1}$. A four-fold increase in corrosion rate was observed at open circuit, thus demonstrating the protection which oxygen evolution provides during electrolysis. Besides the depletion of copper from the anode, they saw a build-up of an alumina-rich surface layer under certain conditions. Pietrzyk and Oblakowsky [21] determined the corrosion rate to be less than 1 cm per year with a metal contamination of about 0.3 wt%, with tin reaching saturation solubility in the bath after 8 hours.

On laboratory scale, Popescu and co-workers examined the current efficiency systematically. Their anode composition was 96 wt% SnO_2 + 2 wt% Sb_2O_3 + 2 wt% CuO. They determined current efficiency by measuring the total amount of oxygen evolved at the anode, and examined the influence of temperature, current density and interpolar distance [39], as well as the influence of electrolyte composition [40] and the behaviour during an anode effect in [41].

The influence of silver oxide additions to tin oxide-based inert anodes on the electrical and chemical properties concluded Galasiu's experiments [42]. Best results were obtained with the following anode composition: 96 wt% SnO_2-2wt% Sb_2O_3-2 wt% Ag_2O. This composition has the lowest electrical resistivity, but the best corrosion resistance in cryolite-alumina baths.

ZnO

Besides inert anodes based on SnO_2, Galasiu et al [43,44] also tried ZnO as an inert anode material adding dopants such as 2 wt% SnO_2, 2 wt% Sb_2O_3, 2 wt% CuO, 2 wt% Fe_2O_3, 2 wt% Bi_2O_3, 1 wt% Cr_2O_3 and 1 wt% ZrO_2. First results look promising with the best dopant being ZrO_2. Dewing et al [45] found the dissolution mechanism to be:

$$3ZnO + 2AlF_3 \rightarrow ZnF_2 + Al_2O_3.$$

$ZnFe_2O_4$

Zinc ferrite was used as an inert anode material by Yu et al [46]. Zinc ferrite materials are corrosion resistant under anodic polarization. The highest corrosion rate appears at an anodic current density of 0.5-0.75 Acm^{-2}. High anodic current densities (more than 1.5 Acm^{-2}), high alumina bath concentrations and low molar bath ratios are the most important factors for using inert anodes.

Cermets

$NiFe_2O_4$ + NiO + Cu

The dissolution mechanism of elements from the anode into the electrolyte and from the electrolyte into the aluminium pad have been examined during recent years. Chin et al [47] dissolved nickel oxide, iron oxide and elemental copper, frequent constituents of inert anodes, in alumina-saturated cryolite melts. They observed that the transfer of these elements from the fluoride melt into the aluminium was complete and that nickel, iron and copper were reduced and alloyed into aluminium in non-electrolytic experiments. This indicates that anodes made from these components are not completely inert with respect to molten cryolite in contact with aluminium.

Olsen and Thonstad [48] tested various compositions of nickel ferrite cermets in laboratory cells, using conventional electrolytes for 50 hours and a current density of 0.8 Acm^{-2}. In the metal product they found typically 2,200ppm Fe, 400ppm Ni and 450ppm Cu with anode corrosion rates of 0.12 cm per year. Xiao et al [49] observed that the normal corrosion is due to chemical dissolution of the anode material and to reduction of the corrosion products into the cathode metal. The corrosion rate increased with increasing cathode surface. At potentials higher than about 2.4V, the anodes showed catastrophic corrosion which the authors ascribe to decomposition of the anode materials by depletion of alumina at the anode surface provoked by low alumina bulk concentration and/or high current density. The mass transfer from oxide anodes into the melt and from there into the metal was then examined by Hives et al [50] and by Pietrzyk and Oblakowski [51]. As described by Chin et al [47] these authors also found that the electrolyte is close to saturation with respect to these species and the rate-determining step of the anode corrosion process is the alloying of the species into the aluminium, where the stability of the elements is in the order Ni>Fe>Cu. If the mass transfer from the electrolyte into the metal could be decreased, this would also decrease the contamination level of anode constituents in the deposited metal [52].

Olsen and Thonstad [53] examined the corrosion behaviour of ferrite anodes in 50 hour electrolysis tests. They found that nickel exhibited significantly lower mass transfer coefficients than iron and copper. The extrapolated corrosion rates of the anode ranged between 1.2-2.0 cm per year, which is acceptable from an industrial point of view. Blinov et al [54, 55] examined the corrosion mechanism independent of bath temperature. Samples with compositions developed by Alcoa ($NiFe_2O_4$-18NiO-17Cu) were tested for more than 130 hours and at an anodic current density of 0.2 Acm^{-2}. The corrosion rate at a bath temperature of 800°C was determined to be less than 10^{-3} $gcm^{-2}h^{-1}$ and at a bath temperature of 950°C was more than 8 x 10^{-3} $gcm^{-2}h^{-1}$. Even at low corrosion rates of anodes during electrolysis, the aluminium produced had fairly high levels of impurities, exceeding standard specifications. The corrosion rate of inert anodes can be reduced significantly by using low-temperature electrolytes.

The solubility of NiO and $NiAl_2O_4$ in alumina-cryolite melts was examined by Lorentsen et al [56] in laboratory experiments. They found the NiO stable solid phase to be NiO at low alumina activities and $NiAl_2O_4$ at high alumina activities, and measured the Gibbs energy of formation for $NiAl_2O_4$ as –28.6 kJ per mol. The solubility of $NiAl_2O_4$ in alumina saturated melts increases with increasing temperature. The solubility of FeO and $FeAl_2O_4$ was measured by Jentofsten et al [57]. FeO was the stable solid phase at low alumina concentrations, while $FeAl_2O_4$ was stable at high alumina concentrations. They determined the Gibbs energy of formation for $FeAl_2O_4$ at 1,020°C to be –17.6 kJ per mol. The solubility of $FeAl_2O_4$ in alumina saturated melts increased with increasing temperature. According to Dewing and Thonstad [58] all iron oxides (FeO, Fe_2O_3, Fe_3O_4 and $FeAl_2O_4$) dissolve in cryolite-alumina melts to give solutions containing both Fe^{2+} and Fe^{3+}. The factor controlling the Fe^{2+}/Fe^{3+} ratio is the oxygen pressure. However, the anode and anode gas of an industrial Hall-Héroult cell appear to be insufficiently oxidizing to cause significant conversion of Fe^{2+} to Fe^{3+}. The authors account for an anomaly in the liquidus diagrams for FeF_2 – Na_3AlF_6 and FeO - Na_3AlF_6 in terms of a solid solution of FeF_2 in cryolite.

$NiFe_2O_4$ + NiO + Cu + Ag

Alcoa improved its composition of inert anodes by adding silver in order to increase electrical conductivity. For the manufacture of inert anodes, a mixture comprises nickel and iron oxide with about 50-90 wt% and a mixture of copper and silver and/or silver alloys preferably up to 30 wt% [59]. The alloy or mixture of copper and silver comprises particles having an interior portion containing 90 wt% copper and 10 wt% silver and an exterior part containing at least 50 wt% silver and less than 10 wt% copper [60]. The starting material for the manufacture of inert anodes comprises a mixture of copper and silver powder with a metal oxide powder containing about 51.7 wt% NiO and about 48.3 wt% Fe_2O_3. About 83 wt% of the NiO and Fe_2O_3 powders are combined with 17 wt% of the copper and silver powder [61]. Reduced bath temperature is preferable in order to improve the corrosion resistance of the electrodes. For a cell operated at 920°C, the preferred molten bath composition is: bath ratio 0.8-1.0, 6 wt% CaF_2 and 0.25 wt% MgF_2. The cermet composite preferably includes an alloy phase and at least part of the ceramic phase has a spinel structure [62]. A solid conductor of oxide ions coats the anode. The solid conductor comprises zirconia stabilised with yttria [63]. The metal base of the inert anode comprises besides copper and silver another noble metal such as palladium [64].

An inert anode resulting in low impurity levels in the aluminium product comprises Fe_2O_3, NiO and ZnO and further comprises at least one metal selected from Cu, Ag, Pd, Pt and Au. The inert anode follows the formula $Ni_{1-x-y}Fe_{2-x}M_yO_4$, where M is Zn and/or Co, x is from 0 to 0.5 and y is from 0 to 0.6 [65]. The aluminium product is said to contain less than 0.18 wt% iron, a maximum of 0.1 wt% copper and a maximum of 0.034 wt% nickel. Besides oxides of nickel and iron, the inert anode may include zinc oxide [66] and cobalt oxide [67]. More generally the composition of the inert anode follows the formula $Ni_xFe_{2y}M_zO_{(3y+x+z)\ +/-b}$ [68] with M being at least one metal selected from Zn, Co, Al, Li and Cu; x is from 0.1 to 0.99; y is from 0.0001 to 0.9; z is from 0.0001 to 0.5; and b is from 0 to about 0.3.

Just recently Alcoa announced that they had delayed deployment of new inert anodes due to thermal cracking problems and issues with electrical connections [69]. Experiments are being performed in an Alcoa smelter in Italy and in September 2001, Alcoa hope to have a full commercial pot operating with inert anodes at a U.S. plant. Alcoa is increasing production capacity of inert anodes to a level corresponding to one pot every 1.5 days. They hope to have one full potroom operating in 2002. Alcoa plans to begin converting their smelters to inert anodes within 2-3 years, conforming to plans elaborated with the U. S. Department of Energy [70]. Part of the engineering development involves numerous tests on the anodes to examine cracking and connection problems. At the time of writing, the longest period Alcoa had operated inert anodes was 300 hours (12.5 days). Alcoa expects to run inert anodes continuously in excess of 6 months to be confident about long term performance.

Metals

Al-Cu alloy

Sadoway [14] believes that metals offer the best potential for inert anode materials. Hryn and Pellin [71, 72] proposed a dynamic anode consisting of a cup-shaped metal alloy vessel filled with a molten salt that contains aluminium. A possible alloy is copper with 5 to 15 wt% aluminium. In the presence of oxygen, aluminium on the metal anode's exterior surface forms a continuous alumina film that is thick enough to protect the anode from chemical attack by cryolite during electrolysis and thin enough to maintain electrical conductivity. However, the alumina film is soluble in cryolite, so it must be regenerated in-situ. Film regeneration is achieved by transport of aluminium from the anode's molten interior through the metal wall to the anode's exterior surface. The transported aluminium oxidises to alumina in the presence of evolving oxygen to maintain the protective alumina film. Periodic aluminium addition to the anode interior keeps the aluminium activity in the molten salt at the desired level.

Ni-Al-Fe-Cu-X Alloys

Stable alloys made of nickel, aluminium, iron and copper were for a long time, an interesting field of research. One way to manufacture such metal alloys was micropyretic synthesis, for which Submarian et al explored the combustion conditions [73]. Inert anodes containing the above mentioned metals were manufactured by combustion synthesis [74] and optional doping elements in amounts of 60-80 wt% nickel, 3-10 wt% aluminium, 5-20 wt% iron, 0-15 wt% copper and 0-5 wt% of one or more of chromium, manganese, titanium, molybdenum etc. The combustion synthesis produced metallic and intermetallic phases. A composite oxide surface is produced in-situ by anodic polarisation of the micropyretic reaction product in molten fluoride electrolyte containing dissolved alumina or by high-temperature treatment in an oxidizing gas [75]. It was reported [76] that best results were obtained with an anode composition Ni-Al-Cu-Fe-X which during electrolysis transforms to a Ni(Fe) porous core and a dense mixed oxide and ferrite on the surface. This anode material evolves oxygen during electrolysis.

After extensive trials, Sekhar et al [77, 78] found the optimal composition to be Ni-6Al-10Cu-11Fe-3Zn (wt%). Anode blocks manufactured micropyretically out of this composition consisted of porous Ni, a Ni_3Al intermetallic core and a mixed oxide surface layer consisting mainly of nickel oxide, nickel zinc ferrite and zinc oxide. Metals such as tin, silicon, cerium or zinc were added in order to decrease the corrosion rate of the inert anode [79]. A steady state between oxidation and dissolution at the inert anode surface was suggested. Zhang [80] used metallic inert anodes, coated with cerium oxide, which resulted in stable cell voltage and very low corrosion rates.

Non-carbon metal-based inert anodes can be made more high-temperature resistant, electrically conductive and electrochemically active with a multilayer surface coating [81]. The surface may be rendered moreelectrocatalytically active when coated with an electrocatalyst [82] such as iridium, palladium and platinum. The surface can be rendered more electronically conductive by coating with a slurry comprising a polymeric carrier oxide and an electronically conductive oxide coating [83]. The applied slurry is then solidified and attached to the substrate by heat treatment to form an adherent, protective, predominantly oxide-containing coating. The active constituents of the coating are oxides such as for example spinels or perovskites, in particular however, ferrites [84].

An anode having a metallic anode body that self-forms during normal electrolysis with an electrochemically active oxide-based surface layer was then proposed [85]. The rate of formation of the surface layer/anode body interface is substantially equal to its rate of dissolution at the surface layer/electrolyte interface, thereby maintaining its thickness substantially constant. Such inert, non-carbon anode electrolytic cells were developed [86, 87]. In one case the electrochemically active anode surfaces are in a coplanar arrangement [86]. The anode members are spaced apart by inter-member gaps forming flow-through openings for the circulation of electrolyte driven by the escape of anodically-evolved oxygen. In the other case, The electrolysis cell is equipped with a drained cathode and operates at a temperature of 730°C to 910°C without formation of a crust or ledge of solidified electrolyte [87]. The electrolyte is substantially saturated with alumina, particularly on the electrochemically active anode surface. Metal anodes with an oxidised surface demonstrate the potential for use as an electrode, however, long-term performance has not yet been demonstrated in an operating environment [88].

Ni-Fe

During the development of Ni-Fe alloys as inert anode materials, Duruz and de Nora [89] proposed a metal-based core structure of low electrical resistance, coated with a series of superimposed, adherent conductive layers. These layers constitute a barrier impervious to mono-atomic oxygen and molecular oxygen; one intermediate layer on the oxygen barrier which remains inactive in the reactions for the evolution of oxygen gas; and one electrochemically active layer for the oxidation reaction of oxygen ions present at the anode/electrolyte interface into nascent mono-atomic oxygen.

Duruz et al [90] proposed this electrochemically active transition metal oxide layer to be a hematite-based layer. The cell operation temperature is required to be sufficiently low to limit the solubility of iron species in the electrolyte. The inert anode body was then proposed to be an iron-nickel alloy body [91], whose surface is oxidised to form a coherent and adherent outer iron oxide-based layer. To reduce erosion, the anode may be kept chemically stable during cell operation by maintaining a sufficient amount of dissolved alumina and iron species in the electrolyte to prevent dissolution of the protective oxide layer on the anode. This protective oxide can be formed on the metal surface before cell operation by heating the iron-nickel anode body in an oxygen-containing atmosphere at a temperature which is preferably more than 100°C higher than the operating cell temperature [92]. This electrochemically-active oxide-based surface layer may also self –form during normal electrolysis [93] whereby the rate of formation of the layer is substantially equal to its rate of dissolution at the surface layer / electrolyte interface, thereby maintaining its thickness substantially constant.

In order to render the metal anode surface more corrosion resistant, Duruz and de Nora [94] proposed to manufacture the nickel-iron anode body such that the metal surface has a nickel-rich outer portion filled with iron oxide containing inclusions. The typical anode was a Ni-30 wt% Fe alloy [95], which was pre-oxidized for 30 minutes at 1,100°C in air to form a protective oxide film. This anode was used in a 72-hour test at a bath temperature of 850°C and at a current density of 0.6 Acm^{-2}. The bath composition was cryolite with an excess of more than 20% AlF_3 and about 3 wt% of alumina. In order to control low alumina concentrations in low temperature baths, Crottaz et al [96] developed a special alumina sensor for the analysis of high AlF_3 electrolytes. During a meeting, de Nora [15] presented results of tests performed in 100 A, 1 kA and 20 kA drained cathode electrolysis cells. Iron contamination in the aluminium product was much less than 0.5 wt%, and this could be reduced by decreasing bath temperature. Only very little nickel contamination was found in the metal as this remains in the metallic anode core.

Oxide Ion Conducting Membrane

A novel non-consumable anode for the electrowinning of aluminium was developed by Rapp [97, 98]. This anode consists of a thin, dense oxide-ion conducting membrane with an electrocatalytic porous internal anode where reformed natural gas is electrochemically oxidized. This concept could potentially reduce carbon dioxide emissions by at least 50% as compared to the current carbon anode, and also eliminate other greenhouse gases at the smelting step. The operation of the new cell requires about one-third less electrical power, further reducing energy requirements. The anode is a thick closed-end ceria-based electrolyte tube coated internally with a porous Ni-CeO_2 slurry and provided with hydrogen or natural gas as reducing gas. The US Department of Energy supports the development of this novel anode with an investment of US$1.7m [99, 100].

Cell design

In order to use an inert anode in combination with a wettable cathode, new cell designs for the production of aluminium seem to be necessary. Electrolysis cells with vertical bipolar inert anodes/wettable cathodes were proposed by La Camera et al [101]. Beck and Brooks [102] propose the use of copper, nickel and iron composite bodies used as vertically arranged electrodes in aluminium reduction cells, and Brown [103] also proposed the concept of a vertical electrode cell for the production of aluminium with reference to current research. Low-temperature electrolysis allows non-consumable metal-alloy anodes to show promise in laboratory cells. With such cells, commercial purity aluminium can be produced with promising high current efficiency.

Future

In an effort to concentrate forces in order to develop inert anodes by 2020, a road map was established in cooperation with the Aluminum Association and the US Department of Energy [104]. The North American aluminium industry is required to consider the desirability of joint efforts in inert anode technology research, as well as possible mechanisms for funding and directing the research efforts. The industry should also consider the government's role in the overall effort to develop inert anode technology. Finally, the industry should consider examining other elements of advanced cell design that could complement inert anode technology and enhance its benefits. However, even before this date it could be possible to have aluminium electrolysis pots equipped with inert anodes and wettable cathodes.

As reported by van Leeuwen [99, 105], such pots could be in operation in commercial scale by 2002 and the industry could adopt such new technology by 2005. It was reported that the shut down Troutdale smelter of Alcoa could be equipped with inert anodes up to the year 2003 [106] and commercialisation could start also in the same year [107, 108]. Even Pechiney wants to use Alcoa's technology for inert anodes, once the development has proven successful but thinks this will take another five to ten years [109]. Alcoa believes the new technology will not consume more energy than the current Hall-Héroult process. Observers expect Alcoa will need to perfect its technology on a larger scale before starting to install inert anode technology in other smelters. Cost savings in constructing a greenfield smelter could be significant [110] and perhaps as much as 35% [99, 108].

Conclusion

Much laboratory work has been performed during the last few years, especially to investigate the solubility of inert anode composites (metals, oxides and cermets) into commercially used fluoride electrolytes. Alcoa and Moltech are the two companies that have achieved some success in the development of inert anodes. Alcoa uses cermet composites probably as described in [66-68], but still has difficulties in manufacturing anodes due to thermal shock and must solve the electrical connection between the cermet and bus bar [69]. The longest period inert anodes have been operated is not more than 12.5 days but Alcoa expects to run inert cermet anodes continuously in excess of six months.

Moltech used inert anodes based on a nickel-iron alloy [15, 89-96] and announced that it operated 100 A, 1 kA and 20 kA aluminium electrolytic cells with such anodes and at bath temperatures at about 850°C [95]. However, according to Kvande and Haupin [13], Sadoway [14], Thonstad and Olsen [16], and Keniry [17] it seems nearly impossible to retrofit existing smelters with inert anodes in combination with wettable cathodes. Keniry [17] also stated that the economic benefits when changing over from carbon anodes to inert anodes are not big enough for largeinvestments. He proposes changes in cell design to the vertical electrode arrangement proposed by Brown [104].

From the above demonstrated state of the art one can conclude that the aluminium industry is years away from a large-scale retrofit of existing aluminium smelters with inert anodes.

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