Chapter Seven

ALUMINUM INDUSTRY

by David W. Richerson

More than 20 billion pounds of aluminum ingot and fabricated mill products are produced each year in the United States. The industry employs over 130,000 people and accounts for over $30 billion per year of the U.S. gross domestic product. The aluminum industry faces stiff challenges of global competition, especially because eastern European countries previously under the control of the former Soviet Union have entered into the world market.

Aluminum production is energy intensive, consuming around 0.4 quad of electrical energy per year in the United States. Aluminum smelting also releases large quantities of carbon dioxide gas into the atmosphere and contributes millions of pounds of solid waste to landfills. Global competition, energy consumption, and pollution are all difficult challenges that are being addressed by the aluminum companies in their internal programs and in partnership with the Industries of the Future program.

The aluminum industry, in collaboration with the Department of Energy's (DOE's) Office of Industrial Technology, has prepared the *Aluminum Technology Roadmap,* which divides the aluminum industry into three sectors: (1) the raw materials sector, also referred to as the primary product sector, (2) the semifabricated sector, and (3) the finished product sector. The following paragraphs briefly describe each sector, review the key processes and the materials challenges in these processes, and discuss the current and potential roles of ceramic-based materials.

7.1 PRIMARY PRODUCT SECTOR

The primary product sector converts raw materials to aluminum metal suitable for subsequent fabrication into products. It includes production of aluminum from ore and also use of recycled aluminum. Most new (primary) aluminum is produced by a sequence of two processes. The first, the Bayer process, extracts aluminum oxide (Al_2O_3) powder from a family of rocks classified as "bauxite." About 40 Bayer plants exist in the world, each producing up to three million tons of aluminum per year. The second, the Hall-Héroult process, smelts the aluminum oxide by electrolytic reduction to metallic aluminum. Ceramic-based materials are required in both of these processes.

The *Aluminum Technology Roadmap* includes the following targets for the primary product sector:

1. Reduce the energy-intensity of aluminum production by the Hall-Héroult process from the current average level of 15.2 kWh(e)/kg of aluminum within 10 years to 13 kWh(e)/kg and beyond 10 years to 11 kWh(e)/kg.
2. Improve productivity of the Bayer process by 20% within 10 years.
3. Reduce/eliminate carbon dioxide emissions during smelting (long-term target, beyond 10 years).
4. Enhance aluminum recycling technologies, including minimizing formation/landfilling of dross and salt cake.
5. Improve metal quality.
6. Develop alternative technologies to reduce the cost of aluminum reduction by 25% (long-term target, beyond 10 years).
7. Develop new uses for wastes and by-products from aluminum processes.

The following chapters describe current primary product sector processes and describe how ceramic-based materials might contribute to achieving the aluminum industry targets.

Bayer Process

Aluminum oxide, the third most abundant compound in the earth's crust, is disseminated in the form of more than 5000 different chemical compositions. The most common compositions from which aluminum metal is produced are aluminum hydroxide (gibbsite) and the closely related oxide-hydroxides (boehmite and diaspore). The term *bauxite* is used for any ore that contains enough of these compositions to be viable for production of aluminum. Worldwide production of bauxite ore for aluminum extraction was about 81 million tons in 1988.

The Bayer process, illustrated in Fig. 7.1, was patented in 1888. The bauxite ore is crushed and ground to produce a slurry of coarse powder particles suspended in water. Sodium hydroxide (caustic soda) is added, and the slurry is heated with process steam to 140°C (for gibbsite) or to 200–300°C (for boehmite or diaspore) in a steel reactor or autoclave at pressures up to 34 atmospheres. The aluminum-containing hydroxides and oxide-hydroxides are dissolved during this digestion process, but other constituents of the bauxite remain solid. Some of the sodium hydroxide is converted to sodium carbonate. Calcium oxide is added to react with the water to hydrate and react with the sodium carbonate to form calcium carbonate plus sodium hydroxide. This latter step increases the efficiency of the operation by recycling / regenerating sodium hydroxide.

The digested bauxite suspension, which contains solids plus dissolved aluminum compounds, is referred to as “green liquor” or “pregnant liquor.” It leaves the digester at about boiling temperature and passes through several stages of filtration referred to as clarification. Coarse particles are removed in a cyclone followed by a sand classifier. Fine particles are removed by a combination of thickening with flocculants and settling, countercurrent decantation washers, vacuum drum filters, and pressure filters. The solids exit the process mixed with water in a slurry that is pumped to a settling pond. The aluminum-containing liquor flows to the precipitation stage of the process.

Precipitation can be batch or continuous, although in modern plants it is continuous. Precipitation is conducted in large flat-bottomed tanks about 30 m high and 10–12 m in diameter with typically 10 to 14 in a series. Cooled supersaturated liquor enters the first tank, and particles of aluminum hydroxide begin to precipitate. Seeds (small particles of aluminum hydroxide) are added to accelerate precipitation.

The next step is classification in which the aluminum hydroxide particles are separated from the liquor by a combination of cyclones and hydroclassifiers. The coarser particles proceed to the calciner. The finer particles are recycled as seeds.

Calcination is the final step of the Bayer process. The particles are dried and heated to 1100°C in either a rotary kiln (a tubular-shaped furnace that rotates as the powder passes through) or a fluidized bed (the kiln is stationary, but the powder is mixed by air bubbled through the powder bed). The aluminum hydroxide is decomposed to form aluminum oxide particles suitable for the Hall-Héroult electrolytic smelting process.

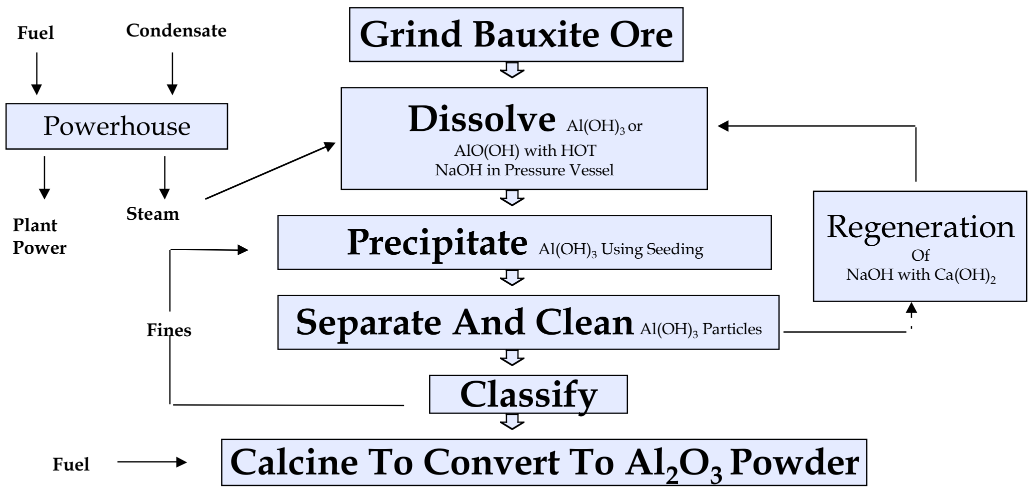

Fig. 7.1. Schematic of the Bayer Process for extracting aluminum oxide powder from bauxite ore.

Ceramic refractories are required as high-temperature linings in the calcining kilns. Incremental improvements have been accomplished over the years to increase thermal efficiency of the kilns, increase the life of the ceramic refractories, and to increase the abrasion-resistance of the refractories. The refractories are currently well-established, although further refinements will probably occur on an incremental basis.

Other areas where ceramics can provide benefits are as wear-resistant and / or corrosion-resistant linings, especially where erosive slurries are pumped or flow through pipes, cyclones, or hydrocyclones. A key issue currently is cost. Some of the advanced ceramics are now lower in cost than they were a few years ago and are worth reconsidering, especially regarding life-cycle-cost and potential reduction in maintenance intervals. A future goal of the aluminum industry is to increase efficiency of the Bayer process by going to higher temperature and pressure during digestion and increasing the sodium hydroxide concentration. This will place an increased burden on materials. Ceramic-based materials may provide viable solutions.

Ceramics may also be beneficial in energy conservation. Most Bayer plants have their own power plant and use the waste heat to produce steam and for other process heating. This cogeneration approach increases fuel efficiency from about 35% to around 85%. Advanced ceramics such as silicon carbide can increase the life and / or efficiency of components such as heat exchanger tubes, burners, and ducts.

Although other processes have also successfully produced aluminum oxide powder for aluminum refining, they are not as cost-effective as the Bayer process. The closest appears to be an acid (HCl) process for extracting alumina from clay. Another process called the lime-soda sintering process has been used for ores with high-silica content such as some bauxite ores in the United States and nepheline ore in Russia. Ceramics might be examined as a means of making these alternate processes more competitive.

Hall-Héroult Process

The Hall-Héroult process, which was discovered in 1886, has undergone over a century of modifications and refinements. As an electrolytic process, it uses electrical energy to separate the aluminum and oxygen in aluminum oxide. As shown in Fig. 7.2, a typical electrolytic cell consists of an anode (positive electrode) made of carbon and a cathode (negative electrode) also currently made of carbon. These are separated at about 960°C by a molten electrolyte of cryolite (sodium aluminum fluoride), which has limited solubility of aluminum oxide. Pure cryolite melts at 1012°C, but additions of fluorides of Ca, Al, Li, and Mg reduce the melting temperature to 920–980°C. A typical cell operates with 1.5–6.0% aluminum oxide in the electrolyte.

A typical cell consists of a rectangular steel shell that is 9–16 × 3–4 × 1–1.3 m. It is lined with several layers of refractory ceramic, usually in the sequence

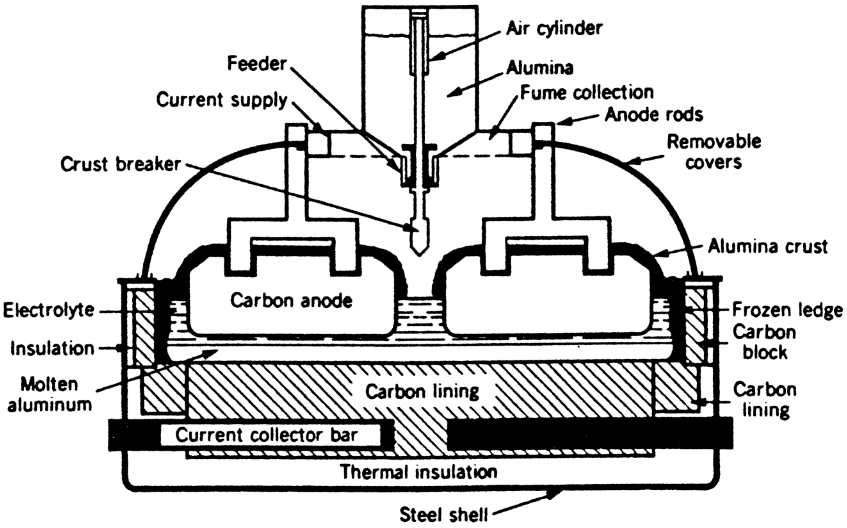

Fig. 7.2. Schematic of a typical Hall-Héroult cell for electrolytic smelting of aluminum metal. *Source:* Kirk, R. E., et al. 1991. *Aluminum*, Wiley Interscience (Wiley), New York (*Encyclopedia of Chemical Technology*, 4th ed., Vol. 2, p. 195).

from the steel inwards of a castable refractory, a porous insulating refractory, a less-porous semi-insulating refractory, and finally firebrick. The firebrick supports the carbon cathode. The carbon cathode is the negative electrode, the host of the electrical current collector bars, and also the bottom of the cell for containment of molten aluminum metal. Because the sides of the cell have less insulation, more heat is lost through the walls. The wall temperature is low enough that the electrolyte in contact with the wall solidifies to form what is referred to as the "frozen ledge," which protects the walls of the cell from the extremely corrosive molten cryolite.

The carbon anodes are consumed during electrolysis and are thus mounted so that they can be lowered to maintain a constant electrolyte gap between the anodes and cathode. Aluminum oxide powder containing substantial sodium hydroxide contamination from the Bayer process is sprinkled onto the molten surface of the cryolite electrolyte, where it dissolves and is distributed through convection currents. Direct current enters the cells through the anodes, passes through the electrolyte carried primarily by sodium ions, passes through the molten aluminum and exits the cell through the cathode and steel current collector bars. About 15,000 kWh(e) are required for each ton of aluminum produced. The positively charged aluminum ions migrate to the electrically negative cathode and pick up electrons to yield aluminum metal. The oxygen ions migrate to the anodes and react with the carbon to produce carbon dioxide gas, which is discharged into the atmosphere. Aluminum metal, which is about 99.6–99.9% pure, is siphoned from the cell at intervals into a crucible for refining and other operations prior to casting into ingots or forming into other shapes.

Much plant design has been conducted over the years to minimize electrical energy use. Modern plants convert alternating current with a silicon rectifier into 600–900 V dc. Each electrolytic cell operates at 4.5–5.0V, so 130 or more cells are linked in series to form a "potline." Depending on the length of the potline, the total current flow can be between 50 and 360 kA. Thus, the electrodes must be good electrical conductors capable of carrying high amperage. Heat dissipated during aluminum smelting is about 8 kWh(t)/kg of aluminum.

The electrodes are obviously key components in aluminum smelting and play a major role in efficiency as well as emissions. Ceramics have the potential to dramatically improve efficiency and reduce carbon dioxide emissions. Before the potential role of ceramics can be understood, the nature of the present electrodes needs to be reviewed.

Two types of anodes are presently used: (1) prebaked carbon anodes, as illustrated in Fig.7.2 and (2) the Soderberg anode illustrated in Fig.7.3. Prebaked anodes are fabricated by forming blocks of about 70 × 125 × 50 cm from a mixture of petroleum coke and coal tar pitch and baking at 1000–1200°C. Petroleum coke is becoming more difficult to obtain each year because of the competition to use petroleum for other products. Coal-based coke is an alternative, but has unacceptable impurities and requires extensive prepurification before it can be used. The advantage of prebaked anodes is low electrical resistance (5–6 Ω-m). The disadvantage is that they are consumed by the carbon-oxygen reaction and must be replaced at intervals. Periodic replacement results in downtime for the cell.

Soderberg anodes were developed to allow continuous operation of a cell. The anode is housed on the sides by a steel casing of 6–8 × 2 × 1 m. A mixture of petroleum coke and coal tar pitch in the form of a paste is added to the top of the casing

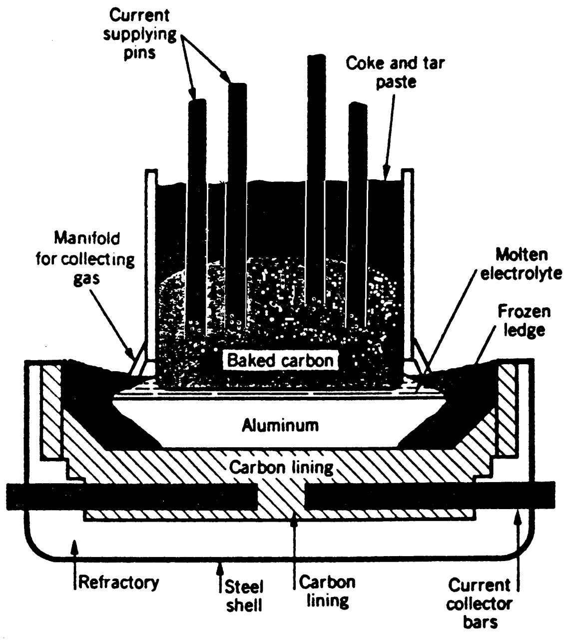

Fig. 7-3. Schematic illustrating an aluminum smelting electrolytic cell with Soderberg anode. *Source:* Kirk, R. E., et al. 1991. *Aluminum,* Wiley Interscience (Wiley), New York (*Encyclopedia of Chemical Technology,* 4th ed., Vol. 2, p. 196).

as the bottom of the anode is consumed. Heat from the process bakes the paste to form carbon in place as it passes slowly through the housing. The Soderberg anode eliminates shutdown, but has higher electrical resistance (about 30% higher than prebaked anodes) and thus reduces electrical efficiency.

The aluminum industry is greatly interested in developing a noncarbon anode that is not consumed by oxygen and that would therefore emit oxygen rather than carbon dioxide. This would eliminate emissions and also reduce the cost of continual replenishment of the carbon anodes. However, finding a material that has high electrical conductivity, does not lose electrical conductivity due to oxidation, and is not attacked by the molten electrolyte bath is a major challenge. Considerable development worldwide has failed to produce a viable material. Many ceramic compositions have been evaluated including nickel oxide, doped tin oxide and zinc oxide, copper-nickel oxides, perovskites (manganites, chromites, and others), titanium diboride, and zirconium diboride. Cermets (metal-ceramic mixtures) have also been explored.

The aluminum industry is also seeking an alternate material to carbon for the cathode. Carbon is not wetted by molten aluminum. A cathode that is wetted by aluminum would allow a dramatic reduction in the gap between the anode and cathode, which would decrease losses from electrical resistance. A consequent increase in electrical efficiency of 10% or greater would be a major breakthrough. The materials challenge is slightly easier for the cathode than the anode. The cathode is not exposed to the molten cryolite, but only to the molten aluminum. Thus, the issues are conductivity, resistance to molten aluminum, and wetability.

Extensive development has occurred during the past 25 years on a ceramic cathode. The best results have been achieved with titanium diboride and mixtures with other ceramics such as graphite and aluminum nitride. The ceramic materials appear to have viable properties, but cost is still an issue. Efforts are currently in progress to modify cathode design to a configuration that can be fabricated at lower cost from promising ceramic compositions.

The combination of a wetable cathode, a nonconsumable anode, and reduced gap between the cathode and anode represent the most important innovations to improve the energy efficiency and reduce pollution for the Hall-Héroult process. However, there are also other areas where ceramics can improve efficiency and reduce maintenance. For example, cell efficiency could be increased with the development of a sidewall that would allow direct contact with the molten cryolite bath, thus eliminating the need for a frozen ledge. The key is to develop a refractory lining that has long life in contact with molten electrolyte. Silicon carbide materials such as nitride-bonded silicon carbide show promise, but there is need for additional development and exploration of other advanced ceramic compositions.

Another concern with the sidewall is leakage of the molten bath past the sidewall into the refractories, eventually requiring replacement of the complete pot lining. Having liquid bath directly in contact with the sidewall will probably make sealing even more difficult than it presently is.

Other areas where ceramics can provide benefits are in instrumentation of the cells. The aluminum industry would like to have instrumentation directly in each cell to continuously measure temperature and concentration of alumina dissolved in the cryolite. For example, currently temperatures in the molten electrolyte and aluminum are measured intermittently by a person dipping a thermocouple. Continuous immersion would allow continuous computerized control of each cell and increase efficiency. The specific need is for thermocouple protection tubes or sheaths that have long life in the molten bath and aluminum. Aluminum nitride is not attacked by molten aluminum but does not have exceptional thermal shock resistance. Nitride-bonded silicon carbide, silicon nitride, and some silicon carbide–based composites have better thermal shock resistance and might be viable thermocouple protection candidates.

Additional areas where ceramics might provide benefits are in the crust breaker (see Fig. 7.2), as a liner for the alumina powder feeder, as electrical insulators, and in the exhaust gas scrubber.

Alternate Processes

A variety of alternate concepts for extraction of aluminum have been evaluated during the past 150 years. A “sodiothermic” process involving reduction of aluminum halides was used commercially between 1855 and 1893 but was discontinued when the Hall-Héroult process was invented. Carbothermic reduction involving high-temperature reaction of carbon with aluminum oxide has also been tried. This is a very high temperature reaction, requiring temperatures between 1930 and

2130°C. Besides the high temperatures, carothermic reduction involves problems with formation of aluminum carbide, evolution of carbon monoxide, and vaporization of aluminum. Experiments have produced potential solutions for these problems, but the process itself has not proved economically competitive.

Around 1976 a process was demonstrated that used about 30% less electrical energy than the Hall-Héroult process. It involved reaction of alumina, carbon, and chlorine to produce aluminum chloride and carbon dioxide. The aluminum chloride was then electrolytically decomposed to yield aluminum plus chlorine. A plant was built and operated for six years, but was shut down because of high maintenance costs and difficulty in reaching projected capacity. An additional problem involved the formation of hazardous polychlorinated biphenyl, which proved to be expensive to remove to environmentally safe standards.

It is possible that advances in materials in recent years, including advanced ceramics, could solve some of the problems encountered in these alternate processes and allow them or other new processes to be safe, efficient, and economical.

Another alternative is to explore different designs for electrolytic extraction of aluminum. An example is the design shown in Fig. 7.4. This design has the anodes and cathodes arranged as alternating flat plates suspended in the molten electrolyte bath, with the cathode plates extending through into the molten aluminum. The electrolyte consists of 64 wt % aluminum fluoride and 36 wt% sodium fluoride. The cathode is carbon and the anode is a cermet with about 17% copper, with the remainder being nickel oxide and iron oxide. The electrolyte was selected for operation at lower temperature (750–850°C) than a Hall cell in conjunction with an inert, nonconsumable anode. The comparison of this design and the Hall-Héroult design implies that there are many configurations for addressing the same basic reaction and that a new design has potential for improved performance, lower maintenance, and reduced pollution emissions. Perhaps advanced ceramic materials can enable an improved design that was not possible with prior materials.

Recycling

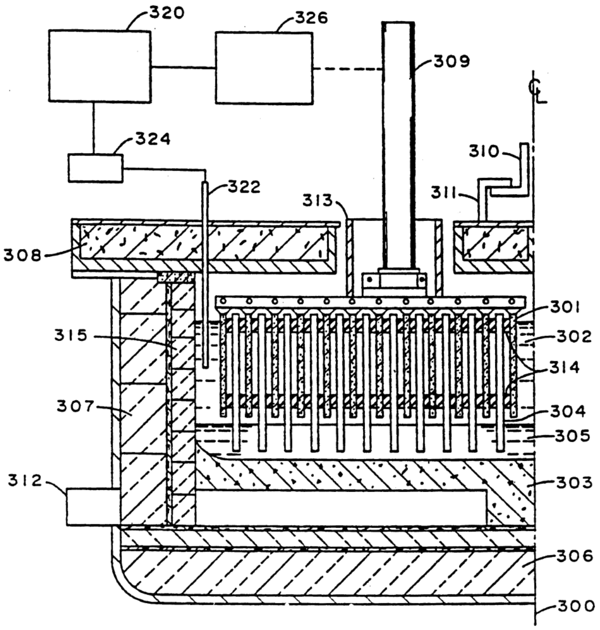

Fig. 7.4. Schematic of an alternative electrolytic cell for extracting aluminum metal from aluminum oxide. The cathode and anode are the alternating vertical plates (304 and 301) in the center of the cell. *Source*: La Camera et al. January 18, 1994. U.S. Patent 5,279,715.

Recycling offers the greatest potential to reduce energy use in the aluminum industry. Processing recycled aluminum consumes only about 5% of the energy of producing primary aluminum. By 1990 about 60% of aluminum beverage cans were recycled. Currently about seven billion pounds of aluminum are recycled annually. Ceramic-based materials are important in the melting, holding, transfer, and forming of recycled aluminum in the same ways they apply to processing of shapes of primary aluminum. Therefore, these applications are discussed in a later general section on semifabricated and finished aluminum. Further discussion is included in Chap.8 on the Metalcasting Industry.

Summary of Potential Applications of Ceramic-Based Materials in the Primary Product Sector

Table 7.1 summarizes areas where ceramics may provide benefits in the primary products sector of the aluminum industry.

Table 7.1. Opportunities for ceramic-based materials in the primary products sector of the aluminum industry

Application	Industry needs	Opportunities for ceramics
Wear- and corrosion-resistant parts in the Bayer process	Incremental improvements in life to decrease maintenance	Monolithic ceramics for valves, seals and pump parts; coating, tiles or liners for high-wear, high-corrosion parts of pipes, vats, filters, cyclones, and hydroclassifiers
Calciner	Incremental improvements in life	Incremental improvements in current refractories; use of ceramic bearings for rotary kilns
Heat exchanger	Increased efficiency of calciner and power plant	Efficient use of waste heat to preheat inlet air using SiC or composite tubular system or oxide ceramic crossflow or counterflow system
Hall cell anode	Nonconsumable anode material with comparable electrical conduction to carbon	Cermets, ceramic composites, and perovskites—probably requiring extensive materials engineering and testing
Hall cell cathode	Cathode material wetted by Al to allow decrease in separation of anode and cathode and decreased electrical losses	Ceramic composite composition such as diborides plus carbon
Hall cell sidewall	Material that can survive for long time in contact with molten cryolite	Possibly a composite construction using nitride-bonded SiC or silicon oxynitride
Thermocouple protection tubes	Tubes that can be immersed in molten aluminum to allow continuous temperature measurement	Silicon nitride; ceramic matrix composites

7.2 SEMIFABRICATED SECTOR

For the purpose of this document, where the emphasis is on reviewing the materials needs and the opportunities for advanced ceramic materials, *semifabricated* is defined to include preparation of aluminum stock ready to then proceed to a final shaping operation. This definition includes preparation of ingot for casting, rolling, and extrusion. It includes the relevant intermediate process steps for primary aluminum directly from the Hall-Héroult cell, as well as remelted scrap and recycled aluminum. These are included together because many of the process steps and key materials issues are identical or similar.

The aluminum industry has identified two working group teams that have prepared and will guide implementation of a semifabricated sector technology roadmap: (1) casting and (2) rolling and extrusion. Some of their improvement targets and major research needs are common to both categories; others are specific.

1. Increase reliability of manufacturer operations to 95%.
2. Improve process control by better models of plant operation and through use of real-time sensors for temperature, pressure, and metal composition.
3. Modify furnaces to improve fuel efficiency and reduce NO_x emissions.
4. Improve understanding and control of continuous casting processes (strip, slab, wire, bar, etc.)
5. Increase efficiency and reliability of molten metal filtration.
6. Fabricate closer to shape and reduce scrap.
7. Reduce energy use and costs associated with extrusion by 20–30%.
8. Increase productivity and quality of extrusions by lowering die cost, improving die technology, achieving higher extrusion speed, and achieving thinner wall capability.

Ceramic-based materials have potential to enable incremental improvements and possibly new tooling / processes that will help the aluminum industry achieve these targets. The following paragraphs review some of the steps in aluminum processing that lead up to semifabricated product and identify some of the current and potential ceramic applications. Key steps include purification, melting / remelting, holding, transfer, degassing, filtration, and ingot casting.

Purification

High-purity aluminum is achieved by electrolytic refining of smelted aluminum or some recycled aluminum in a cell with a carbon bottom and lined with magnesia-based ceramic refractory brick and castable. Ceramic refractories can be used because the temperature is only 750°C. The impure molten aluminum acts as the anode and forms a pool on top of the carbon. A molten electrolyte layer of sodium fluoride plus aluminum fluoride (plus barium chloride in some cells) floats on the aluminum. Purified aluminum forms on top of the electrolyte bath in contact with graphite cathodes. The impurities form fluorides or chlorides and remain in the electrolyte. The current refractories appear to provide adequate life.

Melting and Holding Furnaces and Transfer Troughs

The predominant current application of ceramics in these process steps is refractories. The aluminum industry initially employed the same refractories used by the steel industry, but especially during the past 15–20 years has developed refractories specifically for aluminum. The hearth, which is in contact with molten aluminum, is lined with silicon nitride–bonded SiC. The walls, which are not in contact with molten aluminum, can be mullite, tabular alumina, or other oxide refractory. Aluminum charged into the furnace is directed into the melting zone by the ramp and sill. These must also be lined with refractories but are exposed to greater mechanical and thermal shock abuse than the hearth or walls. Mechanical damage in the sill and ramp region is a significant cause of unscheduled shutdown. Ceramic refractories with improved toughness, impact resistance, and abrasion resistance are needed.

Another critical ceramic component is the tap hole where molten aluminum is released from the furnace. High grades of tabular alumina and silicon carbide refractories have been used in this area.

Melting and holding furnaces have a large range in size. For preparation of ingot, the furnaces typically range in capacity from 50 to 250 tons and can be 25–30 ft in diameter. Furnaces in small casting foundries are much smaller and typically hold less than 15 tons. The larger furnaces are fired with gas combustion burners directed from the roof onto the metal. Advanced ceramics offer potential for increased life of burner components.

Smaller furnaces use either direct firing or ceramic radiant burners. Radiant burners retain the combustion within a tube and radiate the heat to the aluminum. They provide opportunities for controlling the environment in the furnace and perhaps reducing oxidation of the surface of the aluminum. Another option is to immerse the radiant burners in the molten aluminum. This can allow reduced head space above the melt and provide additional benefits. Monolithic ceramics in the silicon nitride and silicon carbide families have been evaluated for both external and immersion burner tubes (Fig. 7.5). Some have performed well while others have shown a need for improvements in durability and reliability. Ceramic matrix composites, currently under development and testing as part of the CFCC program, have potential for increased durability and reliability, but these composite ceramics will cost more than monolithic ceramic burners. A nitride-bonded SiC CFCC reinforced with SiC fibers fabricated by Textron Systems has been tested successfully in 1998 for over 1000 hours as immersion heater tubes.

Fig. 7.5. Silicon nitride tubes used successfully in Japan in an immersion heater for melting aluminum. *Source*: Kyocera Corporation, Kyoto, Japan.

Other functions are performed in melting and holding furnaces besides achieving and maintaining molten aluminum. Especially during remelting of scrap, fluxes such as sodium and potassium chloride are added to react with impurities and oxides and forms a slag that floats to the surface. The slag is typically mixed with aluminum metal, aluminum oxide, and some magnesium oxide and is referred to as dross. Where clean scrap is used, dross may comprise up to 5% of the melt, but is much higher where "litter" scrap and some other types of scrap are involved. The dross, which is skimmed off the surface of the molten aluminum, represents another chemical environment that the refractories must resist. It also represents a waste that must be disposed of or recycled. Efforts are continuing to minimize dross and to reclaim fluxes and metal from the dross.

Even after fluxing and skimming, detrimental impurities remain in the aluminum. Some are dissolved such as hydrogen gas and sodium and calcium. Others are present as insoluble inclusions such as aluminum oxide and pieces of refractory. Two process steps focus on removal of these impurities: degassing and filtration. Degassing involves bubbling a mixture of chlorine gas and argon gas through the roughly 760°C molten aluminum. The degassing unit is a refractory-lined box that contains 500–1000 lb of aluminum at a time. The small size and the argon gas help to minimize further oxidation of the aluminum metal. The gas mixture is typically introduced from the top through a graphite bubbler tube about 40 in. long and 2 in. in diameter. The bubbler tube has an impeller at the end and is rotated (at 200–600 rpm) like a mixer (Fig. 7.6). Advanced ceramics have potential to provide increased life if they are adequately resistant to the chemical environment and to thermal shock.

Metal exiting the degassing unit passes through ceramic filters. Previously a bed of tabular alumina balls was used but has largely been replaced with ceramic reticulated foam filters. These have proven very effective at removing oxide scale, liquid salts, carbides, and solid debris entrained in the aluminum. Further incremental improvements in filter material, structure, and design should result in additional improvements in filter efficiency and reliability.

The molten aluminum flows through refractory-lined troughs between the various process steps. The trough between the melting and holding furnaces is made of steel and lined with about 4 in. of refractory to provide an open area for metal flow about 12 × 12 in. Troughs are typically lined with oxide ceramics such as fused silica or mullite that have relatively low thermal expansion and are resistant to thermal shock, a primary concern with troughs. The refractories have about 10–15% porosity and special additives to resist wetting. They are installed either in board form or as a castable. Erosion and abrasion are other concerns. SiC-based refractories have improved erosion/abrasion resistance and good thermal shock resistance but are more expensive than oxide refractories.

Improvements in the life of all refractory linings are desired. Furnaces are typically designed for a 5-year life, but yearly maintenance shutdowns are performed. Reducing the frequency of planned shutdowns and eliminating unplanned shutdowns would provide significant cost reduction.

Fig. 7.6. Silicon nitride degassing pipe and rotor used to stir molten aluminum and bubble gases for removal of hydrogen. *Source:* Kyocera Corporation, Kyoto, Japan.

Ingot Casting

Aluminum that exits from the ceramic filters or filter bed moves directly into ingot casting. The nature of the ingot depends on the intended application. Smaller ingot are produced for use by foundries for forming of finished products by casting and other processes that are described under

"Finished Product Sector." This includes small ingot (roughly 50–100 lb) referred to as "pig," larger ingot (roughly 500–1000 lb) called "sow," and ingot designed for easy movement by forklift called "T-ingot." Other ingot that are much larger are shaped to be efficient feedstock for subsequent rolling or extrusion operations.

Most ingot for rolling, forging, or extrusion feedstock are produced by the "direct chill" process. The aluminum flows into a mold with a moveable bottom. Water is sprayed directly onto the mold and ingot to achieve rapid cooling and solidification. As additional metal is poured, the mold bottom moves either into a pit (older technology) or along a horizontal path (modern technology) to permit casting of a long ingot. The cross section is controlled by the mold dimensions. Ingot for rolling flat products is typically 40–60 cm thick and up to about 120 cm wide. Ingot for extrusion is produced with a circular cross section up to 90 cm in diameter. Ingot casting is conducted successfully and efficiently with metal tooling. Ceramic-based materials do not appear to be required.

Other processes have been developed for ingot casting. One uses an electromagnetic field to contain the aluminum and is referred to as the electromagnetic casting process. Another, which yields small strip or rod stock for subsequent production of sheet or foil or wire, flows the molten aluminum between rolls or moving steel plates. It provides rapid solidification, which is beneficial for some alloys. Advanced ceramic tooling or inserts might provide increased life or improved surface condition.

Rolling and Extrusion

Rolling and extrusion are employed to convert cast ingot into shapes suitable for subsequent fabrication into finished products. Rolling involves forcing ingot under pressure between sets of metal rolls to produce plate or sheet of a controlled thickness and metallurgical property condition. This process is typically conducted in a sequence of operations at temperatures ranging from about 400°C down to room temperature. Because of the low temperature and limited chemical activity of the solid aluminum, steel rolls are satisfactory. Ceramic materials could potentially improve surface finish and minimize the likelihood of adhesion. However, the rolls are typically so large that they would be difficult and expensive to fabricate from monolithic ceramics. Also, there would be concerns regarding the reliability and durability of such large sections of monolithic ceramic, especially considering the likelihood of high localized contact stresses during rolling and accidentally imposed by handling or impact. Advanced ceramic coatings on steel might provide a viable alternative.

Extrusion has broader potential for use of ceramic materials. Extrusion consists of forcing a large-diameter ingot or rod of metal through a much smaller shaped die. This involves high stresses and an erosive sliding contact between metal and die (compared to rolling contact for rolling). Ceramics such as transformation-toughened zirconia have demonstrated large increases in die life for hot extruding of metals such as copper, brass, and bronze. However, these metals are extruded at much higher temperatures than aluminum (650–870°C compared with below 400°C for aluminum), so the ceramic is replacing relatively expensive metal alloys. Life-cycle cost, quality of extruded product (surface and dimensional control), and die insert reliability all need to be assessed to determine potential benefits of ceramics.

Summary of Potential Applications of Ceramic-Based Materials in the Semifabricated Sector

Table 7.2 summarizes applications in the semifabricated sector of the aluminum industry that might benefit from ceramic-based materials.

7.3 FINISHED PRODUCT SECTOR

The third sector addressed in the *Aluminum Technology Roadmap* compiled by the aluminum industry is the finished product sector. This sector involves aspects of aluminum relevant to competitiveness in end products. This includes properties of aluminum alloys or engineered materials containing aluminum compared to competing materials, final-shape manufacturing technologies, and product design technologies. Some of the specific performance targets and research needs identified in the technology roadmap include:

1. Reduce the costs associated with metal production by 25%.
2. Reduce the cost ratio of aluminum to steel to less than 3 to 1 for auto applications.
3. Increase aluminum use in the automotive market by 40% in 5 years and in infrastructure markets (such as bridges) by 50%.

Table 7.2. Opportunities for ceramic-based materials in the semifabricated sector of the aluminum industry

Application	Industry need	Opportunities for ceramics
Melting and holding furnaces, troughs	Improved life of refractories	Incremental improvements
Burners	Improved life and efficiency of burners in melting, holding, and heat treating furnaces	Ceramic matrix composites; thermal barrier coatings
Purification	Improved life of bubblers, gas lances, skimmers	Ceramic liners or coatings; one-piece ceramic matrix composite constructions
Tap holes, valves	Reduced maintenance	Engineered composition (probably composite) and design
Molten metal filters	Increased efficiency and reliability	Incremental improvement of current ceramic materials and designs
Extrusion dies	Longer life	Engineered tough ceramics
Heat exchangers	Waste heat recycling to decrease fuel costs	SiC or ceramic matrix composite tubular systems and oxide ceramic crossflow or counterflow systems
Reduction in pollution	Minimize particulate and gaseous emissions	Ceramic hot gas filters and ceramic honeycomb substrates for catalytic pollutant decomposition
Reduction in solid waste	Dross reduction	Furnace redesign using ceramic radiant tube immersion heaters, controlled atmosphere and ceramic-lined molten metal pumps

4. Improve competitiveness of aluminum packaging.
5. Develop new alloys and aluminum-containing composites.
6. Improve understanding of effects of composition and processing on microstructure and properties.
7. Increase near-net-shape fabrication capability.
8. Achieve surface defect-free continuous cast 5000 / 6000 sheet.

Ceramic materials can help in several of these areas but mostly in increasing near-net-shape fabrication capability, decreasing production cost, and achieving composites.

Near-Net-Shape Fabrication

Direct fabrication closer to the required shape decreases labor, minimizes tooling, and reduces scrap. Ceramic tooling has the potential to produce smoother surfaces and thinner cross sections, as well as to maintain dimensional stability for an increased number of fabrication cycles. This potential has already been demonstrated commercially for fabrication of aluminum beverage cans. Transformation-toughened zirconia, silicon nitride, and alumina reinforced with silicon carbide whiskers have all been successfully used as tooling sets with demonstrated advantages over prior tool materials. A transformation-toughened zirconia tooling set for beverage cans is illustrated in Chap.2 in Fig.2.16.

Casting, forging, and extrusion are important processes that can fabricate products to near-net-shape. Ceramics are already widely used in the various steps of casting for furnace linings, molten metal pump linings, molds, cores, face coatings, and other components (Figs. 7.7 and 7.8). Metalcasting is discussed in detail in Chap. 8 of this report. Ceramics are also used for extrusion dies for some metals. Advanced monolithic ceramics and some engineered ceramic-metal and ceramic-ceramic composites are not wetted by aluminum and should provide benefits as low friction tooling not requiring release agents. These same ceramic-based materials might also be suitable as inserts for forging dies. Some specific candidates include silicon nitride, new high-fracture-toughness silicon carbide, silicon carbide / aluminum nitride composites, and transformation-toughened zirconia and alumina.

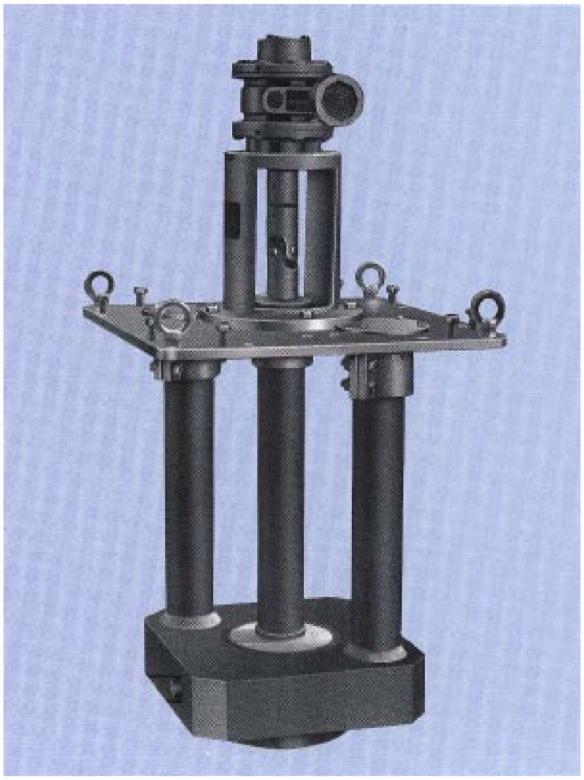

Fig. 7.7. Pump for transfer of molten aluminum, constructed with silicon nitride shaft, impeller, body column, liner ring, and casing liner. *Source*: Kyocera Corporation, Kyoto, Japan.

Fig. 7.8. Silicon nitride sleeves for aluminum die-casting machine. *Source*: Kyocera Corporation, Kyoto, Japan.

Reduction in Production Cost

Achieving closer to net shape will reduce production cost. Increased tooling life will also reduce cost. Other areas where ceramics can reduce production cost are in machining, joining, nondestructive inspection, and heat treating.

Ceramic cutting tool inserts have dramatically decreased the cost of machining many different metals, such as the examples that are cited in Chap.2 for machining of cast ir on with silicon nitride. Other ceramics besides silicon nitride have also been effective as cutting tool inserts for various alloys: aluminum oxide reinforced with titanium carbide particles or silicon carbide whiskers, transformation-toughened alumina, polycrystalline diamond (PCD), cubic boron nitride (CBN), and various ceramic coatings.

New diamond coatings (e.g., from Norton Diamond Film, Northboro, Mass.) appear effective for difficult-to-machine aluminum-silicon alloys and even for new ceramic-reinforced aluminum metal matrix composites. For example, tooling with the diamond coating had 14 times the life of PCD tool inserts for piston outside-diameter machining of A390 aluminum alloy at 1672 m / min. (5,500 surface ft / min). Diamond-coated WC-Co was able to perform at five times the cutting speed (1500 m / min. versus 300 m / min.) of WC-Co for machining 25% SiC-aluminum metal matrix composite brake drums and demonstrated 20 times the life.

Another important application of ceramics that can reduce production costs during machining is ceramic bearings. Silicon nitride bearings increase the rigidity of machine tools and allow higher speeds and greater dimensional accuracy. With their cooler and quieter operation, these ceramic bearings extend equipment life.

Ceramics with controlled levels of thermal expansion and / or thermal conduction have been used in metals-joining operations for tooling such as dimensionally stable support fixtures (e.g., fused quartz and NZP) and quench blocks (beryllium oxide, aluminum nitride). Aluminum oxide and silicon nitride are in commercial production for weld nozzles and induction furnace fixtures. Ceramics have also been successfully used for heat-treating fixtures. Heat treating is discussed in Chap. 8, as is the use of ceramics in inspection.

Fabrication of Aluminum Matrix Composites

Reinforcement of aluminum with ceramic particles or whiskers can improve the properties to a level that can compete with those of iron-based alloys, but at a much lower weight. This opens broad opportunities in the automotive marketplace and also has potential for aerospace, infrastructure, and other product sectors. Besides providing the reinforcement, ceramics will be important for refractories, forming tools, machining, inspection, heat treating, and probably even recycling.

Summary of Potential Applications of Ceramic-Based Materials in the Finished Product Sector

Table 7.3 summarizes some of the opportunities for ceramics to benefit the finished product sector of the aluminum industry.

Table 7.3. Opportunities for ceramic-based materials in the finished product sector of the aluminum industry

Application	Industry needs	Opportunities for ceramics
Casting	See Table 8.2	See Table 8.2
Extrusion dies	Longer life; better surface finish and dimensional control; elimination of release agents	Improved-toughness monolithic and particulate-reinforced composites
Forging tooling	Same	Same
Cutting tools	Longer life, higher cutting speed, improved surface finish of machined metal	Same, plus ceramic coatings such as diamond
Grinding, turning, boring machines	Higher speed; less down-time for tool changes or maintenance; increased rigidity	Silicon nitride bearings
Aluminum metal matrix composites	Decreased cost	Ceramic forming tools, cutting tools, furnace fixtures
Heat exchangers	Waste heat recycling to decrease fuel costs	SiC or ceramic matrix composite tubular systems and oxide ceramic crossflow or counterflow systems
Pollution control	Reduction of particulate and gaseous emissions	Ceramic hot-gas filters and honeycomb substrates for catalytic pollutant decomposition

7.4 REFERENCES

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