



APPLICATIONS FOR ADVANCED CERAMICS IN ALUMINUM PRODUCTION: NEEDS AND OPPORTUNITIES

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Table of Contents

Executive Summaryi	ii
Chapter 1: Introduction	1
Chapter 2: Smelting	7
Chapter 3: Furnaces and Molten Metal Handling 1	5
Chapter 4: Initial Implementation Steps	3
Appendix: List of Contributors 2	5

Applications for Advanced Ceramics in Aluminum Production

Executive Summary

Aluminum production creates some of the most corrosive high-temperature environments in industry today. Advanced ceramic materials are known for their superior performance in high-temperature, corrosive operating conditions. It seems natural that aluminum producers would take advantage of the improved energy efficiency, productivity, and metal quality that advanced ceramics can offer. However, due to a variety of factors, including the high cost relative to traditional materials, the lack of experience in aluminum processes, and durability concerns, advanced ceramics are used very little in aluminum production today, compared to their potential.

Despite these concerns, the most significant reason for their limited use is lack of knowledge and understanding between the two industries on the material requirements of aluminum production and material characteristics that advanced ceramics can offer. This report summarizes a workshop aimed at bringing the two industries together to discuss aluminum needs and advanced ceramic capabilities. By starting a dialogue between the two industries, this report represents the first step in forming a collaborative partnership to take advantage of considerable opportunities to improve production and energy efficiency.

Critical Material Needs and Opportunities

Aluminum producers face a wide and diverse range of material needs. Table ES-1 lists the most critical of these needs for smelting, melting, and molten metal handling. These items represent areas where aluminum production material needs are particularly pressing and where advanced ceramics have significant potential to provide solutions. For each need that appears in the table, Chapters 2 and 3 describe the following five criteria for primary and secondary production, respectively:

- **Performance Requirements** quantitative and qualitative characteristics which the material system must achieve to be considered for that application (operating temperature, resistance to specific corrosive agents, lifetime, wettability characteristics, etc.).
- **Technology Used Today** current material or technology used in aluminum production; advanced ceramics may be used to provide innovative alternatives to this current technology.
- **Most Promising Advanced Ceramic Solutions** the type of advanced ceramic system that is most likely to meet the need or which components are best suited for advanced ceramics.
- **R&D** Needed R&D that must be performed to develop advanced ceramic systems that will meet the specified performance requirements while maintaining cost-effectiveness.
- **Implementation Steps** the initial steps needed to develop an implementation process for advanced ceramic opportunities that meet priority aluminum material needs.

Table ES-1. Top-Priority Needs and Opportunities

Smelting

- Non-consumable, robust anode
- Pre-bake anode stub protection
- Improved sidewall materials
- Joining/sealing mechanisms for cathode components to prevent molten bath and metal from entering cathode (in combination with improved sidewall materials)
- Cathode material that is wetted by aluminum
- Coatings for slowing/stopping erosion in the cathode
- Evaluation and testing of potential materials
- Sensor protection tubes
- Sensors for measuring alumina content of molten electrolyte

Furnaces/Molten Metal Handling

- Standardized testing and appropriate laboratory criteria
- Enhanced surface properties (roughness, coatings, etc.) through surface engineering
- Better understanding of aluminum/ material interface at microscale
- Sensors for process control via accurate temperature measurement

Material Needs by Process Stage

- **Furnace** tap hole blocks, burner blocks, sensors, lining materials, coatings
- Molten Metal Handling coatings and other surface protections systems
- In-line Metal Treatment rotors, shafts, heating elements, coatings
- **Casting** spouts, nozzles, pins, skin dams, distribution headers, flow control valves, molten metal pump parts, coatings

Key R&D Needs and Implementation Steps

Chapters 2 and 3 detail the most critical material needs and opportunities and present R&D needed to take advantage of opportunities and meet smelting, furnaces, and molten metal handling material needs. While needs specific to each process vary, there are several R&D needs which apply to all areas. The following R&D needs and implementation steps are needed to begin the overall process of collaboration between the aluminum and advanced ceramics industries:

- **Standardized testing**—In order to assess material applicability to actual aluminum operating conditions, extensive material testing is required. Standardization of material tests, including identification of what parameters are most relevant to aluminum operating conditions, is critical in enabling aluminum producers to assess appropriateness and performance capabilities of a given material in specific applications.
- Overview of existing materials and efforts Extensive work has already been done within the advanced ceramics industry in material development and testing. Likewise, within the aluminum industry, much materials development work has been done. As a key implementation step for partnering between these two industries, existing materials must be catalogued to easily reference which materials already exist. Also, an overview of previous materials testing efforts within aluminum processes will help avoid "reinventing the wheel."

Executive Summary

V

- **Information exchange on actual aluminum process conditions**—One of the first steps in developing advanced ceramic systems for use in aluminum processes is to exchange information on aluminum process conditions for the application in question. Only with such information can advanced ceramic developers tailor material properties to meet the demands of aluminum production.
- **Post-mortem analyses**—One approach to developing materials well-suited to aluminum processes is to ensure that thorough post-mortem analyses of end-of-life materials are conducted and the results are shared among ceramics and aluminum companies. By performing failure analyses after service life, the next generation of materials can be improved. An iterative approach using post-mortem analyses as a key source of information will ensure advanced ceramic material systems are as effective as possible.
- Sensors protection and development—Significant opportunities exist to use advanced ceramics in the area of sensors. Protection schemes for existing sensors may provide some near-term opportunities that can introduce advanced ceramics into aluminum processes. However, the greater opportunity may lie with new sensor development. Sensor development, particularly a sensor that will allow the molten aluminum and bath temperatures to be directly monitored would be of tremendous value in the aluminum industry.

Applications for Advanced Ceramics in Aluminum Production



Introduction

Aluminum production creates some of the most corrosive high-temperature environments in industry today. A dvanced ceramic materials are known for

their superior performance in high-temperature, corrosive operating conditions. It seems natural that aluminum producers would take advantage of the improved energy efficiency, productivity, and metal quality that advanced ceramics can offer. However, due to a variety of factors, including the high cost relative to traditional materials, the lack of experience in aluminum processes, and durability concerns, advanced ceramics are used very little in aluminum production today, compared to their potential.

Despite these concerns, the most significant reason for their limited use is lack of knowledge and understanding between the two industries on the material requirements of aluminum production and material characteristics that advanced ceramics can offer. This report summarizes a workshop aimed at bringing the two industries together to discuss aluminum needs and advanced ceramic capabilities. By starting a dialogue between the two industries, this report represents the first step in forming a collaborative partnership to take advantage of considerable opportunities to improve production and energy efficiency.

Background

In 1996, the advanced ceramics industry, represented by the United States Advanced Ceramics Association (USACA) with sponsorship by the U.S. Department of Energy's Office of Industrial Technologies (DOE/OIT), undertook a study to assess the opportunities for advanced ceramics to meet key materials needs of major energy-intensive industries. Seven industries, all of which have manufacturing environments with high temperatures, corrosive environments, and processes which incur erosion were examined: aluminum, chemicals, forest products, glass, metal casting, petroleum refining, and steel. The study, published in 1999 and entitled *Opportunities for Advanced Ceramics to Meet the Needs of the Industries of the Future*, identified several opportunities in each industry for advanced ceramics to provide benefits such as increased energy efficiency, reduced maintenance costs, improved environmental performance, and higher-quality products.

One industry in which opportunities for advanced ceramics seem most promising is the glass industry. Glass furnaces operate at high temperatures with corrosive environments – conditions in which advanced ceramics outpace other materials. This conclusion sparked a workshop aimed at sharing the study's results with representatives of the glass industry and starting a dialogue between the two industries. In 1999, a report entitled *Advanced Ceramics in Glass Production: Needs and Opportunities* outlined the results of that workshop, including specific opportunities for advanced ceramics to be used in glass production to realize energy and production efficiency gains.

Advanced ceramics also appear well-suited to the production environments in the aluminum industry. In September 2000, USACA and DOE/OIT, with cooperation from The Aluminum Association, sponsored a collaborative workshop to better understand material requirements in aluminum production. Using the previous glass industry effort as a model, the ceramics and aluminum industries gathered to examine specific opportunities to apply advanced ceramics in aluminum production. The workshop addressed aluminum production via smelting and

melting, as well as molten metal handling. While opportunities for advanced ceramics most likely exist further downstream in the aluminum process (casting, finishing, etc.), those areas were not fully examined at this workshop; what is presented in this workshop report is meant to be a starting point. It is by no means a complete listing of opportunities for use of advanced ceramics in aluminum production and processing.

Overview of Advanced Ceramics

Advanced ceramics encompass a set of materials that offer many of the desirable characteristics of conventional ceramics without many of the flaws. They are best suited for high-temperature

What Are Advanced Ceramics?

Advanced ceramics are distinguished by their purity and performance. They include both oxides and nonoxides and various particulate, whisker, and continuous fiber-reinforced ceramic composites. High-purity ceramic coatings are also part of the advanced ceramics family. applications in power generation, transportation, aerospace, and manufacturing where their superior performance can justify their higher cost. For most purposes, advanced ceramic materials can be classified as **monolithics**, **coatings**, or **composites**.

Monolithic Ceramics

In the refractory industry, monolithics refer to aggregate or cement-type ceramics. In advanced ceramics terminology, monolithic ceramics generally refer to oxide and nonoxide ceramics that are essentially made up of a single material. There is also some overlap between monolothics and ceramic

composites. Advanced monolithic ceramics include oxides (e.g., aluminum oxides, aluminazirconia-silica (AZS), and transformation-toughened zirconia), carbides (e.g., silicon carbide and boron carbide), and nitrides (e.g., reaction-bonded, sintered, and pressure-densified silicon nitride).

Monolithic ceramics can have complex microstructures and are produced using many different processes. Although many companies produce monoliths, monoliths all share some common properties that are attractive to manufacturing customers. For example, they are resistant to high temperatures, corrosion, thermal shock, abrasion and wear, and oxidation, and they are light weight and have high stiffness.

Although there has been significant materials development over the past 25 years, there are two key barriers to commercialization: reliability (monolithic ceramics are still considered brittle) and cost-effectiveness. However, the industry continues to aggressively pursue R&D to remove these barriers.

Ceramic Coatings

Ceramic coatings offer an alternative approach for meeting demanding material needs. The concept is to allow the substrate material to provide structural strength while the ceramic coating provides protection against the environment. The objective of this concept, however, is the same as creating an entire part from advanced ceramics: high reliability for the life of the part. Some standard ceramic coating technologies that are used today include plasma spray, high-velocity oxy-fuel (HVOC), flame spray ceramic coating, electron beam physical vapor deposition (EBPVD), and chemical vapor deposition (CVD).

Advanced ceramic coatings are now at the point where the reliability and cost-effectiveness have been demonstrated. For example, thermal barrier coatings are routinely used in gas turbine engines. The industry is on the verge of other significant commercial breakthroughs to produce advanced ceramic-coated components in a variety of applications.

Ceramic Composites

Ceramic composites, which include ceramic matrix composites and continuous fiber ceramic composites (CFCCs), are designed to overcome the catastrophic failure mode that can occur in some monolithic ceramics. Composites produce a controlled failure by using ceramic fibers to carry the load across a developing crack. The ceramic fiber can be oxide or nonoxide in a continuous phase of oxide or nonoxide ceramics.

CFCCs are extremely tolerant materials. Not only do they perform well at standard baseline conditions, they also perform well in extreme conditions. For example, during a burst strength test of a two-inch CFCC tube at 1200 °C (2200 °F), seals started to leak at 700 psi but the tube did not burst until the pressure exceeded well over 2000 psi. When damage does occur in ceramic composite components, it is predictable, allowing designers to use controlled failure as an advantage. Furthermore, ceramic composites are custom materials that can be tailored to meet operating conditions of various process environments, including those found in aluminum production.

Numerous resources are available to provide more detailed information about advanced ceramics. Two sources easily found on the Internet are the United States Advanced Ceramics Association web page (www.advancedceramics.org), and the recently completed *Advanced Ceramics Technology Roadmap: Charting Our Course*, also available from the USACA web site.

Overview of North American Aluminum Industry

The aluminum industry in North America is comprised of three principle sectors. The raw materials sector produces alumina from bauxite (the ore of aluminum) and primary and secondary (scrap-based) molten metal and ingot. The semi-fabricated sector produces sheet, plate, foil, forgings, castings, wire, rod, bar, extrusions, elemental and alloyed powders, and alumina-based chemical products. The finished products sector uses products from the first two sectors to manufacture a wide variety of consumer/commercial components and products, including aircraft, automobiles, building components, and packaging for food products. This report focuses on the first of these three sectors, breaking the raw materials sector into smelting and furnaces used for melting scrap, and molten metal handling applications. The aluminum industry has developed several technology roadmaps that describe their technology priorities over the next twenty years. These sources provide additional information about the aluminum industry and the direction of technology development. They can be found on the OIT web page at www.oit.doe.gov.

Ore-Based Aluminum Production

Ore-based aluminum is produced by the electrolysis of alumina (Al_2O_3) dissolved in a molten cryolite-based (Na_2AlF_6) electrolyte. In this smelting process, called the Hall-Heroult process, electric current is passed through an anode to a cathode in order to separate the alumina into aluminum and oxygen. The predominant products from the cell are molten aluminum and carbon dioxide (formed by the oxygen reacting with the carbon anode).

Applications for Advanced Ceramics in Aluminum Production

Alumina is itself extracted from bauxite, a natural ore, by the Bayer process. In the Bayer process, the crushed ore is slurried with caustic soda (a liquor containing dissolved sodium carbonate and sodium hydroxide), heated, and reacted at a high temperature under steam pressure. The result is a mixture of dissolved aluminum oxides and insoluble bauxite residues. These residues are separated out, after which the filtered aluminate solution is seeded with aluminum hydroxide crystals in a precipitation tank. The seeding process stimulates the precipitation of solid crystals of aluminum hydroxide, which is recovered and calcined to alumina at temperatures of about 980 $^{\circ}$ C (1,800 $^{\circ}$ F).

In the Hall-Heroult process the alumina is fed into the aluminum reduction cells, or "pots." A pot consists of a rectangular steel shell lined with refractory thermal insulation, and some 150 to 250 pots are electrically connected in series to form a "potline." Each pot can produce 360 to 2,350 kg of aluminum metal per day. Primary aluminum operations are differentiated by the type of anode used and the method by which the pot is worked. The majority of primary aluminum plants use prebake anode technology, in which the anodes are formed and baked prior to consumption in the pots. The inner carbon lining of the cell and the molten aluminum itself act as the cathode in the cell.

Depending on the pot chemistry and other factors, the optimum operating temperature of the cell is between 940 and 985 °C (1,724 to 1,805 °F). Using direct current, cells operate at 65,000 to over 300,000 amperes. Anode current densities range from 600 to 800 amperes per square foot. The voltage drop across a single cell is 3.9 to 5.0 volts and may reach 1000 volts across an entire potline.

Scrap-Based Aluminum Production

Because producing aluminum from scrap uses 95% less energy than producing it from ore, scrap-based aluminum production holds an important role within the industry. Aluminum produced from recycled material makes up one-third of the total aluminum produced, and in 1999 totaled 8,265 million pounds of metal. About half of the scrap used in aluminum production is so-called "new" (industrial) scrap generated by plants making end products. The rest is "old" (consumer) scrap recovered from used consumer goods such as beverage cans.

Furnaces

Melt furnaces can create very harsh conditions in which materials must resist high temperatures, thermal shock, high impact, erosion, and corrosion. Typical operating temperatures in a melting furnace are around 700 to 1400 °C (2200 to 2550 °F). The basic furnace configuration has three distinct zones, each of which poses unique challenges to materials. The top portion of the furnace is the no-metal contact zone, where thermal shock, mechanical abuse, and the atmosphere are a concern to materials. The atmosphere usually contains carbon monoxide, water vapor, unburned fuel, and corrosive salt vapors. The bottom is where the liquid aluminum is contained, and thus furnace walls and hearth are in contact with molten aluminum, a highly corrosive agent.

The region in the middle is the problematic "belly band" zone, which typically ranges from 8 to 14 inches deep and is the most corrosive, erosive portion of the entire furnace environment. Because the level of molten aluminum fluctuates within this region, materials are not only subject to the corrosion found in the constant contact zone, but to erosion via metal level variation. The aluminum-atmosphere-refractory interface is particularly harsh in this region, due in part to the reactivity and corrosive nature of aluminum. Severe thermal shock and mechanical abuse is common within melting furnaces, as up to 30,000 pounds of scrap metal at ambient temperature are pushed into or dropped onto the hearth of the furnace. In short, aluminum melting furnaces have unique conditions that require special materials with a unique collection of properties.

Molten Metal Handling

Molten aluminum is transferred from the furnace to various direct or roll casting operations by being poured through spouts into troughs and allowed to flow via gravity. Spouts, troughs, and other molten metal handling components and systems which are in contact with flowing molten aluminum must have specific technical qualities to withstand the corrosion, erosion, and thermal shock that occurs during transfer while not adversely affecting metal purity or quality.

Many resources are available to provide a more detailed description of primary and secondary aluminum production. Two resources easily found on the Internet are the Aluminum Association web page (www.aluminum.org) or Chapter 4 of the *Energy and Environmental Profile of the U.S. Aluminum Industry*, sponsored by the Office of Industrial Technologies and available for download at www.oit.doe.gov. The previously mentioned *Opportunities for Advanced Ceramics to Meet the Needs of the Industries of the Future* (available for download at www.advancedceramics.org) also provides additional details about aluminum processes and opportunities for advanced ceramics to meet selected material needs of aluminum producers. Additionally, the aluminum industry family of technology roadmaps, including the *Aluminum Industry Technology Roadmap, Inert Anode Roadmap*, and *Applications of Aluminum in the Automotive Market* are available for download from the OIT home page.

Applications for Advanced Ceramics in Aluminum Production



Smelting

Aluminum smelting and related processes present numerous opportunities for the application of advanced ceramics. Many of these

involve the development of improved anodes and cathodes that can better withstand the corrosive cryolite environment found in the Hall-Heroult cell. Ceramics also have potential to improve cell structure and other components such as sidewalls, joints, and sensors, with additional applications for the more corrosive subunits of the Bayer process.

Critical Material and Technology Needs

The most critical material needs in smelting and related processes have been organized into nine categories:

- **Bayer Process**—improving the reliability and service life of the calciner and other equipment operating in corrosive environments.
- **Anode**—developing materials that can be used for the production of non-consumable, robust anodes with performance superior to today's carbon anodes or for anode stub protection that can extend the life of carbon anode stubs by a factor of five or greater.
- **Cathode**—building on existing efforts to develop advanced ceramic cathodes that are wetted by aluminum and resist erosion and corrosion from the aluminum/fluoride components of the electrolyte.
- **Sidewall**—developing improved ceramic sidewall materials with improved corrosion resistance and longer service life.
- **Sensors**—investigating the use of advanced ceramics for sensor protection schemes to extend sensor life and the range of variables that can be measured.
- **Testing**—establishing protocols for standardizing materials testing and evaluation and conducting joint aluminum industry/ceramic industry tests on promising materials for aluminum production applications.
- **Other Hall-Heroult Issues**—enhancing the performance of alumina feeding systems and investigating cryolite bath additives that may allow the cell to operate at lower temperatures.
- Alternative Approaches—examining the materials requirements of alternative aluminum reduction technologies.
- **Auxiliary Systems/Other**—considering the factors affecting the recyclability of spent potlining materials and examining possible opportunities for ceramics in auxiliary smelting equipment.

These needs are discussed more comprehensively in Table 2-1. The table also indicates the relative priority given each item by the aluminum and ceramics industry representatives participating in the workshop. The priorities distinguish between most critical needs for the aluminum industry and top opportunities for the advanced ceramics industry.

Opportunities for Advanced Ceramics

The largest opportunity to lower the energy requirements and cost of primary aluminum production is through the use of advanced electrolytic cell technology. Advanced cell technology has been one of the top research priorities of the aluminum industry for several decades. Advanced ceramics have a central role in the development of both inert anodes and stable wetted cathodes,

★ = Top Priorities; ● = Top Opportunities							
Bayer Process	Anode	Cathode	Sidewall	Testing	Alternative Approaches	Auxiliary Systems	
Incremental improvements in life to decrease maintenance of wear- and corrosion- resistant parts in the Bayer process Incremental improvements in life of calciners Increased efficiency of calciner and power plant for heat exchanger More robust refractory blocks for rotary hearth kilns	Non- consumable, robust anode ★★★★●● Prebake anode stub protection ★★★● Protection of anode pins from sulfide corrosion (Soderberg) Nonconsum-	Cathode material wetted by Al *****••••• - Progress towards bipolar cell Coatings for slowing/ stopping erosion in the cathode ****•• Prevention of molten materials from penetrating cathode, with focus on sealing seam	Improved sidewall materials ★★★★ Materials that can survive for long time in contact with molten cryolite in Hall cell sidewall Material that resists corrosion at the Al-cryolite interface	Development of test standards for materials and procedures ★★★●●● Evaluation of potential materials— conduct more testing ★★ - Joint operation for testing - Get around proprietary issues - Meaningful results from lab-scale tests	Materials and designs for alternate cell designs/ approaches ● Materials for carbothermic reduction "Rapp's paradigm" smelting concept (and lower temperature bath)	Recycle spent pot-lining materials • Heater for Al remelt and crucible • Gas collection system— coatings for protection	
	able anode material with comparable	 Joining mechanism for different cathode 			Other Hall- Heroult Issues	Sensors	
	conduction to carbon in the Hall cell anode	Carbonless cathode Better insulation capability combined with ability to withstand attack from Al/fluoride components of the electrolyte • Coatings for wettability and corrosion- resistance in the cathode Barriers to sodium penetration into the cathode Identification of other materials as effective as TiB ₂ Closer anode to cathode spacer - Maintain Al distance at a controlled level		Testing of materials in cryolite interface ● - Location and protocol for testing at the interface	Development of material resistant to corrosion in alumina feeding Alternative additives to lower temperature of the cryolite bath	Thermocouple protection tubes that can be immersed in molten Al to allow continuous temperature measurement ●● Sensors for measuring Al ₂ O ₃ content of molten electrolyte ★●	

Table 2-1. Major Material and Technology Needs in Smelting

key components of advanced cell designs. They also have the potential for use in improved sidewall materials and cell sensor applications.

The greatest technical challenge to improving the environmental performance and energy efficiency of electrolysis is the development of a **nonconsumable (or inert) anode**. A typical Hall-Heroult cell currently uses a carbon anode that is consumed over a period of weeks and then must be replaced. Inert anode technology will eliminate the need for consumable carbon anodes, thereby reducing carbon dioxide and perfluorocarbon

Most Critical Material Needs in Smelting

- Non-consumable, robust anode
- Pre-bake anode stub protection
- Improved sidewall materials
- Joining/sealing mechanisms for cathode components to prevent material (liquid) from entering cathode (in combination with improved sidewall materials)
- Cathode material that is wetted by aluminum
- Coatings for slowing/stopping erosion in the cathode
- Evaluation and testing of potential materials
- Sensor protection tubes
- Sensors for measuring alumina content of molten electrolyte

emissions significantly. A dditionally, when inert anode technology is coupled with that of stable wetted cathodes, significant energy savings are possible.

A framework for the development of inert anodes was laid out by the Technical Advisory Committee of The Aluminum Association in the 1998 *Inert Anode Roadmap*. The framework describes the required performance characteristics and development requirements of inert anode technology. The encouraging results from Alcoa's recent trials of a new inert anode material suggests that the industry may take a wait-and-see approach to initiating any new research efforts in inert anode materials at this time.



The likelihood of a successful inert anode technology is difficult to assess. One alternative concept is **ceramic coatings used to cover conventional prebaked carbon anodes**. The coatings would provide some protection from the corrosive cell environment, extending the life of the anode by a factor of 5 to 10. Existing coatings used in the aerospace industry could provide a starting point for evaluating potential materials to determine their compatibility with Hall-Heroult cell operating conditions.



Top priorities for ceramic-based cathode research include the development of **improved cathode material that is wetted by aluminum**, **coatings to protect cathodes from erosion**, and **joining or sealing mechanisms for different cathode components**. In the standard Hall-Heroult cell, molten aluminum acts as the upper surface of the electrochemical cathode. Electric current collection is provided by cathode blocks located below the aluminum pool. The integrity of these blocks usually determines cell life, and failure is most often the result of erosion or expansion caused by penetration of sodium or highly corrosive cryolite into the carbon material of the block.



Technology Need Coatings for slowing/stopping erosion in the cathode **Performance Requirements Most Promising Opportunities** Additive to graphite block · Extended life of graphitic block based on economic Internal factors Surface layer · Electrical conductivity (the higher the better) Other Minimal contamination of aluminum produced R&D Needed · Identify potential materials · Investigate methods of application/fabrication/impregnation · Conduct exposure testing **Current Technology** Implementation Steps · None proven · Initiate cooperative effort between aluminum industry, ceramics industry, cathode supplier, and national labs · Look for opportunities at testing facilities

The cathode also plays a large role in determining the electricity requirements of the smelting process. Because the aluminum pool does not "wet" the cathode blocks, an undesirably thick layer of aluminum is required to ensure electrical contact throughout the operation of the cell. The uneven, wavy surface of the metal layer, in turn, requires an anode-cathode (AC) gap that is much greater than what would normally be electrically efficient. The current AC gap could be reduced significantly if the cathode base materials were wetted by the molten aluminum, saving power requirements and costs.

Technology Need

Joining/sealing mechanisms for cathode components to prevent material (liquid) from entering cathode (in combination with improved sidewall materials)



Other limitations of graphite cathode materials include disintegration and deformation during cell operation, poor joints between cathode blocks and poor fitting to the side wall, sludge formation, inefficient cathode configuration, short life, high cost, and pollution from cathode manufacture and disposal. The industry does not believe that carbon-based cathode materials can overcome all of these limitations. Non-carbon materials for cathode applications must exhibit good wettability, high electrical conductivity, low solubility and chemical inertness to aluminum and molten cryolite, oxidation resistance and corrosion resistance to reactive gases, good resistance to penetration by molten cryolite-alumina, adequate mechanical strength and thermal resistance, satisfactory adhesion to cathode substrates, low thermal conductivity, accept-

Applications for Advanced Ceramics in Aluminum Production

able cost, easy fabrication into required shapes, and good erosion resistance ("Evaluating a New Material for Hall-Heroult Cathodes" by T. Mroz in JOM, August 1997). The purity of the aluminum produced in the cell must also be maintained.

Substantial efforts have already been put into evaluating alternative materials for the cathode blocks, with the prime candidates being ceramics. Wetted cathodes made from titanium diboride (TiB_2) have already been demonstrated by Comalco in Australia and are nearing commercialization. Additional research is needed to determine optimal TiB_2 /carbon composites and lower cost methods of manufacturing both the ceramic and cathode element.

The cell lining has evolved considerably in recent years with the use of alternative materials such as ceramics. Silicon-carbide **sidewalls** are increasingly being used in cell linings to avoid problems with sidewall oxidation. More work is needed to develop materials such as nitride-bonded silicon carbide that can survive a minimum of five years in continuous contact with cryolite and aluminum. Thermodynamic modeling using information on material properties and processes coupled with accurate experimental data on cell behavior will provide a basis for material choice and cell design.



The operation of the electrolytic cell can also be improved through better monitoring and control of key chemical and physical parameters. This would require sensors capable of operating continuously in the molten bath for approximately one carbon anode lifetime, or approximately three to four weeks. A tube composed of an advanced ceramic material could serve as a **protective shield for existing sensors**, such as those measuring the temperature of the cryolite/aluminum bath. **New ceramic-based sensors** could also be developed to measure the alumina content of the bath, allowing tighter control of bath chemistry and thus reducing harmful "anode effects," among other benefits. Developing specifications and screening candidate ceramics would require close coordination between the aluminum industry and ceramic companies.

Technology Need

Sensor protection tube

Performance Requirements

- Capable of surviving molten cryolite/molten aluminum
 For control purposes, minimum life equal to anode cycle (approximately 3 weeks)
- Thermal shock resistance
- · For accurate reading of temperature

Most Promising Opportunities

- Silicon nitrides
- Boron nitrides
- Diamond and other coatings

R&D Needed

- · Identify methods to improve the life of existing sensors
- Screen and evaluate candidate materials
- Develop program to get material ready for testing

Current Technology

Implementation Steps

- TiB
- Sialon

Initiate partnership between several aluminum and ceramic companies

Technology Need

Sensors for measuring alumina content of molten electrolyte

Performance Requirements

- Intermittent sensor for troubleshooting applications
- Accuracy within 0.2% of actual content
- Probable feed-through requirement
- Continuous sensor for process control with life of approximately 3 to 4 weeks (long range goal)

Current Technology

Disposable tip sensor

Most Promising Opportunities

- Silicon nitrides
- Boron nitrides
- · Diamond and other coatings

R&D Needed

- · Evaluate potential sensor capabilities with ceramics (i.e., zirconia)
- Screen and evaluate materials

Implementation Steps

- Initiate education effort between aluminum and ceramics industries and sensor companies on available technology
- Present topic to Aluminum Association Technical Advisory Committee
- Conduct future OIT sensor program solicitation

Smelting

Standardized test procedures and protocols must be developed for use in evaluating advanced ceramics for applications in aluminum production. Prior to initiating any testing programs, the aluminum and ceramics industries must jointly establish the standards and methods that will be used to ensure the validity of the results. Testing methods to measure key materials characteristics must be carefully identified and adapted to reflect the actual conditions in which the materials would be expected to operate in the plant. Additional suggestions for evaluation and testing of potential materials are discussed in Chapter 3.





Furnaces & Molten Metal Handling

Aluminum melting and molten metal handling are the processes used to create aluminum ingot primarily from scrap and transfer the molten metal

to subsequent casting operations. These processes create unique operating conditions that require cost-effective materials capable of withstanding severe environments. Aluminum furnaces and molten metal handling equipment have many material limitations, some of which may be cost-effectively addressed using advanced ceramics. This chapter describes the material needs that have been identified as important and opportunities to use advanced ceramics to provide an advantage over materials currently being used.

Critical Material and Technology Needs

The critical material and technology needs in aluminum furnaces and molten metal handling can be categorized into four general areas:

- **Design/Concept Validation**—gathering the data, design and testing criteria and material development approaches to ensure advanced ceramics are designed, manufactured, and tested to suit aluminum industry material requirements.
- **Parts**—creating advanced ceramic components or coatings that can be used to perform the task that existing parts do not adequately fulfill due to the challenges associated with aluminum melting furnaces and molten metal handling systems.
- **Process**—using advanced ceramics to improve the performance of processing equipment throughout the molten metal handling.
- **Materials Properties**—developing cost-effective materials which exhibit specific properties such as high thermal shock resistance, corrosion and erosion resistance, non-wettability, and compatibility with other material types of critical importance in aluminum melting and molten metal transfer.

Table 3-1 presents the entire range of material and technology needs identified during the workshop and reflects relative priority of need for aluminum producers and opportunity for advanced ceramic producers.

Table 3-1. Major Material and Technology Needs in Furnaces/Molten Metal Handling ★ = Top Priorities; ● = Top Opportunities						
Design/Concept Validation		Parts	Process	Materials Properties		
Standardized testing ************************************	Center of excellence approach to identify criteria for different applications Non-destructive condition assessment of components in batch operations (between cycles) Parts made from multiple materials/ partial coatings to reduce costs Consideration of different materials in the fumace of the future Ceramics focused on continuous, minimal human contact applications – Paradigm shift Method to handle material data reporting—interest list to describe what data is desired Entire advanced ceramics fumace lining Considering changing only surfaces in molten metal contact rather than bulk material for metarial in refractory fumace (with thermocouple sheaths, sensors) One material for multiple applications "Parts supplying" mentality focused on supplying components of a system – Better additives or raw materials	Detection of temperature in refractory furnace (thermocouple sheaths and sensors) ★★★●● Components in spouts that are in constant molten metal contact ★★★●● - Prevention of oxide interfere with metal purity - Metal level control, particularly with high-Mg alloys Casting nozzles (must last 3 to 4 days) ★●● Flow control valves (similar to steel) ★●● Baghouse filters capable of filtering 3 microns ★● Pump parts ●● Pump parts ●● Rotary units have many moving parts that may benefit from advanced ceramics ●● Header distribution systems for continuous casting ★ Dies, rolls, other downstream applications that lower temperatures ● Furnace dampers that do not use cooling water Bonding systems that hold refractories together are weakest part Spout floats Furnace tools of all sizes - Improved life	Metal contact/ machining areas downstream (e.g., scalping, transfer roll tables) ● Surface finishing of rolling mill rolls (roll grinding) Sides of remelt furnaces should be capable of quick heating/ reheating - Minimization of lag time Billet casting Robust repair technology to ensure minimal contaminate introduction Recuperation systems	Non-wetting materials ************************************		
		safety, and serviceability				

Opportunities for Advanced Ceramics

Advanced ceramics offer several promising opportunities to improve the efficiency, productivity, and profitability of aluminum furnaces and molten metal handling operations. The eight items detailed in the following pages depict those opportunities which hold the most promise for success or represent an area where secondary aluminum producer needs are particularly critical. Included in the figures are:

- performance requirements to meet aluminum industry needs
- current technology being used
- · most promising opportunities for advanced ceramics
- R&D needed to capitalize on those opportunities
- key implementation steps

Standardized testing and appropriate laboratory criteria

are critical to ensure that the performance of advanced ceramics in operating conditions relevant to aluminum production is assessed. The critical properties to test are thermal shock, corrosion, mechanical impact, and erosion on scales found in actual aluminum production. While existing testing procedures can measure three of these variables at once, monitoring all four concurrently is difficult in a laboratory setting. The first step in the R&D to address this need must be to compile an overview of existing testing procedures. One barrier to progress in testing is the lack of available test furnaces, as aluminum producers are hesitant to use their production furnaces as test beds for

Most Critical Material Needs in Melting and Molten Metal Handling

- Standardized testing and appropriate laboratory criteria
- Enhanced surface properties (roughness, coatings, etc.) through surface engineering
- Better understanding of aluminum/material interface at microscale
- Sensors for process control via accurate temperature measurement

Material Needs by Process Stage

- **Furnace** tap hole blocks, burner blocks, sensors, lining materials, coatings, etc.
- Molten Metal Transfer coatings and other surface protections systems, etc.
- In-line Metal Treatment rotors, shafts, heating elements, coatings, etc.
- **Casting** spouts, nozzles, pins, skin dams, distribution headers, flow control valves, molten metal pump parts, coatings, etc.

new technology. Accordingly, the industry should look to the glass industry user facility as a model for what can be done to establish an industry-wide testing facility. An alternative approach to actual laboratory testing is developing advanced modeling capability that will allow "virtual" testing.

Technology Need

Standardized testing and appropriate laboratory criteria

Performance Requirements

- Set of test procedures and standards that can be validated
- · Concurrent testing for:
- Corrosion
- Abrasion/erosion
- Thermal shock
- Mechanical impact
- Factory-scale testing
- Testing in alloys
- Cup tests for penetration
- Erosion/corrosion test in fluorine and non-fluorine salts
- Simulation tests
- · Account for all interactions in the furnace
- Analogies with other industries (e.g., auto, aerospace—system-wide tests)
- Bench scale test indicating whether material has chance for survival

Current Technology

- Total immersion test and crucible test; test under thermal gradient between atmosphere and metal for erosion
- Aluminum treatment furnace below metal line; atmosphere-refractories-metal interface
- Test for thermal shock, corrosion, mechanical impact all at once, but not erosion
- · Final test: real furnace for a year

Most Promising Opportunities

To be defined

R&D Needed

- · Compile overview of existing tests as first step
- · Conduct separate effort to address test standardization
- · Undertake thorough post-mortem analyses
- · Adopt center of excellence approach to assemble technical expertise
- · Involve mechanical and design engineers in R&D process
- Understand overall system interactions for developing holistic systems tests
- · Share test manuals
- Establish a test furnace (approximately 1/2 scale)
- Explore modeling opportunities for virtual testing
 Chemical aspects are challenging
- · Quantitatively define specific desired material properties

Implementation Steps

- Assemble existing testing procedures led by representatives of USACA and The Aluminum Association
- · Consider glass industry user facility as a model
- Combine refractory effort with OIT Best Practices program for furnaces
 - New Industrial Materials of the Future effort will include refractories
- Propose test guidelines (The Aluminum Association)

Advanced ceramics need **enhanced surface properties through surface engineering** to meet certain requirements in aluminum production, particularly in troughs and other molten metal transfer applications, where surface properties and finish directly affect product quality Coatings may be the most appropriate approach to enhancing surface properties using advanced ceramics. Initial R&D should include in-depth consideration of troughs and their design by both advanced ceramic providers and aluminum producers. Advanced ceramic providers must understand trough design in order to enhance their performance, while aluminum producers must consider how to retrofit or redesign troughs to take full advantage of the enhanced material properties advanced ceramics can provide. Because the temperatures required in this application are only around 1000 °C (1800 °F) low-grade silicon nitride may be used to reduce material costs.

Enhanced surface properties (roughness, coatings, etc.) through surface engineeering

Performance Requirements

- High performance at approximately 1800 °F/1000 °C
 Thermal shock: Room temperature to 1500 °F in three seconds
- · Long-term cost competitiveness with existing materials

Most Promising Opportunities

- Coatings that are more resilient than current technology
 Porosity may allow impregnation with beneficial materials
- Low grade silicon nitride (1800 °F/1000 °C) may make it cost-effective
- · Boron nitride additives

Implementation Steps

R&D Needed

- · Better understand liner thickness requirements
- Reconsider designs of troughs and other equipment to take advantage of ceramic options
- Retrofit designs of troughs and other equipment to accommodate new material introduction
- · Better understand bonding mechanism for coatings
 - Bonding is more problematic with dense substrate—some porosity is needed
- · Conduct thorough post-mortem analyses
- Conduct metal corrosion testing of various grades of ceramic materials
- Develop capabilities to consider entire system interaction
- · Near-term solutions are to coat existing material to protect it

Current Technology

- Sialon, silicon nitride, boron nitride (excellent materials, but expensive)
- May make financial sense in long term for certain applications
- Define material requirements through collaboration between ceramics and aluminum industries
- National labs are unbiased sources of technical expertiseDevelop design teams to address needs
- Determine existing gaps in research capabilities
 Expand upon existing work
- First step: Compile inventory of materials available

Developing a **better understanding of aluminum-material interface** is a third crucial area of research. The materials being used in aluminum production today perform well under most conditions, but many fail when in direct contact with molten aluminum because it is highly corrosive. Coatings are used in many areas, but they often wear away, particularly when under continuous metal flow such as during continuous casting. In order for advanced ceramics to help address these material shortcomings, a more thorough understanding of the fundamental interactions between aluminum and advanced ceramic materials on a microscale is needed. The first steps in cultivating such knowledge is to quantitatively define and focus on the properties which are most critical to aluminum producers. Researchers should also look to the science of aluminum metal matrix composites, where much has been learned about how aluminum interacts with non-metallic particulates.

Technology Need

Better understanding of aluminum-material interface at microscale

Performance Requirements Most Promising Opportunities To be defined · For aluminum contact, strong, smooth, non-wetting, non-reactive material that resists thermal shock · For non-aluminum-contact, resistant to salt disposition, **R&D** Needed vapor attack, splash, corundum growth, thermal cycling, mechanical abuse · Investigate aluminum-fiber interactions in MMCs as first step to - Consider reducing atmosphere as alternative understanding microscale interactions · Reactivity-resistant to spinel formation and corundum · Conduct thorough post mortem analyses of materials to undertand formation failure modes; retrieve test results for evaluation · Mechanical abuse-quantifiable extent of crack · Develop baseline data for desired properties propagation · Define ideal properties and understand microscale implications - Location specific · Consider materials specific to certain applications · Consider interaction among all properties Aggregates may hold opportunity · Extend science of anti-wetting additives to extend range of material choices Implementation Steps **Current Technology** · Initiate long-term university program (rigorous R&D is required) - Take consortium approach involving industry, academia, and · Today's materials perform well for some properties but fail laboratories when in contact with molten aluminum - Identify experts in the field · Coatings-wear away in continuous casting due to · Look at reactions in refractories in existing furnaces to compile metal flow: some materials are not treated at all baseline data

Sensors for process control via accurate measurement of temperature in furnaces are needed to improve product quality and production efficiency. Aluminum producers would like to monitor the temperature of the aluminum bath directly, but because of the harsh environment, thermocouple protection tubes are subject to severe erosion and corrosion. Existing oxygen sensors that monitor rich/lean atmosphere qualities do not work well to control quality. In this particular application, the sensor material must be resistant to thermal shock, corrosion, and high temperatures.

Because the coated cast iron sensors used today are so inexpensive, sensor protection using advanced ceramics may not be a viable approach. However, new sensor development does hold significant promise and may be the focus of a separate effort, possibly starting with a workshop (similar to that held for this report) to initiate cooperative efforts among the sensor development community, advanced ceramic producers, and aluminum producers.

Technology Need

Sensors for process control via accurate measurement of temperature in refractory furnace

Performance Requirements

- Atmosphere: 4000 °F/2200 °C, natural gas, water, carbon monoxide, unburned fuel, salt fumes
- Minimum life 1 year (comparable to Sialon)
- · Ultimately in-line sensing and analysis for metal quality
- · Non-contact metal sensors (lasers, electromagnetic, etc.)
- Salt vapor sensors, monitor vapor evolution during cycle

Most Promising Opportunities

- Ceramic coatings on cast iron to reduce surface failure
- Self-cleaned or easily cleaned to minimize potential abuse
- Minimize worker interaction by good design
- Silicon nitride, Sialon, boron nitride, or other materials with similar properties
- · Sensor development, as opposed to sensor protection

R&D Needed

- Educate and train workers to reduce abuse
- Consider optic sensing of molten metal temperature
- Explore inclusion detection, oxygen detection, salt detection, sensor development
- Develop contacting probe with molten aluminum to detect refractory particles in bath
- Consider casting headers, valves, diffusers, etc.

Current Technology

- Oxygen sensors to monitor rich/lean atmosphere do not work well
- In-roof thermocouples to control roof temperatures (aluminum silicon carbide)
- Cannot measure bath temperature
- Three two-foot long sensors in roof made from coated cast iron
- · Abuse is main reason for failure
- · Cast iron is used (2 week lifetime)

Implementation Steps

- Consider sensors for process control (workshop, etc.)
- Involve sensor development community in R&D process

In addition to the four priority needs described above, each major process step in aluminum melting, treatment, and transfer has additional material needs which may be fulfilled by advanced ceramics. The diagram on the following page depicts the performance requirements, technology used today, most promising opportunities for advanced ceramics, R&D needed, and key implementation steps for four major process stages in scrap-based aluminum production (furnace, molten metal transfer, in-line metal treatment, and casting operations). Because the focus of the workshop held for this report was furnaces and molten metal handling, the other two areas are only discussed in a preliminary capacity. Undoubtedly, additional opportunities exist for advanced ceramics in downstream applications; future efforts may explore these opportunities.

	Furnace	Molten Metal Handling	In-Line Metal Treatment	Casting Operations	
Performance Re	equirements				
Operating Temperature	Approximately 2200°- 2500°F/1100°-1300°C	Approximately 1400°F/750°C	Approximately 1400°F/750°C— easy to maintain uniform temp • Metal line variation is 6-8 inches ****	Lower than approximately 1400°F/700°C	
Thermal Shock	2000°- 1200°F/ 1100°-650°C	Room to service temperature instantly	Cool down for repair, so not main consideration	Very high	
Impact Resistance	High impact compressive impact shear 1500 lb ingot	Not major issue, better design can reduce impact	Not an issue	Lot of handling, and abuse, sheeting with spouts is particularly at risk	
Erosion/Wear Resistance	Furnace sidewall, circulation leads to high erosion due to particulates	Critical in some places (e.g., impact pad, outlet tap hole)	Rotors and shafts erode	Mold package, spouts high resistance	
Corrosion	Everywhere, especially metal contact zone	Moderate corrosion in continuous casting	Same as troughs, slightly worse	Critical because metal contamination is possible	
Surface Finish	Not relevant	Important so cleaning is easy	Similar to troughs	Critical	
Thermal Mass	Low thermal mass, not critical factor	Important— Heat cannot be drawn out of metal at beginning of trough	Not an issue—preheated	Fairly low	
Thermal Conductivity	Furnace design makes it important	Low	Need low conductivity	Very low	
Salt/Chloride Resistance	Sidewall furnaces must be resistant to salt, chloride contact	Not an issue	Degassing-salts - Filters and degassing operations - 75% goes through porous form filters (CFF) - Fluting gases are used: argon, argon chlorine	Not an issue	
Other	None	Must be easy to change on fly (1 year service life is good)	Spin at 200-600 rpm rotors and shafts (three feet long) Graphite lasts 2 weeks	None	
Material Used T	oday				
Material OSec 1	Refractory life (4 to 5 years) depends on location - High alumina - 4 to 6 hour change Fused silica castables — corrosion resistance is not good enough, boron nitride coating helps	None	Similar to furnace materials (anti-wetting materials), rotors and shafts	Dense fused silicas, fused silica castables, aluminum titanate	
Most Promising	Opportunities				
	Tap hole burners, sensor linings New coatings for existing material Zone in center of furnace (8 to 14 inches wide)	Coatings or other surface protection	Rotors and shafts in degassing, heater elements, coatings	New materials, zero thermal expansion (ZTE), is example, impregnated with non-wetted agent	
R&D Needed					
	Specific tests to determine how materials react in the actual environment Understanding of failure mechanisms of existing materials—post-mortem analyses	Surface engineering (relatively easy to test in field)	Design changes to alleviate problems with producing threaded ceramic components Tougher materials	Similar to rotors—metal corrosion, immersion testing	
Implementation	Steps				
	Establish overview of existing test methods	Identify alternatives (e.g., plasma spray, vapor decomposition, etc.) — overview of protection schemes	Establish partnerships between aluminum and ceramics industry Allow ceramics industry to observe current technology being used	Allow ceramics industry to see what today's parts look like— part shape is somewhat inflexible	

Material Needs in Aluminum Melting/Molten Metal Transfer Processes



Initial Implementation Steps

While the specific needs described in the preceding chapter all have unique requirements, a number of implementation steps can be taken

to begin the overall process of collaboration between the aluminum and ceramics industries. These cross-cutting implementation steps will be central to a successful strategy aimed at realizing significant energy and productivity gains in aluminum production by using advanced ceramics.

- Establish partnerships between advanced ceramics and aluminum companies and industries as a whole. This is the first step in adapting advanced ceramics for applications in aluminum production. Only through close cooperation and collaboration will material developers become familiar with real aluminum production environments, existing technology, and process limitations that will dictate material and component design parameters. The Aluminum Association and USACA should act on behalf of their members to help foster such partnerships by continuing to stimulate a dialog between the industries.
- **Collect and organize baseline data and existing efforts.** In many of the priority need areas, work has already been done with advanced materials and ceramics. Additionally, performance data are not always available for existing materials, forcing material developers to sometimes repeat mistakes made in the past. A comprehensive inventory of materials already available with appropriate data for parameters relevant to aluminum producers is an crucial first step in matching aluminum needs to advanced ceramic capabilities. Similarly, an overview of existing test methods would be beneficial in determining where improvements are needed.
- Educate and train workers to handle advanced ceramic components. Advanced ceramic components are often significantly more expensive than traditional materials, a cost that is justified by their superior performance. However, worker handling of these components can sometimes result in premature breakage or material degradation due to mechanical impact or abuse. Training is needed to reduce the frequency at which workers inadvertently damage a component. Mishandling is particularly common during cleaning of components; materials that require less frequent cleaning may reduce worker-related damage.



Appendix: List of Contributors

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