Report on the Process Heating Advanced Materials Forum



Sponsored by

U. G. Department of Energy Office of Energy Efficiency and Renewable Energy and Industrial Heating Equipment Association



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Note: Because of their large size, the presentations and research briefs are included on the CD-ROM rather than in this printed version of the report.



Process Heating Advanced Materials Forum



Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee February 5–6, 2003

Dear Colleague:

On behalf of The Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE) and the Industrial Heating Equipment Association (IHEA), we welcome you to the Process Heating Advanced Materials Forum.

The forum agenda focuses on use of advanced materials including high-temperature alloys, ceramics and composites, and refractories and insulation to achieve greater energy efficiency, as well as to lower operating costs, increase reliability and productivity, and improve safety.

The forum attendees include representatives from the process heating industry, the associated user community, and scientists and researchers from DOE national laboratories. The agenda has been structured to allow for both formal and informal opportunities to exchange information. We encourage you to discuss and share information on your specific needs, recent research and development results, and the future research needs of the process heating industry in the area of advanced materials.

We hope that your participation in the forum activities and your visit to the Oak Ridge National Laboratory will be productive and enjoyable.

Ramesh Jain Office of Energy Efficiency and Renewable Energy U.S. Department of Energy Mario Ciampini, President Industrial Heating Equipment Association

Executive Summary

An advanced materials forum was held at Oak Ridge National Laboratory (ORNL) February 5–6, 2003, under the sponsorship of the Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE) and the Industrial Heating Equipment Association (IHEA).

This summary report was prepared under the guidance of the Process Heating Advanced Materials Subcommittee. It identifies areas of research and development that demonstrate particular promise for the process heating industry and comments on a strategy for DOE and the national laboratories to work with the industry to proceed with the research and development (R&D) that meet future needs of the industry.

The forum was attended by 56 representative end users from Industries of the Future, equipment suppliers, and research scientists and engineers from DOE national Laboratories. The purpose of the forum was to provide an environment in which representatives from the process heating industry, the associated user community, and scientists and researchers from the national laboratories and elsewhere can share information on recent R&D and discuss the future research needs of the process heating industry in the area of advanced materials.

The forum agenda (Appendix A) was structured to allow for both formal and informal opportunities to exchange information. The topics of discussion included use of advanced materials such as high-temperature alloys, advanced ceramics, and refractories and insulation in process heating equipment. Representatives from DOE-EERE and IHEA, as well as members of industry and scientists from the national laboratories, made presentations on various areas of materials technology and their application to process heating systems. The agenda included a tour of the Materials Research Laboratories at ORNL.

Three round table discussions involving representatives from industry, materials suppliers, and the national laboratories addressed the future needs of the industry and possible areas of research and developments. The three areas of focus were (1) High-Temperature Alloys; (2) Insulation and Refractories, and (3) Advanced Ceramics. These sessions identified the following research needs that could help U.S. industries make significant improvements in energy efficiency and related areas such as productivity, waste reduction, emission reduction, safety, and production cost reduction.

The recommendations and research needs identified in the round table discussions for the three areas follow:

1. High-Temperature Alloys

- Creep rupture property improvements.
- Extension of temperature limits to 2300°F+
- Better life prediction/monitoring
- Enhance resistance to aggressive environments

2. Refractories and Insulation

- Modeling of phases and reactions and corrosion modeling
- New refractory application and mounting methods
- Advanced coatings for current refractories
- The use of bonded-spinel refractories, or very pure silica refractories coated with spinel or mullite for use in furnace crowns
- Development and application of preformed refractory shapes
- Utilization of low-thermal-conductivity materials

3. Advanced Ceramics

- Advanced ceramics to eliminate or reduce erosion of material used in handling of liquid or solid fuels.
- Oxidation and coking resistance ceramics or coatings on alloys for burner parts (i.e., flame stabilizers)
- Special coatings with customize spectral characteristics to enhance radiation heat transfer in high-temperature furnaces using rare earth oxides or other ceramic coatings for refractories.
- Advanced ceramic materials for tubular (or other shapes) heat exchangers and associated joining technologies to recover heat from high-temperature corrosive stack gases.
- Ceramic materials for catalyst base to avoid poisoning of catalyst.
- New ceramic materials for sensors and probes that can survive in stack gases containing hightemperature, highly corrosive gases.

Details for each of the round table sessions are given in this report.

The information obtained from this forum will be discussed by the advanced materials subcommittee and would be used for defining potential R&D and other activities that could meet he industry requirements.

Introduction

Almost every product that we purchase, use, and consume in daily life requires process heating. Process heating accounts for nearly 17% of all U.S. industrial energy use. Improving the efficient operation of process heating systems through use of advanced materials such as high-temperature alloys, ceramics and composites, and refractories and insulation will contribute to greater energy efficiency. It should also help lower operating costs, increase reliability and productivity, and improve safety. For these reasons, DOE-EERE and IHEA jointly sponsored the Process Heating Advanced Materials Forum held at ORNL February 5–6, 2003.

The forum was attended by 56 representative end users from Industries of the Future, equipment suppliers, and research scientists and engineers from DOE national laboratories. The purpose of the forum was to provide an environment in which representatives from the process heating industry, the associated user community, and scientists and researchers from our national laboratories and elsewhere can share information on recent R&D and discuss the future research needs of the process heating industry in the area of advanced materials. The forum provided an opportunity for the attendees to visit R&D facilities at ORNL and to discuss various means available to pursue collaborative R&D and other activities at ORNL.

The forum agenda (Appendix A) was structured to allow for both formal and informal opportunities to exchange information.

Prior to this meeting, a white paper (matrix) was prepared to describe materials needs for process heating equipment and components. This information was sent to DOE national laboratories to help them identify research areas that could serve needs of the industry and could be presented at the forum.

In response to this request, several national laboratories submitted abstracts to the Process Heating Advanced Materials Subcommittee. The subcommittee selected five of these proposed papers for presentation at the forum.

The forum included presentations on the current status of the process heating industry, status of the technology for three major areas (high-temperature alloys, refractories and insulation, and advanced ceramics) of materials used in process heating, new developments in materials at the national laboratories, and the industry-government collaboration opportunities. The attendees visited various laboratories performing research and application-related activities at ORNL.

Following the presentations and laboratory visit, forum participants broke out into three separate sessions, one for each of the topics of interest mentioned above, to discuss the industry needs and future R&D activities that could meet the industry needs.

The following sections provide summaries of the presentations, details of discussions at each of the three round table meetings, and additional remarks on methods of collaborative activities between industry and DOE national laboratories. Additional information on the forum is provided in the end of the report: Appendix B: Speaker/Presenter Information, Appendix C: List of Forum Attendees, Appendix D: Research Briefs, and Appendex E: Forum Presentations.

The forum arrangements were made by ORNL with help from Mr. Peter Angelini and Ms. Gwen Sims. The Process Heating Advanced Materials Subcommittee would like to express their sincere thanks for their efforts.

Materials Requirements for Process Heating Industry

Prior to the forum the subcommittee compiled a list of materials needs for the industrial heating systems. The process included three steps: (1) defining material selection criteria, (2) identifying areas for improvement, and (3) identifying components or subsystems that require one or more of the considerations identified in step 1.

Define Material Selection Criteria

The first step was to define specific considerations that are used in selection of materials used in furnaces. The material selection criteria that were identified are numbered in the following list. Numbers associated with the criteria are also used under the heading "Major criteria for material section" in Table 1.

Material selection criteria

- 1. Strength at operating temperature tensile, compressive, and shear
- 2. Creep at operating temperature
- 3. Thermal fatigue cycling
- 4. Thermal fatigue cycling
- 5. Oxidation resistance
- 6. Corrosion resistance halogens (cholorine, fluorine, etc.), sulfur and acidic environment
- 7. Reducing atmosphere resistance
- 8. Liquid metal steam resistance
- 9. Solid-metal reactions
- 10. Other specify

Identify Specific Areas For Improvement

The second step was to identify specific areas for improvement that would improve performance of the process heating equipment and components. The areas identified follow:

Areas for improvement

- Longer life for heating elements, radiant tubes, etc.
- Weight reduction for trays, fixtures, baskets, etc.
- Increased life of insulation and refractory for combustion chamber, furnace walls, and burner blocks
- High-strength, high-temperature materials for recuperators, regenerators, heat exchangers, etc.
- Reduction or elimination of water air cooling through use of improved material for load support, rails, rollers, etc. (nonmetallic – ceramics)
- Materials for high-temperature fans (metallic, ceramics or composite material)
- Long-life sensor and protection materials
- Increased life of heater tubes, heat exchanger elements (matrix), etc., for high- and low-temperature heat recovery systems.

Identify Components or Subsystems Requiring Considerations in Step 1.

The third step involved identifying components or subsystems such as burners, fans, and material-handling systems that require one or more of the considerations identified in step 1. The list is provided

in Table 1. The table divides the materials in three general categories: high-temperature alloys, refractories and insulation, and advanced ceramics including composite materials.

This information was sent to the DOE national laboratories with active programs in materials area through the Laboratory Coordination Council. Laboratories includes ORNL, Lawrence Berkley National Laboratory (LBNL), Argon National Laboratory (ANL), Albany Research Center (ARC), and Sandia National Laboratory.

Twelve abstracts, listed in Appendix D, were received. They were reviewed by the subcommittee consisting of the following seven members:

- 1. Mario Ciampini, President, IHEA.
- 2. Jason Wilson, Technical Marketing Manager, Rolled Alloys, Inc.
- 3. Robert Licht, Manager Government Programs Group, Saint-Gobain Ceramics & Plastics, Inc., and Chairman, USACA
- 4. Gary Deren, Unifrax Corporation
- 5. Peter Angelini, ORNL
- 6. Arvind Thekdi. President, E3M, Inc.
- 7. Russ Mosher, President, Mosher and Associates

Five abstracts were selected for presentation at the forum. The selection was made based on the research topic and its match with the industry requirements, it potential for commercial application, and the timeframe for availability of the technology. A list of the selected papers is provided in the next section.

Table 1. Advanced materials requirement in process heating systems

	Criteria for	Metals/high-	Engineered	l materials	
Application area	material selection ^a	temperature alloys	Refractories/ insulation	Ceramics/ nonmetallic	Composites
		Heat generati	on		
Burners/combustors - normal	1,2,3,4,5,6,7	Nozzles	Blocks	Nozzles	Nozzles
Burners – IR and panel	1,2,3,4,5	Matrix for IR burners	Matrix for IR burners	Matrix for IR burners	Matrix for IR burners
Radiant tubes	1,2,3,4,5,7,9	Tube		Tube	Tube
Immersion tubes	1,2,3,4,5,8	Tube		Tube	Tube
Combustion chamber	1,3,4,5,6,9		Exposed surfaces		
Heat transfer surfaces	1,2,3,4,5,6,7,8,9	Surface coating		Surface coatings	
Electrical heating elements	1,2,3,4,5,6,7	Elements		Elements	Elements
Mounting system	1,2,3,4,5,7		Mounting panel (MP)	Elements and MP	

Table 1. Advanced materials requirement in process heating systems (cont.)

Table 1. Advanced materials requirement in process heating systems (cont.)					
	Criteria for	Metals/high-		d materials	
Application area	material selection ^a	temperature alloys	Refractories/ insulation	Ceramics/ nonmetallic	Composites
		Heat transfe			·
Furnaces, heaters, etc.	1,2,3,4,5,6, 13	Nozzles		Nozzles	Nozzles
		Fans		Fans	Fans
		Radiation schields		Radiation schields	Radiation schields
		Baffles Retorts		Baffles	Baffles
		Heat containme	ent		
Furnances, heaters, etc.			Furnace walls, crowns	Furnace walls, crowns	Nozzles
Water/air cooling		Matrix for IR burners	Matrix for IR burners	Matrix for IR burners	Matrix for IR burners
		Waste heat reco	very		
Recuperators		Tubes / separators		Tubes / separators	Tubes / separators
		Fins / extended surfaces		Fins / extended surfaces	Fins / extended surfaces
Regenerators	Heat transfer (HT) matrix		HT matrix	HT matrix	HT matrix
Heat transfer surfaces		Surface coatings		Surface coatings	
		Emission cont	rol		
Scrubbers		Corrosion resistant packing, etc.		Corrosion resistant packing, etc.	Corrosion resistant packing, etc.
SCRs for NO _x control		Substrate Coatings		Substrate Coatings	
			Refractories/ insulation	Ceramics/ nonmetallic	
Material handling					
Load support		Trays, fixtures, etc.		Trays, fixtures, etc.	Trays, fixtures, etc.
Transfer		Rails, belts, pushers, flights, etc.		Rails, belts, pushers, flights, etc.	Rails, belts, pushers, flights, etc.
Rolls, rollers, etc.		Rolls, rollers, etc.		Rolls, rollers, etc.	
		Coatings		Coatings	

Table 1. Advanced materials requirement in process heating systems (cont.)

Application area	Criteria for material selection ^a	Metals/high- temperature alloys	Engineere Refractories/ insulation	d materials Ceramics/ nonmetallic	Composites
Material handling					
Waste containment		Crucibles, holders, etc.	Crucibles, holders, etc.	Crucibles, holders, etc.	
Sensors and controls					
		Protection tubes Probes		Protection tubes Probes	

^a See the section titled "Define Material Selection Criteria" for a numbered list of criteria.

The Forum Presentations

The forum agenda was structured to allow for both formal and informal opportunities to exchange information. It was intended to give an overview of the materials program supported by the DOE–EERE and the status of the process heating industry and its general needs, followed by a review of the current status of materials used by the industry. The review was divided into the three categories of the materials mentioned earlier.

The speakers and their presentations are listed below.

- 1. Advanced Materials Programs/DOE/National Labs. Dr. Sara Dillich, DOE-OIT
- 2. A Look at the U. S. Process Heating Industry: Today and Tomorrow Mr. Mario Ciampini, President, IHEA. (presented by Arvind Thekdi, President E3M, Inc.)
- 3. High-Temperature Alloys Jason Wilson, Technical Marketing Manager, Rolled Alloys, Inc.
- 4. Advanced Ceramics Robert Licht, Manager Government Programs Group, Saint-Gobain Ceramics & Plastics, Inc. and Chairman USACA
- 5. Refractories and Insulation for the Heating Equipment Industry Gary Deren, Unifrax Corporation

Following papers, selected by the subcommittee, were presented by the DOE national laboratories.

- 6. High-Temperature Alloys Vinod Sikka, ORNL
- 7. Low-Cost Ceramic Composite Fan Materials Ronald Ott, ORNL
- Monolithic and Surface Modified Ceramics Andrew Wereszczak, ORNL
- Advanced Nonporous Composite Materials for Industrial Heat Applications Michael Ayers, LBNL
- 10. Advanced Refractory Materials Research Program Cindy Dogan, ARC
- 11. Materials Degradation Processes in Elevated-Temperature Environments Relevant to Process Heating Peter Tortorelli, ORNL

Additional presentations included:

- 12. Welcome and Introduction to ORNL Marilyn Brown, Director, EERE Program, ORNL
- 13. Working with DOE National Laboratories Lou Dunlap, Deputy Director Technology Transfer and Economic Development
- 14. Dinner Presentation: Superconductivity: Evolution of a Research and Development Project Donald M. Kroeger, ORNL

All of these presentations, with exception of the dinner presentation, are listed in Appendix E. Because of their large size, the actual presentations are provided on the CD-ROM.

Round Table Break-Out Sessions Reports

Three breakout sessions were held during the forum. The three topics were (1) High-Temperature Alloys, (2) Insulation and Refractories, and (3) Advanced Ceramics.

The following reports prepared by the session chairpersons describe the summary of discussion and R&D program recommendations suggested by the session attendees.

High-Temperature Alloys

Session Chair: Jason Wilson - Rolled Alloys

Participants

Jason Wilson Rolled Alloys
Ahmed Abada Steel Tech Ltd.

Russ Mosher R.N. Mosher & Associates

Bill Scott ASM International Malcomb Gordge Spirax Sarco, Inc.

Vinod Sikka ORNL

David Collier Eclipse Combustion

Dennis Bickford Westinghouse Savannah River Rick Sisson Worcester Polytechnic Institute

Don Voke Duraloy Technologies
Bruce Kelly Sandia National Laboratory

Richard Alstott Bloom Engineering

Jim McLaughlin ExxonMobil Research & Engineering Phil Anderson ExxonMobil Research & Engineering

Stated meeting objectives

- Provide interaction between the user of heat-resistant metals (i.e., the Process Heating Industry) and the R&D community (i.e., ceramic suppliers, national laboratories, and universities).
- Identify future materials needs to improve performance of process heating equipment systems.

Overview and approach

The group was composed of a good cross section of heat-resistant alloy suppliers: Wrought & Castings (3), national laboratories (2), universities (1), trade associations (1), equipment suppliers [burners, boilers) (3)], end use industries [(refining, nuclear (2)], and consulting (1).

Each participant was asked to volunteer two life-limiting issues related to heat-resistant metallics.

Heat-Resistant Metallic Areas for Improvement

- Creep rupture properties
- Toughness properties (long-term aging)
- Scaling resistance/oxidation resistance
- Resistance to halogens/salts

- Extension of temperature limits from 2200°F by 100-200°F
- Thermal shock resistance
- Improved tools for materials selection
- Ductility castings
- Life prediction/assessment tools or software
- Sulfidation resistance

A discussion ensued to determine which areas were felt to be of greatest importance. Four items were agreed upon.

- I. Creep rupture property improvements
- II. Extension of temperature limits beyond 2200°F by 100 to 200°F.
- III. Life prediction/assessment tools or software
- IV. Aggressive environment resistance (sulfidation)

Potential areas of study for these four items were then discussed.

- I. Creep rupture property improvements
 - A. Nanophase strengthening
 - 1. Inexpensive means of strength improvement capable of use in traditionally melted alloys if better understood.
 - B. Greater data generation
 - 1. More accurate design capabilities for long-term service.
 - 2. Computational software for greater long term modeling of high-temperature alloys.
- II. Extension of temperature limits to 2300°F+
 - A. Improved intermetallics usability
 - 1. Joining methods
 - 2. Wrought products
 - B. Oxide dispersion alloys
 - 1. Fe-Cr-Al type offer high melting points up to 2600°F
 - a. Lack ability for joining by conventional arc welding
 - b. Need production improvements to reduce costs
- III. Better Life Prediction/Monitoring
 - A. Collaboration with sensors group to apply newer inspection technologies to high-temperature components to assess the materials condition and predict remaining life.
 - B. Better data collection for specific types of units (boilers, ethylene furnaces, crude heaters, recuperators)
 - C. Better modeling tools
 - D. Integrate the above 3 items to create a better overall picture of what is occurring in these units.
- IV. Enhance resistance to Aggressive Environments
 - A. Surface treatments or Coatings suitable for high temperatures

Summary

A recurring theme in the discussion was the need for better data collection and compilation of this information for engineers to use for better design and, once in service, greater life prediction. The ability to better use existing information to select the proper alloy initially and then to design with these alloys more accurately seems to be a first step while newer alloy technologies are maturing.

Insulation and Refractories

Session Chairs: Peter Angelini and James Hemrick, ORNL

Participants

Peter Angelini, ORNL (angelinip@ornl.gov)

Michael Ayers, Lawrence Berkeley National Laboratory (LBNL) (mrayers@inreach.com)

Michael Binni, Bloom Engineering (mbinni@bloomeng.com)

Gary Deren, Unifrax Corporation (gderen@unifrax.com)

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Jim Shell, Shell Glass Consulting, Inc. (jshell@columbus.rr.com)

Carsten Weinhold, Schott Glass Technologies (carsten.weinhold@us.schott.com)

Current Areas and Issues of Refractory Use

Several industries where identified where improved refractories can result in improved processing and energy efficiencies. These are highlighted below.

Steel

About 20–40% of the refractories found in the steel industry are used in ladles for both integrated mills and minimills. This use accounts for the single largest application of refractories in the steel industry. Large amounts of energy are required to preheat ladles prior to their being filled with molten metal; otherwise, the refractories may fracture from mechanical and thermal shock and separate from their anchoring systems. Currently, the heating times for ladles are high, and heating efficiency is low. Additionally, ladles are often held at operating temperature for long periods of time (8–12 hours) before use to avoid reheating. Energy is required to hold the ladles at temperature, and heat losses from the refractory during this time can be substantial. Preformed refractory systems may reduce the heating time and improve thermal efficiency substantially, which could also lead to lower hold times and losses for heated ladles.

Another area where refractories are used in the steel industry is as protective coverings on metallic skids. These refractories must provide both mechanical and thermal protection to the metallic skid material beneath it. Currently, most skids are water-cooled, a process that leads to substantial energy losses. Additionally, up to 30% breakage of the refractory due to abrasion, and erosion occurs in less than 2 years of service life.

Also, blast furnaces use large amounts of refractories. The refractories in this case are generally bricks. These furnaces can cost up to \$100 million and require extensive repairs every 10 to 12 years to extend the operational lifetime of the units. Additionally, maintenance issues must be addressed during the operational period. Some of the current major refractory issues include (1) use of gunnable or castable refractories in place of bricks, (2) mounting designs for the refractories used, (2) requirements for improved thermal insulation, (4) lack of understanding of the corrosion and chemical reactions of the refractories in that environment, (5) lack of sensors for determining the thickness and recession of the refractories during service, and (6) energy losses associated with the thinning of refractories.

Glass

Crown materials for glass melting furnaces are also an area of great interest. Improvements in these materials could lead to higher operating temperatures (through conversion to oxy-fuel firing), better thermal efficiency, and longer refractory service lives in these types of furnaces. Improved insulation aspects of crowns are especially needed with respect to the use of higher conductivity fused cast refractories versus the use of traditional lower conductivity pressed silica based refractories. In some cases water-cooling is needed on the cold face of the refractories to cool them as they are corroded, in order to maintain integrity of furnaces. This can lead to substantial energy losses. Mounting designs of refractories are also critical to successful longevity of the refractories.

Molten metal line corrosion in sidewall refractories is another area of concern. Such corrosion can lead to inclusions in the glass due to particles of refractories in the bath and can severely impact overall productivity and yield. For example, the current yield of some types of glass is only 25%. Therefore, improved yield could result in direct energy savings. Additionally, metal line corrosion can lead to reduced thermal efficiency due to the refractory recession. There is interest in addressing these issues by applying hot gunning techniques for the repair and maintenance of furnaces during service.

Aluminum

In the aluminum industry there are also various areas where improved refractories lead to significant energy and production benefits. One of these is in the Hall-Heroult process where cells are designed with a steel shell lined with castable refractory, porous insulating refractory, less-porous semi-insulating refractory, and finally firebrick. The sides of the cell are designed with less insulation to promote heat loss through the walls resulting in a lower wall temperature that causes electrolyte in contact with the wall to solidify forming a "frozen ledge" which protects the walls of the cell from the corrosive molten cryolite. Yet, it is thought that cell efficiency could be increased by developing a sidewall that would allow direct contact with the molten cryolite bath eliminating the "frozen ledge." This development could result in less heat loss from the cells along with reduced corrosion of the refractories.

A second area of interest is in the use of fibrous or foam linings in areas such as doors and linings in aluminum reheat furnaces. These materials provide excellent thermal insulation but do not resist erosion and corrosion well. They are also currently limited in their use by an upper service temperature of 980–1090°C.

Identified Research and Development Topics

Basically, the discussion identified two primary areas for refractory research and development: (1) preformed shapes and (2) low-thermal-conductivity materials.

Development and Application of Preformed Shapes

Currently refractory preformed shapes, procured from the refractory manufacturers, are finding limited application in areas of the steel industry as protective coverings on skid rails, pipes, and risers. Some preformed shapes are also used in high-wear regions on the bottom of ladles. However, various issues can arise relative to the premanufactured nature of these materials when they are implemented in process heating systems. In addition to the research and development of preformed shaped refractories, it is imperative to address various approaches on how to implement these new types of refractories in industrial systems.

Use of preform shapes, compared to the use of castable or gunnable materials, can lead to the following improvements:

1. Less downtime as compared to castables when used in furnaces and easier installation. Additionally refractory dry out cycle is not needed.

- 2. Improved corrosion resistance and mechanical performance (i.e., coverage is maintained for a longer period of time).
- 3. Decreased breakage of the refractory due to improved thermal shock and system design.
- 4. Improved productivity from their being easier to utilize in a larger number of applications.
- 5. Enables the use of insulating refractories to back up the preformed refractory, thus leading to improved energy efficiencies.
- 6. Improved energy efficiency due to shorter preheat times and lower energy used to maintain them at temperature due to improved thermal resistance.
- 7. Improved quality control of the refractory.
- 8. Improved damage control of refractory components.

Utilization of Low-Thermal-Conductivity Materials

These materials include fibers and porous materials, along with low-density materials coupled with higher density refractory materials on their exposed surface.

As highlighted above, one of the major issues with these types of materials is chemical attack. In reheat burners for example, the fibers are not stable near the flame environment, thus leading to high corrosion rates. Similarly when the fibers corrode, the burner can also be compromised, leading to unexpected shutdowns. One of the great advantages of fibrous materials, however, is their inherently low thermal conductivity. This property leads to shorter heat up times to furnace operating temperatures and, due to superior thermal efficiency, to less energy use once at operating temperature. For example, the use of fibrous insulation can decrease the heat up schedule of a steel reheat furnace by nearly 6 hours. The major issue, however, is that the fibers have a service temperature of less than ~1900°C and a service life of only about 5 days under the specific temperature and operating environment in the furnaces.

Therefore, a refractory systems approach is needed where a fibrous or porous refractory material is teamed with a dense surface refractory layer on its exposed surface. At the present time, efforts related to increasing the upper use temperature of fibrous or low-thermal-conductivity materials are required. Through this approach, the insulating properties of the fibrous (or porous) materials are exploited while the dense surface layer can provide chemical, thermal, and mechanical protection from the detrimental furnace environment. These systems could then be applied to many of the industries and problems highlighted above. Implementation of these types of systems is expected to lead to increased furnace efficiency and productivity that could result in better thermal efficiency and the use of fewer furnaces.

Future Needs

- 1. Modeling of phases and reactions and corrosion modeling, as well as sensors for monitoring of refractory wall condition and thickness and recession.
- 2. New refractory application and mounting methods, including the preformed shape approach, to enable easier installation, greater wear resistance, and longer refractory life.
- 3. Advanced coatings for current refractories. These may be possible through new corrosion resistant material coatings, surface modified refractories incorporating the properties of fiberous/foam materials with those of dense corrosion resistant materials, or glass-coated refractories for use in metal line applications. The use of bonded composites or refractory systems will have significant benefits because these types of materials could have lower thermal conductivity, higher corrosion resistance, and similar thermal insulating properties relative to monolithic silica refractories. Another area which needs further investigation is in situ reaction processed refractories-.
- 4. The use of bonded spinel refractories, or very pure silica refractories coated with spinel or mullite for use in furnace crowns. This could especially have significant benefits in flat glass manufacturing. These types of materials may also have a cost benefit over fused cast refractories such as alumina and spinel.

- 5. Focused efforts are needed in the areas of
 - a. Development and Application of Preformed Refractory Shapes
 - b. Utilization of Low Thermal Conductivity Materials

Advanced Ceramics

Session Chair: Bob Licht, - Saint-Gobain Ceramics & Plastics, Inc.

Participants

Bob Licht, Meeting Chairman Saint-Gobain Ceramics & Plastics, Inc.

Arvind Thekdi, Co-Chair E3M, Inc.
Beth Armstrong ORNL
Andy Wereszczak ORNL

Roberto Ruiz John Zink Co.

Ramesh Jain DOE
Sam Arcara Honeywell
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Andy MacQueen Ceradyne, Inc. Biljana Mikijelj Ceradyne, Inc.

Stated Meeting Objectives

The objectives of this meeting were (1) to provide interaction between the users of advanced ceramics (i.e., the process heating industry) and the R&D community (i.e., ceramic suppliers, national laboratories, and universities) and (2) to identify future materials needs to improve performance of process heating equipment systems.

Overview and Approach

As shown by the list of attendees, there was a good mix of representatives: three from ceramic suppliers, three from the process heating industry and four from government/national labs. The group

- Reviewed the nine major Segments of the Process Heating Industry. The three representatives
 from the process heating industry were in agreement as to the top three priority segments to address
 in the time allowed: fluid heating; melting; and heat treating.
- Listed the six Process Heating Elements common to all segments, with the 7th, Materials, common to all the other elements.
- Reviewed Critical Materials Problems and Potential Advanced Ceramics Solutions in the highest priority segment (fluid heating) by the major process elements.
- Developed a Summary and Next Steps.

Notes and Results

Segments of the Process Heating Industry

A. Fluid Heating (g, v, l) (chemical and petroleum) Priority #1

B. Melting Priority #2

C. Sintering

D. Heat Treating Priority #3

E. Preheating (e.g., for metal forging)

F. Calcining

G. Boiling/Evaporating (phase change, e.g. boilers)

H. Drying

I. Curing

Process Heating Elements, (common to all Segments)

1. Heat Generation

2. Heat Transfer

3. Heat Containment

4. Heat Recovery

5. Environmental

6. Sensors and Control

--

7. Materials (common to all)

Critical Materials Problems and Potential Advanced Ceramics Solutions

Segment A: Fluid Heating Process Element 1. Heat Generation

Need: a. Flame stabilizer for burner; need oxidation resistance and longer life.

Current material: high-temperature alloy, large part 18–20 in. (Roberto Ruiz drew a schematic of this part.)

Possible solutions: ceramic, CMC, ceramic coating on alloy. First step is to analyze properties and failure probability to determine materials solution. The advanced ceramic part could be made in segments to reduce cost, but this approach requires design collaboration.

Need: b. Nozzle–coking resistance, high-temperature oxidation, ceramic – metal fastening. Current material: high-temperature alloy

Need: c. Erosion of material when liquid or solid fuel.
Possible solution: advanced ceramics.

Process Element 2. Heat Transfer

Need: a. Enhanced heat transfer, prevent heat escape, increase reflection.

Current materials: refractories.

Possible solutions: rare earth oxides, coatings on refractories, tailor spectral characteristics.

Process Element 3. Heat Containment

Current materials: refractories (no advanced ceramic solutions discussed).

Process Element 4. Heat Recovery (e.g. heat exchangers)

Need: a. High-temperature corrosion of alloys, industry specific.

Possible solution: advanced ceramics.

Need: b. Higher temperature capability

Possible solution: advanced ceramic tubes. Requires sealing technology.

Unknown variable for ceramics in heat recovery: Viability (cost-effectiveness dependent on

energy cost.

Process Element 5. Environmental Problems

Need: a. Solve problem of the poisoning of catalyst.

Current material is not a ceramic.

Need: b. Reduce high-temperature corrosion of construction materials.

Current materials: metal, very large components.

Possible solutions: ceramics or refractories. Size limitations.

Need: c. High-temperature sensors for NOx. Improved corrosion/high-temperature capability.

Possible solutions: New ceramic materials to survive in stack.

Summary and Next Steps

The brainstorming was very effective, but we could have used more time. We covered only one of the nine process heating segments, fluid heating, which was the highest priority. It was believed that other segments would have similar material needs (e.g., high-temperature capability and corrosion resistance) and similar advanced ceramics solutions.

There is a benefit to teaming among the process heating industry, material suppliers and R&D support groups such as national laboratories, to find solutions to high-value problems. The DOE Industry of the Future programs could provide the structure for this teaming.

It was agreed that the approach to a specific materials substitution program should occur in two phases. Phase 1 would evaluate currently available advanced ceramic materials, which had not been tried in the program application. Laboratory and field testing would be needed and would include failure analysis. Phase 2 would be the improvement of these materials or development of new advanced ceramics to meet the requirements determined from Phase 1.

Appendix A: The Forum Agenda



DOE/IHEA Materials Forum



Oak Ridge National Laboratory
Oak Ridge, Tennessee

AGENDA

Wednesday February 5, 2003

Wednesday i estadiy 6, 2000						
11:00 AM 11:45 AM	•		Garden Plaza Hotel (Front Entrance) Jason Wilson, Sub-Committee Chair Building 4515, Conference Room 240			
40.45 DM	Welcome & Introductions	DOE-ITP ORNL IHEA	Sara Dillich, Lead Technical Manager, MMP Marilyn Brown, Director, EERE Program, ORNL Mario Ciampini, President, IHEA			
12:15 PM	Advanced Materials Programs/DOE/National Labs. Sara Dillich, DOE-OIT					
	•	A Look at the U. S. Process Heating Industry: Today and Tomorrow – Mario Ciampini, President, IHEA				
	High-Temperature Alloys – Jason Wilson, Technical Marketing Manager Rolled Alloys, Inc					
	Advanced Ceramics –Robert Licht, Manager Government Programs Group, Saint-Gobain Ceramics & Plastics, Inc. and Chairman USACA					
	Refractories and Insulation for the Heating Equipment Industry – Gary Deren, Unifrax Corporation					
	High-Temperature Alloys – Vinod Sikka, ORNL					
	Low Cost Ceramic Composite Fan Materials – Ronald Ott, ORNL					
		Monolithic and Surface Modified Ceramics – Andrew Wereszczak, ORNL				
		Advanced Nonporous Composite Materials for Industrial Heat Applications –Michael Ayers, LBNL				
		Advanced Ref Dogan, ARC	fractory Materials Research Program – Cindy			

Materials Degradation Processes in Elevated-Temperature

Environments Relevant to Process Heating – Peter Tortorelli,

ORNL

5:15 PM General Discussion Jason Wilson, Discussion Leader

5:45 PM Session

Adjournment

6:00 PM Bus Returns to Garden Plaza Hotel

7:00 PM Reception Museum of Science and Energy, Oak Ridge, TN

Near the Garden Plaza Hotel

8:00 PM Dinner Museum of Science and Energy, Oak Ridge, TN

Near the Garden Plaza Hotel

Speaker and Presentation: Donald M. Kroeger, ORNL – Superconductivity: Evolution of a Research and Development

Project

Thursday February 6, 2003

7:30 AM Bus pick-up Garden Plaza Hotel (Front Entrance) 8:15 AM Tour of Oak Ridge (Meet in Lobby of Bldg. 4515)

National Laboratories

10:40 AM Presentation: Working with DOE National Laboratories – Lou Dunlap, Deputy

Director Technology Transfer and Economic Development

Building 4515, Conference Room 240

11:00 AM Lunch

12:00 PM Breakout Sessions An opportunity for interaction between industry, DOE and

national laboratory representatives to discuss R& D needs and

future actions and activities.

Session 1 – High-Temperature Alloys

Building 4515, Conference Room 240

Session 2 – Advanced Ceramics

Building 4500S, Conference Room Z62

Session 3 – Insulation and Refractories

Building 4515, Conference Room 114

1:45 PM Summary Session Summary by leader from each breakout session

Building 4515, Conference Room 240

2:15 PM Summary Session Jason Wilson – Discussion Leader

Building 4515, Conference Room 240

2:45 PM Conference

Adjourns

3:00 PM Bus Returns to Garden Plaza Hotel

Appendix B: Speaker / Presenter Information

- **Michael Ayers** received his Ph.D. in inorganic chemistry from the University of Massachusetts-Amherst. His research focuses on the synthesis, characterization, and applications of nano-porous materials, especially aerogels. Recent projects have included aerogel nanocomposites, aerogel-based gas sensors, laser speckle characterization of gels, microgravity effects, and thin porous films for semiconductor applications. Current projects involve the synthesis of porous refractory oxides from low-cost raw materials for high-temperature insulations.
- Marilyn Brown is the director of Oak Ridge National Laboratory's (ORNL's) Energy Efficiency and Renewable Energy Program. During her 18 years at ORNL, she has researched the design and impacts of policies and programs aimed at accelerating the development and deployment of sustainable energy technologies. She currently manages a \$125 million/year program of research to develop and assess advanced energy efficiency and renewable energy technologies. Before coming to ORNL in 1984, she was a tenured associate professor in the Department of Geography at the University of Illinois at Urbana-Champaign. She has a Ph.D. in geography from the Ohio State University where she was a University Fellow, a master's degree in resource planning from the University of Massachusetts, and a bachelor's degree in political science (with a minor in mathematics) from Rutgers University. She has authored more than 140 publications and has received awards for her research from the American Council for an Energy-Efficient Economy, the Association of American Geographers, the Technology Transfer Society, and the Association of Women in Science. Dr. Brown sits on the boards of several energy and environmental organizations and serves on the editorial boards of several journals.
- **Mario Ciampini** is president and C.E.O. of Ipsen International, Inc., Rockford, Illinois. In addition, he is president of LINAC Holdings, Inc., a member of the board of directors for LOI, Inc., and chairman of Hauck Manufacturing Company. Mr. Ciampini has a degree in business management and majored in finance from Ryerson University of Toronto, Canada. He is a certified management accountant in the Province of Ontario, Canada.
- **Gary Deren** is the manager of marketing operations for the Unifrax Corporation in Niagara Falls, New York. After graduating from the State University College at Buffalo, Mr. Deren taught public school for the first five years of his career. He joined the Carborundum Company (currently Unifrax Corporation) in 1979. In his current position he manages a staff responsible for identifying and commercializing new products, as well as developing new business opportunities. Mr. Deren has published several articles addressing furnace-lining issues.
- Sara Dillich is the lead technology manager for Materials and Materials Processes in the DOE-EERE Office of Industrial Technologies (OIT). Previous responsibilities within OIT have included leading the Aluminum Industry of the Future program and initiating the Supporting Industries program in OIT. Her prior work experience includes Materials Research program management with the U.S. Bureau of Mines, teaching materials engineering at the undergraduate and graduate level, and a National Research Council–sponsored postdoctoral appointment at the Naval Research Laboratory. She received her Ph.D. in Materials Science from the University of Virginia and has performed research in the areas of electrical contacts, surface modification and tribology.
- Cynthia Powell Dogan is a materials research engineer and the project leader for the Advanced Refractories for Gasification project at the U.S. Department of Energy's Albany Research Center. She has more than a decade of research experience in the areas of high-temperature phase and microstructural development in ceramic materials and the effect of these phase changes on the bulk mechanical properties of the material. She received her Ph.D. in materials science from Case Western Reserve University in 1989, preceded by an M.S. and B.S. in ceramic engineering from Clemson University in 1985 and 1983, respectively. Her research has also addressed microstructure/property and microstructure/processing relationships in a wide range of intermetallic, metallic, and composite materials, and the influence of microstructure on the tribological

performance of ceramics and ceramic-based composites. She currently has more than 40 publications in these areas, including the paper "Improving Refractory Service Life in Slagging Coal Gasifiers," which was recognized for technical merit at the 2001 International Pittsburgh Coal Conference in Newcastle, Australia.

Louise Dunlap is associate director of Technology Transfer and Economic Development at Oak Ridge National Laboratory. This organization is responsible for a wide range of technology transfer and industrial outreach activities. Her previous assignments include serving as director of the Office of Science and Technology Partnerships, where she was responsible for the guest research and user programs, and as business manager for the High Temperature Superconductivity Pilot Center Program, where she assisted in establishing the first industrial partnership program at the Laboratory. Ms. Dunlap has a B.S. Degree in Chemistry from the University of Tennessee and has completed numerous management courses. She is immediate past president of the Technology Partnerships Working Group, a national organization of technology transfer professionals in the DOE laboratory system. In addition to her professional activities, she is involved with many community groups including the Oak Ridge City Council, Pellissippi State Community College Foundation, Rotary Club, and the Methodist Medical Center Foundation.

Donald Kroeger received his B.A. in physics from Washington University and his Ph.D in physics from Vanderbilt University. He is a distinguished research staff member and leader of the Superconducting Materials Group in the Metals and Ceramics Division at Oak Ridge National Laboratory (ORNL). He is responsible for coordination of the conductor development activities within the Superconducting Technology Program. He is principal investigator for, or has supervision over, ORNL's collaborative projects with industry on conductor development.

During 35 years as a member of the research staff at ORNL, Dr. Kroeger has conducted research and development programs on superconducting materials and related technology, atomic transport in solids, rapid solidification processing and metallic glasses. He has published about 100 papers on superconducting materials and related technology and has made numerous invited presentations at conferences, universities, and research laboratories in the United States and abroad, and has participated in the organization of several symposia and workshops on superconductivity. He is a member of the Materials Research Society and the Minerals, Metals and Materials Society. Dr. Kroeger is the holder of one U.S. patent and has received ORNL awards for inventions and publications.

Robert Licht has been with Saint-Gobain and Norton Company (acquired by Saint-Gobain in 1990) for over 20 years. His primary responsibilities lie in research and development management in advanced materials, ceramic processing, machining and abrasive products. Mr. Licht holds two patents and is the author or co-author of several technical papers. He has an M.S. in Ceramic Science from Penn State University and a B.S. in Ceramic Engineering from Rutgers University.

Ronald Ott graduated from the University of Alabama at Birmingham (UAB) with an undergraduate degree in mechanical engineering in 1991, with emphasis on mechanical systems. At UAB he also earned a master's degree in materials engineering in 1994 and a Ph.D. in 1997. Ron conducted his dissertation research at the High Temperature Materials Laboratory (HTML) at Oak Ridge National Laboratory (ORNL) under the HTML graduate fellowship program (1994–1997). Following graduation, he held a postdoctoral research fellowship at the Materials for Information Technology (MINT) Center at the University of Alabama where he conducted nano-tribology research associated with the computer hard disk industry. After completion of the postdoctoral work, Ron began work at Oak Ridge National Laboratory in Surface Processing and Mechanics (SPM) group in 1999, performing research in the area of tribology. He transferred to the Materials Processing Group in 2002 and is currently involved with research associated with the Infrared Processing Center.

Vinod K. Sikka received a Ph.D. in metallurgical engineering from the University of Cincinnati. He is a Fellow of ASM International; has received six R&D 100 Awards, and the Federal Laboratory Consortium Award of Excellence in Technology Transfer award; and is a Corporate Fellow, leader of

the Materials Processing Group, Oak Ridge National Laboratory. He has worked in developing metallic and intermetallic alloys for high-temperature applications and developed materials processes including Exo-Melt and infrared processing for manufacturing of advanced materials. He has 33 patents and over 200 publications and has extensive experience in working with industry and the transfer and implementation of materials technologies.

Arvind Thekdi has over 30 years of experience in design and development of process heating equipment such as high-temperature furnaces used by all major industries. His areas of expertise include design and application of combustion and heating systems, waste heat recovery systems for high-temperature furnaces and heaters, emission (NOx) reduction systems, and use of combined heat and power systems. He has worked on a number of programs related to development and commercialization of innovative furnace designs for the metals industry to improve energy efficiency and reduce emissions. During the past five years, he has prepared tools and training courses that offer instructions on practical and cost-effective methods to reduce energy use in process heating equipment. He holds 25 U.S. and foreign patents related to high-temperature processes and equipment. Dr. Thekdi has conducted several technology related studies, published more than 50 technical papers, and contributed to two books in the area of combustion, process heating, and application of improved technologies in industries.

Peter Tortorelli has a Ph.D. in metallurgy from the University of Illinois at Urbana-Champaign. He has extensive research experience in the areas of high-temperature oxidation and corrosion of alloys, metal matrix composites, ceramics and ceramic composites, the mechanical behavior of oxide scales, and liquid metal corrosion in support of energy efficiency in key industrial applications and enabling technologies for advanced fossil-fuel-based power plants and other energy systems. He is employed in the Metals and Ceramics Division of Oak Ridge National Laboratory, where he has research responsibilities as a principal investigator and serves as the manager of the Corrosion Science and Technology Group. He is a Fellow of ASM International and is also a member of TMS, the American Ceramic Society, and the Materials Research Society. He has published more than 130 scientific or technical papers and made more than 140 presentations at conferences or workshops.

Andrew Wereszczak is a senior research and development staff scientist in the Structural Ceramics Group at Oak Ridge National Laboratory (ORNL). He rejoined ORNL in September 2002 and is presently performing research on structural ceramics for heat engine applications and materials for power electronic devices. From 2000 to 2002, Andy worked at the U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, and researched ceramic gun barrel technology and the microstructure - mechanical performance relationship in armor ceramics. From 1991 to 2000, Andy was a staff ceramic scientist in ORNL's Mechanical Characterization and Analysis Group and researched mechanical performance and reliability issues associated with monolithic structural ceramics under consideration for components in (primarily) diesel and gas turbine engines, mechanical reliability of ceramics used in electronic components, and high-temperature performance of refractories used in glass melting furnaces. He received a PhD in materials science and engineering from the University of Delaware and a BS in ceramic engineering from Alfred University. Andy has authored or co-authored more than 90 publications and given over 60 presentations on his work and is a member of the American Ceramic Society (Engineering Ceramics Division, Committee Member) and ASTM C28 (Advanced Ceramics).

Jason Wilson received his BSME from the University of Toledo. He began his career with Rolled Alloys in Temperance, Minnesota, as a materials engineer in 1991. He is currently the Technical Marketing Manager at Rolled Alloys. Mr. Wilson has published four papers on heat resistant alloys and their use in heating equipment.

Appendix C: List of Forum Attendees



DOE/IHEA Materials Forum



Oak Ridge National Laboratory Building 4515, Room 240 Oak Ridge, Tennessee February 5-6, 2003

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Appendix D: List of Research Briefs

The following research briefs were received from various DOE national Laboratories. Note that the presentations and research briefs are included on the CD-ROM rather than in this printed version of the report.

Advanced Nonporous Composite Materials for Industrial Heat Applications

Michael Ayers and Arlon Hunt (Lawrence Berkeley National Laboratory)

Advanced Refractory Materials Research Program, DOE Albany Research Center Cynthia Powell Dogan (Albany Research Center)

Advanced Wrought Alloys with Improved High-Temperature Performance for Waste Heat Recovery Systems

Philip J. Maziasz (Oak Ridge National Laboratory)

High-Temperature Alloys

Vinod K. Sikka (Oak Ridge National Laboratory)

Low-Cost Ceramic Composite Fan Materials Ron Ott (Oak Ridge National Laboratory)

Materials Degradation Processes in Elevated-Temperature Environments Relevant to Process Heating Peter F. Tortorelli (Oak Ridge National Laboratory)

Materials for Low-Cost Sensor Array System for High-Temperature Gas Measurement Tim R. Armstrong and James E. Hardy (Oak Ridge National Laboratory)

Materials Test Methods, Alloy and Ceramic Selection and Development for Elevated Temperature and Aggressive Environments

Dennis Bickford (Savannah River Site)

Modeling of Thermo-Chemical-Kinetic Reactions Between Gas – Liquid – Glass – Metal in Industrial Process Heating Environment

Theodore M. Besmann and Sudarsanam S. Babu (Oak Ridge National Laboratory)

Monolithic and Surface Modified Ceramics

Andrew A. Wereszczak (Oak Ridge National Laboratory)

PNNL High-Temperature Materials Capabilities

Charles H. Henager, Jr. and Russell H. Jones (Pacific Northwest National Laboratory)

Surface Modification and Thermomechanical Properties of Refractory and Insulation Materials
Terry Tiegs (Oak Ridge National Laboratory)

Appendix E: List of Forum Presentations

Industry Presentations

A Look at the U. S. Process Heating Industry: Today and Tomorrow - Mario Ciampini, President, IHEA

High-Temperature Alloys – Jason Wilson, Technical Marketing Manager, Rolled Alloys, Inc.

Advanced Ceramics – Robert Licht, Manager , Government Programs Group, Saint-Gobain Ceramics & Plastics, Inc. and Chairman USACA

Refractories and Insulation for the Heating Equipment Industry – Gary Deren, Unifrax Corporation

DOE National Laboratory Presentations

High-Temperature Alloys – Vinod Sikka, ORNL

Low Cost Ceramic Composite Fan Materials - Ronald Ott, ORNL

Monolithic and Surface Modified Ceramics - Andrew Wereszczak, ORNL

Advanced Nonporous Composite Materials for Industrial Heat Applications - Michael Ayers, LBNL

Advanced Refractory Materials Research Program - Cindy Dogan, ARC

Materials Degradation Processes in Elevated-Temperature Environments Relevant to Process Heating – Peter Tortorelli, ORNL

Other Presentations

Introduction to Oak Ridge National Laboratory - Marilyn Brown