

Industrial Technologies Program Industrial Materials for the Future







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FINAL TECHNICAL REPORT

Project Title:	High-Density Infrared Surface Treatments of Refractories	
Award Number:	CPS #1758; FWP #CEED001	
Project Period:	September 30, 2001–December 31, 2004	
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High-Density Infrared Surface Treatments of Refractories

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March 2005

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Acknowledgments and Disclaimer

Acknowledgements

This report is based upon work supported by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Industrial Technologies Program, Industrial Materials for the Future, under Award No. CPS1758.

Research was sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

The authors wish to thank Mr. David Harper for performing all of the experiments for IR heating of the refractories. The authors also wish to thank Dr. Peter Angelini for reviewing the document and Ms. Millie Atchley for preparation of documents.

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Contents

	List of Figures Abbreviations and Acronyms	v vii
1.	Executive Summary	1
	1.1 Project Results	1
	1.2 Technology Transfer	2
	1.3 Commercialization	2
	1.4 Recommendations	2
2.	2. Introduction	3
3.	B. Background	5
	3.1 Potential Economic, Energy, and Environmental Benefits	
	3.1.1 Economic Benefit	
	3.1.2 Energy Benefit	
	3.1.3 Environmental Benefit	7
	3.2 Project Areas	7
	3.3 Industrial Partners	8
4.	Results and Discussion	11
	4.1 Reduction of Surface Porosity	11
	4.1.1 Experimental Results	11
	4.1.2 Summary	
	4.2 Fabrication of Corrosion-Resistant Coatings	
	4.2.1 Experimental Results	
	4.2.2 Summary	23
	4.3 Production of High-Emissivity Coatings	24
	4.3.1 Experimental Results	24
	4.3.2 Summary	29
	4.4 Cost Estimate	29
5.	. Accomplishments	
	5.1 Technical Accomplishments	
	5.2 Technology Transfer	31
	5.3 Publications. Presentations. and Patents	
	5.3.1 Publications	
	5.3.2 Presentations	32
	5 3 3 Patent Disclosure	32
	5.4 Commercialization	
6.	5. Conclusions	35
7.	7. Recommendations	37
8.	3. References	

Appe	endix A	A: Posters	41
	A.1	Surface Treatment of Refractories Using High-Density Infrared Heating	41
	A.2	Surface Treatment of Refractories Using High-Density Infrared Heating	41
	A.3	Surface Treatment of Refractories Using High-Density Infrared Heating	41

List of Figures

4.1	High-alumina castable before and after high-density infrared (HDI) treatment	12
4.2	Aluminosilicate with low cement content castable after HDI treatment	12
4.3	High-alumina castable surface after HDI treatment	13
4.4	Cross section of aluminosilicate with low-cement-content castable (a) before and	
	(b) after HID treatment	14
4.5	X-ray diffraction of aluminosilicate with low-cement-content castable	15
4.6	Surface region of high-alumina castable refractory without HDI treatment	16
4.7	Surface region of high-alumina castable refractory after HDI treatment	16
4.8	Surface region of aluminosilicate refractory without HDI treatment	16
4.9	Surface region of aluminosilicate refractory after HDI treatment	16
4.10	Interface between copper and high-alumina castable refractory without HDI treatment	17
4.11	Interface between copper and high-alumina castable refractory with HDI treatment	17
4.12	Interface between copper and aluminosilicate refractory without HDI treatment	17
4.13	Surface of aluminosilicate refractory with HDI treatment after contact with molten copper	17
4.14	FC AZS-33 before and after HDI treatment	19
4.15	CS AZS-20 before and after HDI treatment	19
4.16	Cross section of coated FC AZS-33 after HDI treatment	19
4.17	Cross section of coated CS AZS-20 after HDI treatment	19
4.18	Microstructure of as-received FC AZS-33	20
4.19	Microstructure of FC AZS-33 after HDI treatment	20
4.20	Microstructure of as-received CS AZS-20	20
4.21	Microstructure of CS AZS-20 after HDI treatment	20
4.22	Cross section of as-received FC AZS-33 after corrosion testing for 15 h	21
4.23	Cross section of HDI coated FC AZS-33 after corrosion testing for 15 h	21
4.24	Microstructure of as-received FC AZS-33 after corrosion testing for 15 h	21
4.25	Microstructure of HDI-coated FC AZS-33 after corrosion testing for 15 h	21
4.26	Cross section of as-received CS AZS-20 after corrosion testing for 15 h	22
4.27	Cross section of HDI-coated CS AZS-20 after corrosion testing for 15 h	22
4.28	Microstructure of as-received CS AZS-20 after corrosion testing for 15 h	22
4.29	Microstructure of HDI-coated CS AZS-20 after corrosion testing for 15 h	22
4.30	Cross section of as-received FC AZS-33 after corrosion testing for 80 h	23
4.31	Cross section of HDI-coated FC AZS-33 after corrosion testing for 80 h	23
4.32	Microstructure of as-received FC AZS-33 after corrosion testing for 80 h	23
4.33	Microstructure of high density-infrared coated FC AZS-33 after corrosion testing for 80 h	23
4.34	Cross section of as-received CS AZS-20 after corrosion testing for 80 h	24

4.35	Cross section of high density-infrared coated CS AZS-20 after corrosion testing for 80 h .	24
4.36	Microstructure of as-received CS AZS-20 after corrosion testing for 80 h	24
4.37	Microstructure of high density-infrared coated CS AZS-20 after corrosion testing	
	for 80 h	24
4.38	Appearance of noncontact fiber insulation after HDI of rare-earth-coated surfaces	25
4.39	Surface of HDI-treated aluminosilicate fiber insulation with a Nd ₂ O ₃ coating	26
4.40	Cross section of HDI-treated aluminosilicate fiber insulation with a Nd ₂ O ₃ coating	26
4.41	Cross section of HDI-treated zirconia fiber insulation with a Nd_2O_3 coating	26
4.42	Visual spectrum emittance from aluminosilicate (51% SiO ₂ -48% Al ₂ O ₃) insulation	27
4.43	Visual spectrum emittance from zirconia (ZrO ₂ -8% Y ₂ O ₃ -3% SiO ₂) insulation	27
4.44	Samples after emittance testing	28
4.45	Average intensity from 550 to 1100 nm of samples at 1250°C	29

Abbreviations and Acronyms

AZS	alumina zirconia silicate
CS	cast and sintered
CVD	chemical vapor deposition
FC	fused-cast
HDI	high-density infrared
IOF	Industries of the Future
NMAB	National Materials Advisory Board
NRC	National Research Council
ORNL	Oak Ridge National laboratory
R&D	research and development
T.D.	theoretical density
UMR	University of Missouri-Rolla
YAG	yttrium aluminum garnet

1. Executive Summary

Refractory materials play a crucial role in all energy-intensive industries and are truly a crosscutting technology for the Industries of the Future (IOF). One of the major mechanisms for the degradation of refractories and a general decrease in their performance has been the penetration and corrosion by molten metals or glass. Methods and materials that would reduce the penetration, wetting, and corrosive chemistry would significantly improve refractory performance and also maintain the quality of the processed liquid, be it metal or glass.

This report presents the results of an R&D project aimed at investigating the use of high-density infrared (HDI) heating to surface treat refractories to improve their performance. The project was a joint effort between Oak Ridge National Laboratory (ORNL) and the University of Missouri—Rolla (UMR). HDI is capable of heating the near-surface region of materials to very high temperatures where sintering, diffusion, and melting can occur. The intended benefits of HDI processing of refractories were to (1) reduce surface porosity (by essentially sealing the surface to prevent liquid penetration), (2) allow surface chemistry changes to be performed by bonding an adherent coating onto the underlying refractory (in order to inhibit wetting and/or improve corrosion resistance), and (3) produce noncontact refractories with high-emissivity surface coatings.

1.1 Project Results

During the first year of the project, the HDI treatment of commercial refractories to reduce surface porosity (by essentially sealing the surface to prevent liquid penetration) showed that the surface properties can be altered. With the refractories, surface melting was plainly evident at moderate power levels (\geq 1375 W/cm²). During solidification of the surface melted region on aluminosilicate materials, the mullite grains that formed were highly oriented with the *c*-axis perpendicular to the surface. Corrosion testing showed that the HDI treatment was effective in reducing penetration by molten copper.

Work during the second year of the project showed that bonding an adherent coating onto the underlying refractory produced surface chemistry changes that would inhibit wetting and/or corrosion. It was demonstrated that zirconia-rich coatings could be formed on the surfaces of alumina zirconia silicate (AZS) refractories using HDI thermal treatments. During high-temperature processing, the surfaces are melted and mixing occurs between the applied zirconia coating and the underlying refractory. The coatings are characterized by the formation of fine dendritic ZrO_2 grains and some porosity. Corrosion testing in a container glass-NaCO₃ mixture at 1400°C showed that the coatings helped form boundary layers on the surfaces and reduced dissolution of the refractory.

During the final year of the project, high-emissivity coatings were produced on noncontact refractories by bonding rare earth oxides onto fibrous materials using the HDI system. These types of coatings are used extensively in heat-treating furnaces. The results showed that the surface coatings could alter the emissivity of fibrous ceramics. Reducing the emissivity reduces the energy absorbed by the fibrous ceramic, leading to a reduction in heat transfer. The coatings dominated the change in emissivity. No difference could be found between the emissivity of the coatings on zirconia-based and aluminosilicate fibrous ceramics even with the large differences in emission between the uncoated base materials. All of the samples (uncoated and coated) followed Plank's law with respect to temperature.

1.2 Technology Transfer

The industrial partners in this project were Allied Mineral, Inc. (Columbus, Ohio); Emhart Glass Co. (Owensville, Mo.); Magneco-Metrel, Inc. (Addison, Ill.); Allvac, Inc. (Monroe, N.C.); and Albany Research Center (Albany, Ore.). These companies provided refractory samples used in the HDI processing and testing. They were involved in the project from the standpoint of being informed of the results on their products and being able to give their input on the results and the methods used in testing the samples after HDI processing.

The HDI technologies developed in the project demonstrated improved refractory performance by surface treating with HDI heating. The results demonstrating improved refractory performance by surface treating with HDI heating were of interest to several refractory, glass, and metal melting companies. However, several hurdles prevented commercial implementation of the technologies, the most significant of which was cost (both capital and operating). As the use of HDI increases in several other areas, the capital costs will decrease, and this technology will become more available for use in treating refractories. Operating costs were also an issue, mainly because refractories are a commodity product and the profit margins are small. The large volumes of materials used offset the small margins. Thus, any increase in manufacturing cost has a significant impact on the profitability of the products.

1.3 Commercialization

This project was exploratory to determine the feasibility of various surface modifications of refractories. Technology transfer activities are discussed in Sect. 1.2, above.

1.4 Recommendations

While the results were positive for improving refractory performance, all the testing was done on a laboratory scale. For industrial implementation of the HDI surface treatment technologies, larger-scale testing is necessary to determine scale-up. Consequently, an additional two years of funding would be needed to get the technologies into a commercial application.

2. Introduction

Refractory materials play a crucial role in all energy-intensive industries and are truly a cross-cutting technology for the Industries of the Future (IOF). Refractories are key materials in glass furnaces, metals refining and casting, pulp and paper processing, boilers for power generation, and petrochemical processing. Refractory materials have remained largely unchanged for many years, and industrial users are beginning to realize that it is time to look for fundamentally new refractory systems because most current materials are reaching their ultimate performance limits. Areas where economically viable breakthroughs are needed are in corrosion/erosion resistance, improved mechanical properties, and the ability to act as a host or support for high-emissivity coatings and advanced catalysts.

One of the major mechanisms for the degradation of refractories and a general decrease in their performance has been the penetration and corrosion by molten metals or glass. Methods and materials that would reduce the penetration, wetting, and corrosive chemistry would significantly improve refractory performance and also the quality of the processed liquid, whether metal or glass.

This report presents the results of an R&D project aimed at investigating the use of high-density infrared (HDI) heating to surface treat refractories to improve their performance. The project was a joint effort between Oak Ridge National Laboratory (ORNL) and the University of Missouri—Rolla (UMR). HDI is capable of heating the near-surface region of materials to very high temperatures where sintering, diffusion, and melting can occur. The intended benefits of HDI processing of refractories were to (1) reduce surface porosity (by essentially sealing the surface to prevent liquid penetration), (2) allow surface chemistry changes to be performed by bonding an adherent coating onto the underlying refractory (in order to inhibit wetting and/or improve corrosion resistance), and (3) produce noncontact refractories with high-emissivity surface coatings.

The HDI technology, as described below, is relatively new to the materials processing area and is gradually being exploited in coatings and surface modification application area mainly for metals. Until the start of the current project, the technology had not been applied to the surface treatment of refractory materials in any systematic way. The HDI processing facility at ORNL utilizes a unique technology to produce extremely high-power densities of 3.5 kW/cm² with a single lamp, which is currently the most powerful one in the world.

The specific goals of the project were to (1) reduce open surface porosity on commercially available refractories and demonstrate improved penetration resistance; (2) fabricate corrosion-resistant surface layers on refractories by selective sintering of secondary layers and show improved corrosion behavior; and (3) produce noncontact refractories with high-emissivity surface coatings.

3. Background

Ceramic refractories are widely used in high-temperature, chemically demanding applications and obviously are critical construction materials for energy-intensive industries. Recognizing their central role in numerous industries, the National Materials Advisory Board (NMAB) of the National Research Council (NRC) report entitled *Materials Technologies for the Process Industries of the Future* specifically identified refractories as important or very important for the aluminum, glass, metal casting, steel, and chemical industries [1]. Thus, refractories are truly a cross-cutting technology common to multiple industries. All of the industries mentioned above are involved with the handling and containment of molten metals and/or glass. The need for research and development (R&D) efforts in refractories are also noted in the glass and aluminum industry roadmaps.

Refractories are made in many forms for a variety of applications. They have remained largely unchanged for many years, and industrial users are beginning to realize that it is time to look for fundamentally new refractory systems because current materials are reaching their ultimate performance limits with respect to chemical and mechanical wear and tear. Areas where economically viable breakthroughs are needed are in corrosion/erosion resistance, improved mechanical properties, and the ability to act as a host or support for high-emissivity coatings and advanced catalysts. While advanced ceramics have been the subject of numerous R&D efforts, studies on refractories have not received adequate attention for many years. While incremental improvements in the thermal properties and durability of refractories do continue to be made, these are small and quite often application-specific. No dramatic improvements in refractory performance have been made in a number of years. In part, this is because the refractory industry is very cost sensitive and will not tolerate materials or processes that add significantly to the cost of the end product. While advanced ceramics could make improvements in refractory performance, their cost has been prohibitive to their widespread use. On the other hand, the proposed HDI surface treatments have the potential to be used with current base materials and add only minimally to the overall economics since they can be done at a fast rate. Although refractories might not seem glamorous compared to other highperformance materials, the cost of rebuilding a glass furnace or relining a recovery boiler in a paper mill is huge, partly because of the associated downtime for the rest of the facility. (Scheduled downtime for a paper mill recovery boiler runs around \$250,000/shift and unscheduled downtime is substantially more expensive.) The time between rebuilds is directly related to the ability of the refractory to resist creep or sagging, corrosion, erosion, and other slow degradation processes.

Several studies have examined the surface modification of refractories to reduce surface porosities [2-6]. For the most part, these studies have relied on laser melting of the surface. With that technology, the area actually being treated is quite small, with usual spot sizes of <6 mm. To cover a large area, the laser must be scanned across the part at speeds of 0.05-0.5 cm/s with typically a 20-50% overlay from the previous scan. To do a large area requires several minutes, and in some cases, hours. In addition, the overlapping of the scans also affects the resulting microstructure and causes significant microcracking of the surface. Thus, while this technique is of academic interest, it is not attractive for widespread industrial use. On the other hand, HDI is capable of covering a much larger area (up to 35 cm across) at reasonable scan speeds (~1 cm/s), making it a viable industrial technique that is capable of continuously processing a large number of parts.

3.1 Potential Economic, Energy, and Environmental Benefits

3.1.1 Economic Benefit

Refractories are used throughout many industries, including glass, aluminum, chemical, metal casting, petrochemical, steel, agriculture, mining, and forest products. Most applications are in the area of high-temperature corrosion resistance. Examples of where benefits occur from increased knowledge of the thermodynamics of glass and refractories are described in two industry roadmaps: glass and aluminum. The calculations used to determine the energy benefits are derived from Ref. 7.

In the glass industry the benefits can be realized by the identification of improved refractories relative to improved high-temperature behavior and corrosion resistance and thermal management. Benefits from HDI surface treatments of refractories would include reducing penetration, wetting, and corrosive chemistry, all of which would significantly improve refractory performance and the quality of the processed liquid, whether metal or glass.

The use of improved refractories designed to enable oxy-fuel firing in the glass industry would result in significantly less capital equipment and operations, in that regenerators would not be necessary as they are in air-fired furnace systems. This means that the recuperators would not be necessary, and thus capital costs would be saved. In addition, all of the costs relative to recuperator maintenance and rework could also be saved. The glass industry savings in energy costs alone in switching from air firing to oxy-fuel firing would be ~\$475 million/year by 2020. Improved refractories in the aluminum industry would also lead to new and more energy-efficient enabling technologies, for example, improved air-fired furnace designs and new oxy-fuel designs. Results of an analysis of these various costs are shown in Table 3.1.

3.1.2 Energy Benefit

The high-temperature properties of refractories are critical to the design, structural and chemical stability, and service life of various components of glass furnaces, including the crowns. HDI surface treatments of refractories will lead to refractories with better performance under higher operating temperatures and increased corrosion resistance under various environmental conditions. The stability and corrosion resistance of refractories

Table 3.1. Energy cost savings from use of improved refractories by 2020

Industry	Energy savings (million \$/year)
Glass	120
Aluminum	25
Both industries	145

is critically important as the glass industry moves from conventional air-firing to oxy-fuel firing. Thus, validated, new, or modified refractory materials will be necessary. Oxy-fuel firing is 20 to 40% more efficient than air firing, and there are over 290 glass melting furnaces in the United States. By 2020 the implementation of oxy-fuel firing in the glass industry can have an impact of over 90 trillion Btu/year of primary energy savings (2 billion kWh/year of electricity; 70 billion cubic feet of natural gas saved per year; and 50 million barrels of oil saved per year). The portion of those savings attributable to this project is estimated to be nearly 25% of the total.

Refractories also have an important role in the aluminum industry for aluminum melting furnaces. Refractory linings are critical for corrosion resistance and thermal management of the melting furnaces. Currently, the thermal efficiency of gas-fired melting furnaces is $\sim 25\%$. Improved refractories would lead to improved furnace designs. Further improvements can be anticipated with current air-fired furnaces and will also enable new oxy-fuel firing. The contributions from this project are estimated to be a 12.5% relative improvement over conventional aluminum melting furnaces. Details are shown in Table 3.2.

Vision industry	Electricity (billion kWh)	Gas (billion ft ³)	Oil (million barrels)	Total energy savings (trillion Btu)
Glass	0.5	18	0.12	23
Aluminum	—	7	—	7
Total savings	0.5	25	0.12	30

Table 3.2. Energy savings from use of refractories in the glass and aluminum industries by 2020

3.1.3 Environmental Benefit

Oxy-fuel firing uses much less nitrogen than is used in conventional air firing, leading to lower emissions of NO_x . Just in the glass industry, NO_x emissions would be reduced by 3000 tons/year by enabling oxy-fuel firing throughout the industry.

Implementation of HDI surface treatments will also lead to enhanced energy-efficient furnace designs and significant environmental benefits as a direct result of the energy savings. The data in Table 3.3 is for the estimated environmental benefits in 2020 and highlights the benefits relative to two gases, CO_2 and NO_x .

3.2 Project Areas

It is well known that some refractory compositions are more resistant to corrosion by molten metals and glass than the materials currently used in industrial facilities. However, the more resistant refractories are not utilized for a number of reasons, primarily because they are usually

Table 3.3. Environmental benefits from use of refractories
in the glass and aluminum industries by 2020: reductions
in emissions (thousand tons/year)

Vision industry	CO ₂ emissions	NO _x emissions
Glass	345	3
Aluminum	90	0.8
Total	435	3.8

more expensive and/or have some other undesirable attribute such as poor thermal shock behavior. Another aspect of the research in the current project was to use the HDI surface coating process to produce corrosion-resistant surfaces on commercial refractories. There are several advantages to altering only the refractory surface vs changing the entire refractory material. Altering the surface only leaves bulk properties, such as thermal shock resistance and thermal conductivity, unchanged. Also there may be a huge cost barrier to manufacturing the entire refractory out of particular compound, whereas using the compound for a coating would be significantly less.

Coatings on refractories can be developed by sintering and bonding of an applied coating. For applied coatings, a powder layer would be HDI-sintered to densify and form an adherent coating, but to have only minor interaction with the underlying refractory. As examples, either a ZrO_2 -based or Y_2O_3 -based slurry (very stable oxides) can be applied onto aluminosilicate refractories and HDI-treated to sinter and bond the coating to the surface. In this project, appropriate combinations of refractories and coatings were chosen to minimize thermal expansion mismatches and chemical interactions. Such coatings can also be in the form of higher-purity, dense materials that are applied over low-cost, less pure, porous materials. In general, higher-purity refractories exhibit better performance than lower-purity counterparts of the same general composition. For example, a high-purity, dense mullite could be coated over a cheaper, higher-porosity aluminosilicate refractory. In such an instance, problems of thermal expansion mismatches and chemical compatibility are minimized. The advantage of the HDI treatment over other coating processes is that bulk properties are unchanged. In addition, in comparison to processes such as chemical vapor deposition (CVD), the HDI coatings should be much more economical.

Another area where surface treatments of refractories have great potential is in the application of highemissivity coatings. This topic was investigated in the last year of the project. High-emissivity coatings have been reported to improve the furnace output in the metallurgical, petrochemical, and ceramic industries in China and reduce the energy consumption 5 to 10% [8]. In the current project, coatings based on rare-earth oxides were formulated and applied to oxide refractories. The selection of materials was based on the prior research in the project and attempted to maximize both chemical stability and optical emissivity. It is also possible that the rare-earth oxides exhibit surface catalytic activity at elevated temperatures, adding to the benefits of their addition to the yttrium aluminum garnet (YAG) family of materials, although this possibility was not investigated as a part of the current project.

The project was conducted in a series of tasks over a three-year period. The objectives of the three tasks were to (1) demonstrate the ability to reduce open surface porosity on commercially available refractories and evaluate the corrosion behavior, (2) fabricate corrosion-resistant surface layers on refractories by either diffusion coating or selective sintering of secondary layers, and (3) produce refractories having high-emissivity surface coatings (in addition to low porosity and high corrosion resistance).

Task 1. Demonstrate the ability to reduce open surface porosity on commercially available refractories and evaluate the corrosion behavior

The first task involved the varying the HDI parameters to produce a crack-free nonporous structure. Some of the parameters studied were lamp intensity, scan speed, sample pre-heat temperature, and cooling rates. The refractories tested were high alumina, aluminosilicates and mullite. After HDI processing, the refractories were characterized to determine the effects of the variables on the materials' microstructure and phases. On the basis of these characterizations, selected refractories were treated to produce optimum surfaces for the best combination of low porosity and surface integrity. The samples were then exposed to simulated process environments at both ORNL and UMR.

Task 2. Fabricate corrosion-resistant surface layers on refractories by either diffusion coating or selective sintering of secondary layers

Initial testing examined coating on refractories for both glass and metal applications. Some aspects of the approach were based on prior results from Task 1. Compositions and processing conditions were selected to minimize the effects of thermal expansion mismatch and chemical interactions. The coatings were characterized for microstructure, bonding of the surface layer, and chemical interactions between the surface and the bulk material. The samples were then subjected to exposure to simulated process environments at both ORNL and UMR.

Task 3. Produce refractories having high-emissivity surface coatings (in addition to low porosity and high corrosion resistance)

Aspects of the experimental approach in Task 3 were based on prior results from Tasks 1 and 2. Compositions and processing conditions were selected to minimize the effects of thermal expansion mismatch and chemical interactions while maximizing the emissivity. The coatings were characterized for morphology, emissive characteristics, and chemical interactions between the surface and the bulk material. The samples were then tested for emissive behavior at UMR.

3.3 Industrial Partners

The industrial partners in this project were Allied Mineral, Inc. (Columbus, Ohio); Emhart Glass Co. (Owensville, Mo.); Magneco-Metrel, Inc. (Addison, Ill.); Allvac, Inc. (Monroe, N.C.); and Albany

Research Center (Albany, Ore.). These companies provided refractory samples used in the HDI processing and testing. They were involved in the project from the standpoint of being informed of the results on their products and being able to give their input on the results and the methods used in testing the samples after HDI processing.

In addition, several other companies were contacted and visited during the course of the project to be introduced to the technology and obtain their viewpoints. These companies included St. Gobain/Norton (Buckhannon, W.Va.) and Minteq, Inc. (Slippery Rock, Pa.).

4. Results and Discussion

4.1 Reduction of Surface Porosity

Because surface porosity is one of the major mechanisms for the degradation of refractories and a general decrease in their performance, through penetration and corrosion by molten metals or glass, the initial emphasis of the HDI treatment of refractories was to reduce surface porosity and improve corrosion resistance.

4.1.1 Experimental Results

Instead of using an electrically heated resistive element to produce radiant energy, we used a controlled and contained plasma. The lamp consists of a 3.175-cm-diam quartz tube, which can be 11.5, 20, or 35 cm long. The lamp has a typical life of approximately 1200 h, and failure occurs in the anodes and cathode, which are inexpensive and can be changed in approximately 15 min. Furthermore, the lamp has a consistent spectral output independent of lamp life and power level. The lamp was configured with a reflector to produce a line focus or an area of uniform irradiance. The width of the beam in the present experiments was ~1 cm; maximum power density at that condition was approximately 2675 W/cm². The HDI lamp is mounted on a large five-axis robotic manipulator arm. A state-of-the-art robotic controller controls the arm. This controller is capable of using computer-aided drawing data files of large parts to generate instructions to manipulate the source over a complicated geometry in a predetermined, systematic way. For the tests performed in the present studies, scan rates over the surfaces ranging from 0.5 to 2 cm/s were used.

The refractories treated in the study were commercial castable materials: (1) high alumina with a nominal starting composition of 90% Al_2O_3 -5% SiO_2 -5% calcium aluminate, and (2) aluminosilcate with low cement content and a nominal composition of 60% aluminosilicate-30% Al_2O_3 -8% SiO_2 -2% calcium aluminate. These were calcined to \geq 800°C prior to surface treatment.

The surfaces of the refractories were exposed to the HDI treatment at various power levels, with the scan speed held constant at 1 cm/s. Examples of the appearances of the refractories are shown in Figs. 4.1 and 4.2. Surface melting is readily evident at exposures $\geq 1375 \text{ W/cm}^2$. At lower power levels, little visual effect was observed, as indicated in Fig. 4.2. Also apparent in the visual examination was the formation of gas bubbles in the melted surface layer. Weight changes observed during HDI treatments did not indicate any severe decomposition. The gas bubbles are believed to be generated from internal porosity in the refractories where gas is trapped after the surface region becomes molten. Closer inspection of the surfaces also indicated that some surface cracking takes place (Fig. 4.3).

A cross section of a typical surface region on the refractories is shown in Fig. 4.4. The as-fabricated material consists of large aggregates bonded together with the finer materials. The HDI-treated material (Fig. 4.4b) has a 1- to 2-mm-thick melted surface coating and an underlying reaction zone that extends another 1 to 2 mm. The cross section also shows that the bubbles are predominantly near the bottom of the melted region, which reinforces the idea that the gas that forms them is derived from internal porosity. It should also be noted that the melted surface has a highly oriented morphology with grains extending from the reaction zone interface to the surface.



Fig. 4.1. High-alumina castable before and after high-density infrared (HDI) treatment. Surface melting was evident, and gas bubbles were present. Treatment conditions as shown.



Fig. 4.2. Aluminosilicate with low cement content castable after HDI treatment. Surface melting was evident and gas bubbles were present at power levels \geq 1375 watts/cm². Treatment conditions as shown.



<u>2 mm</u>

Fig. 4.3. High-alumina castable surface after HDI treatment (at 1375 W/cm²). In addition to surface melting and gas bubbles, some cracking was also observed.

This oriented structure was confirmed by X-ray diffraction (Fig. 4.5). Comparison of a conventionally heated brick ($1500^{\circ}C$ for 1 h) and one that was HDI-treated shows they are considerably different. The conventionally heated material showed the presence of mullite and residual raw materials, with all of the mullite peaks indicating no preferred orientation. On the other hand, the HDI-treated material showed the formation of highly oriented mullite and no detectable residual raw materials. The two major peaks for the mullite on the HDI-treated surface were the 001 and 002 peaks, indicating that the grains were oriented with the *c*-axis perpendicular to the surface. Evidently, after the surface is melted, crystals nucleate at the reaction zone interface and grow towards the surface.

Further studies to determine the corrosion resistance of HDI-treated refractories used two commercial materials. The first was a high-alumina castable with a nominal starting composition of 88% Al_2O_3 -4% SiO_2 -4% calcium aluminate cement-4% MgO. It had a density of ~3.2 g/cm³ and about 12% porosity. The second material was a pumpable aluminosilicate with a nominal composition of 88% Al_2O_3 -12% SiO_2 . It had a density of ~2.9 g/cm³ and contained ~16% porosity. These were calcined to 800°C prior to HDI surface treatment.

Cursory corrosion testing was done by melting copper onto the surfaces of test samples much like a sessile drop. The non-HDI-treated materials were preheated to 1500°C for 1 h to simulate a conventional thermal cycle prior to contact with the molten metal. The corrosion exposure was done at 1200°C for 100 h in argon.

The surface region of the high-alumina castable refractory without HDI treatment is shown in Fig. 4.6. Typically, the refractory consists of a mixture of aggregates and finer bonding phases. X-ray diffraction confirmed that a combination of the raw materials (Al₂O₃, etc.) and some mullite formed during the conventional thermal treatment to 1500°C. After HDI treatment, the appearance of the surface region is quite different (Fig. 4.7). Surface melting is readily evident at the exposure level used (a double scan at 2350 W/cm² and 1 cm/s), and the thickness of the melted region was \geq 500 µm. The rapid thermal transients inherent with the HDI processing result in the formation of a dendritic grain morphology. X-ray diffraction identified the surface as mullite; based on the peak intensities, the grains were

preferentially oriented with the *c*-axis perpendicular to the surface. Weight changes observed during HDI treatments did not indicate any severe decomposition took place. Some porosity is evident; however, it is not as much as observed in earlier work. While there is no conclusive correlation, it should be noted that this sample was HDI-treated with a double scan sufficient to melt the surface twice. Previous work has shown a reduction in trapped porosity by multiple HDI scans.



(a)



Fig. 4.4. Cross section of aluminosilicate with low-cement-content castable (a) before and (b) after HID treatment (at 1700 w/cm²). A reaction zone is observed below the melted surface region.



Fig. 4.5. X-ray diffraction of aluminosilicate with low-cement-content castable: (a) after conventional heating to 1500°C for 1 h, and (b) after HDI treatment (at 1700 W/cm²). Mullite and residual raw materials are observed after conventional heating. Only mullite is observed after HDI treatment; the major peaks at 001 and 002 indicate a highly oriented structure.



Fig. 4.6. Surface region of high-alumina castable refractory without HDI treatment.



Fig. 4.7. Surface region of high-alumina castable refractory after HDI treatment (double scan at 2350 W/cm² and 1 cm/s). Surface melting and some gas bubbles were observed.

A cross-section of a typical surface region on the aluminosilicate refractory is shown in Fig. 4.8. The asfabricated material consists of large aggregates bonded together with the finer materials. As before, the HDI-treated surfaces reveal the melted surface coating, which is \geq 500 µm thick and exhibits an oriented grain structure (Fig. 4.9). Also observed is the presence of significant trapped porosity beneath the molten surface layer. The gas bubbles are believed to be generated from internal porosity in the refractories by gas that is trapped after the upper surface region becomes molten. The cross section also shows that the bubbles are predominantly near the bottom of the melted region, which reinforces the idea that they are derived from internal porosity. In addition, there is an underlying thermally affected zone that extends another 1 to 2 mm. Evidently, in this region the raw materials react with one another but do not become molten. Although no characterization in this region was performed, it most likely that some mullite is formed, but it is not oriented like the mullite in the surface region.



Fig. 4.8. Surface region of aluminosilicate refractory without HDI treatment.



Fig. 4.9. Surface region of aluminosilicate refractory after HDI treatment (single scan at 2350 W/cm² and 1 cm/s). Surface melting and gas bubbles were observed.

After corrosion testing, the interface between the molten copper and refractory were examined. The interface for the conventionally heated high-alumina castable is shown in Fig. 4.10. A shallow penetration zone of $\sim 10 \,\mu$ m extending into the refractory was observed. The copper-refractory interface for the HDI-treated high-alumina castable showed very little to no penetration into the refractory (Fig. 4.11). For this sample, the interface was difficult to observe because of the high relief between the ceramic and metal phases.

The behavior of the non-HDI-treated aluminosilicate refractory is shown in Fig. 4.12. Copper penetration into the refractory was $\leq 15 \ \mu$ m. This is a little more than the other refractory tested and may be related to a slightly higher porosity level. However, this would need to be confirmed with additional testing. In contrast, the behavior of the HDI-treated aluminosilicate refractory was very different. The molten copper did not wet the surface and actually fell off at the end of the test. The HDI-treated surface of the aluminosilicate showed no penetration or interaction with the molten copper (Fig. 4.13).



Fig. 4.10. Interface between copper (below) and high-alumina castable refractory without HDI treatment. Some penetration of copper into refractory can be observed.



Fig. 4.11. Interface between copper (below) and highalumina castable refractory (above) that had HDI treatment. Very little or no penetration of copper into refractory can be seen.



Fig. 4.12. Interface between copper (below) and the aluminosilicate refractory (above) without HDI treatment. Some penetration of copper into refractory can be observed.



Fig. 4.13. Surface of aluminosilicate refractory with HDI treatment after contact with molten copper. No penetration into refractory or interaction with molten copper is seen.

4.1.2 Summary

The HDI system offers a unique method for surface treatment of ceramics. It is characterized by the extremely high heating and cooling rates that are possible. Surface melting is observed in many ceramic systems where the melting point is $>1400^{\circ}$ C.

The surface treatment of commercial refractories has shown that surface properties can be altered. With the refractories, surface melting was plainly evident at moderate power levels (\geq 1375 W/cm²). During solidification of the surface melted region on alumino-silicate materials, the mullite grains that formed were highly oriented with the *c*-axis perpendicular to the surface. Corrosion testing showed that the HDI treatment was effective in reducing penetration by molten copper.

4.2 Fabrication of Corrosion-Resistant Coatings

In the glass industry, alumina zirconia silicate (AZS) refractories have been used for many years for glass contact applications. Previous work has shown that corrosion resistance improves with increasing zirconia content [9]. A study was initiated to demonstrate the fabrication of zirconia coatings on AZS refractories to improve the corrosion resistance.

4.2.1 Experimental Results

The refractories treated in the study were commercial AZS materials: a fused cast AZS with 33% ZrO₂ (referred to as FC AZS-33), and a cast and sintered AZS with 20% ZrO₂ [referred to as cast and sintered (CS) AZS-20]. The characteristics of each are presented in Table 4.1. The samples were approximately $1 \times 1 \times 2$ in. (2.5 \times 2.5 \times 5 cm) and were cut from larger blocks. While the sample surfaces may be slightly different from what would be found in an actual cast material, for an initial study the samples were considered adequate. The coatings were made with slurries of ZrO₂ (3% Y₂O₃) powder and ethanol (10 vol % solids plus 1 wt % polyvinylpyrrolidone binder). The slurries were painted on by hand and dried. The weight of powder applied to each surface was estimated to produce a dense coating of zirconia ~200 µm thick.

The surfaces of the refractories were exposed to the HDI treatment at various power levels. Several infrared thermal treatments were conducted to determine an appropriate powder level to use to bond the coating to the underlying refractory. Because of the high thermal expansion of the AZS refractories, a preheat of the surface was used prior to the high-power bonding step. To determine the effects of the HDI treatment on the underlying refractory, several uncoated samples were treated using similar conditions for producing the coatings. In the case of the FC AZS-33, the surface exhibited a coating due to the exudation phenomenon that is typically observed when these types of refractories are heated. The sample also turned buff colored, which is also normal. On the other hand, the

Table 4.1. Characteristics of alumina zirconia
silicate (AZS) refractory samples

Characteristic	FC AZS-33	CS AZS-20
Porosity (%)	3–9	17–20
Density (g/cm ³)	3.7	3.1
Composition		
ZrO ₂ (%)	33	20
SiO ₂ (%)	13.5	10.7
Al ₂ O ₃ (%)	52	69
Na ₂ O (%)	1.3	—
Other (%)	0.14	0.3

Abbreviations: FC = fused cast; CS = cast and sintered

less dense CS AZS-20 sample showed very little morphological changes when HDI-treated at conditions sufficient to produce melted coatings with the FC samples. The CS AZS sample required an additional infrared exposure to produce a surface coating. This difference in behavior may be due to the higher SiO₂ and impurity contents in the dense FC AZS-33.

The appearances of the refractory samples at different stages are shown in Figs. 4.14 and 4.15 for the different refractories. Surface melting is readily evident for the HDI-treated samples. Weight changes observed during HDI treatments did not indicate that any severe decomposition took place. Cross sections of the HDI coatings are shown in Figs. 4.16 and 4.17. The HDI-treated surfaces on the FC AZS-33 sample revealed that the melted surface coating was 1–2 mm thick. For the CS AZS-20 sample, the HDI-affected zone was 0.5–1 mm. It should be noted that these thicknesses are considerably more than the 200-µm thickness estimated for the coatings on the basis of the weight of zirconia powder that was applied to the surface prior to HDI processing. Evidently, significant mixing occurs between the applied zirconia powder coating and the underlying material. While the mixing could be viewed as detrimental, it probably helps to reduce the thermal expansion mismatch between the coating and refractory and should also improve the bonding. The cross section also shows bubbles that are generally located near the bottom of the melted region. A predominant source for the gas bubbles is believed to be from internal porosity in the refractories where gas is trapped after the upper surface region becomes molten. Another source of the bubbles could be from trapped gases in the glass phase that have been reported for FC AZS refractories.



Fig. 4.14. FC AZS-33 before and after HDI treatment. *Left to right:* as-received sample; painted sample prior to HDI treatment; sample after HDI treatment. Surface melting was evident. HDI treatment consisted of a preheat from zero power to 220 W/cm² in 5 min, followed by a high-power treatment at 400 W/cm² for 4 s.



Fig. 4.15. CS AZS-20 before and after HDI treatment. *Left to right:* as-received sample; painted sample prior to HDI treatment; sample after HDI treatment. Surface melting was evident. HDI treatment consisted of a preheat from zero power to 220 W/cm² in 5 min, followed by a high-power treatment at 400 W/cm² for 4 s and an additional 375 W/cm² for 2 s.



Fig. 4.16. Cross section of coated FC AZS-33 after HDI treatment.



Fig. 4.17. Cross section of coated CS AZS-20 after HDI treatment.

Significant microstructural changes occur during the HDI thermal treatments of the coated samples, as shown in the comparisons in Figs. 4.18 through 4.21. Normally, FC AZS microstructure consists of primary ZrO₂ (monoclinic) grains, Al₂O₃ grains with secondary ZrO₂, and a glassy silicate intergranular phase. The HDI-treated zirconia coatings in the present study were significantly different. Evidently, there is a melting of the zirconia coating as well as of the top region of the underlying refractory. Mixing occurs during the liquid stage, and high-aspect-ratio ZrO₂ dendrites precipitate. X-ray diffraction identified tetragonal as well as monoclinic ZrO₂ in the HDI-treated coatings. Porosity, which is probably due to shrinkage, is also observed.

The microstructure of the as-received CS AZS-20 material shows large Al_2O_3 aggregates surrounded by a finer structure of ZrO_2 and aluminosilicate grains. HDI treatment of a coated sample showed melting and some mixing with the underlying refractory similar to that observed with the FC AZS. Dendrites of alumina and zirconia were observed in the HDI-affected surface region along with some residual Al_2O_3 aggregates from the underlying material. Porosity was also observed.



Fig. 4.18. Microstructure of as-received FC AZS-33.



Fig. 4.19. Microstructure of FC AZS-33 after HDI treatment.



Fig. 4.20. Microstructure of as-received CS AZS-20.



Fig. 4.21. Microstructure of CS AZS-20 after HDI treatment.

Corrosion testing was done at 1400°C using a mixture of a typical soda-lime-silica window glass plus 10 wt % NaCO₃. It was thought this mixture would provide an aggressive test of the effectiveness of the coatings. Samples were exposed for either 15 or 80 h. Macroscopic views of the surfaces of the FC AZS-33 uncoated and coated samples after 15 h showed some degradation of the refractories (Figs. 4.22 and 4.23). Closer inspection revealed the formation of a boundary layer consisting of undissolved ZrO_2 grains, which is normal behavior for this type of refractory (Figs. 4.24 and 4.25). For the uncoated FC AZS-33, the boundary layer was ~300 µm. For the coated FC AZS-33, the boundary layer was not readily apparent. However, dissolution of the intergranular phase between the high-aspect-ratio ZrO_2 dendrites appeared to have occurred to a depth of ~300 µm below the surface. The CS AZS-20 also showed degradation during the 15-h glass mixture exposure (Figs. 4.26 and 4.27). The uncoated sample exhibited significant dissolution and release of undissolved grains, as shown in Fig. 28. The coated CS AZS-20 showed some degradation, however; a boundary layer of undissolved ZrO_2 was still observed on the surface (Fig. 4.29).



Fig. 4.22. Cross section of as-received FC AZS-33 after corrosion testing for 15 h.



Fig. 4.23. Cross section of HDI coated FC AZS-33 after corrosion testing for 15 h.



Fig. 4.24. Microstructure of as-received FC AZS-33 after corrosion testing for 15 h.



Fig. 4.25. Microstructure of HDI-coated FC AZS-33 after corrosion testing for 15 h.



Fig. 4.26. Cross section of as-received CS AZS-20 after corrosion testing for 15 h.



Fig. 4.28. Microstructure of as-received CS AZS-20 after corrosion testing for 15 h.



Fig. 4.27. Cross section of HDI-coated CS AZS-20 after corrosion testing for 15 h.



Fig. 4.29. Microstructure of HDI-coated CS AZS-20 after corrosion testing for 15 h.

As expected, the 80-h exposure tests revealed significantly more degradation of the refractories (Figs. 4.30 and 4.31). On the uncoated FC AZS-33 materials, the boundary layer had a thickness of ~900 μ m and a considerable amount of undissolved ZrO₂ grains within the glass melt due to material loss from surface (Fig. 4.32). The coated material showed a larger boundary layer due to retention of fine ZrO₂ from the HDI coating a significant dissolution of the alumina grains and glassy grain boundary phase in the underlying refractory (Fig. 4.33).

The CS AZS-20 material showed severe degradation after the 80-h glass mixture exposure (Figs. 4.34 and 4.35). In fact, the HDI-coated sample had the coating on one surface, and those areas not covered nearly disintegrated during the test. Microscopic examination reveals the severity of the degradation, with both fine ZrO_2 and larger Al_2O_3 grains being dislodged from the surface (Fig. 4.36). The HDI-coated surface of the CS AZS-20 sample showed the retention of fine ZrO_2 in the coating, forming a significant boundary layer (Fig. 4.37).



Fig. 4.30. Cross section of as-received FC AZS-33 after corrosion testing for 80 h.



Fig. 4.31. Cross section of HDI-coated FC AZS-33 after corrosion testing for 80 h.



Fig. 4.32. Microstructure of as-received FC AZS-33 after corrosion testing for 80 h.



Fig. 4.33. Microstructure of high density-infrared coated FC AZS-33 after corrosion testing for 80 h.

4.2.2 Summary

It was demonstrated that zirconia-rich coatings can be formed on the surfaces of AZS refractories using HDI thermal treatments. During high-temperature processing, the surfaces are melted, and mixing occurs between the applied zirconia coating and the underlying refractory. The coatings are characterized by fine dendritic ZrO₂ grains and some porosity. Corrosion testing in a container glass–NaCO₃ mixture at 1400°C showed that the coatings help form boundary layers on the surfaces that inhibit penetration by the molten glass.



Fig. 4.34. Cross section of as-received CS AZS-20 after corrosion testing for 80 h.



Fig. 4.36. Microstructure of as-received CS AZS-20 after corrosion testing for 80 h.



Fig. 4.35. Cross section of high density-infrared coated CS AZS-20 after corrosion testing for 80 h.



Fig. 4.37. Microstructure of high density-infrared coated CS AZS-20 after corrosion testing for 80 h.

4.3 Production of High-Emissivity Coatings

High-emissivity coatings on noncontact refractories were produced by bonding rare earth oxides (e.g., yttria and ceria) onto fibrous materials using the HDI system. These types of coatings are used extensively in heat-treating furnaces. An added benefit of the HDI treatment would be to seal the surfaces of the porous refractories, which should also reduce thermal heat losses.

4.3.1 Experimental Results

Two commercial fiber insulation types were tested: an aluminosilicate (51% SiO₂-48% Al₂O₃) with a density of 0.32 g/cm³ and a maximum use temperature of 1400°C, and a zirconia (ZrO₂-8% Y₂O₃-3% SiO₂) with a density of 0.48 g/cm³ and a maximum use temperature of 1700°C. The thicknesses of the coatings were estimated by the weight of rare earth powder applied to the surfaces prior to treatment in the HDI. Coating thicknesses ranged from 20 to 90 μ m. The appearance of coated and HDI-treated samples is shown in Fig. 4.38. Good bonding was observed for all of the coatings.



Fig. 4.38. Appearance of noncontact fiber insulation after HDI of rare-earth-coated surfaces. *Top row:* aluminosilicate (51% SiO₂-48% Al₂O₃); *bottom row:* zirconia (ZrO₂-8% Y₂O₃-3% SiO₂). From left to right in each row the coatings are of ceria, lanthana, yttria, neodymia, and a lanthanide mixture.

The HDI power used to bond the coatings onto the fibrous insulation was significantly less than the power required for HDI treatments of other dense refractories. Previous work showed that powers of \geq 1500 W/cm² were necessary to bond coatings on dense refractories, but the coatings in the present study needed powers of <500 W/cm² for adequate bonding. This is a significant improvement in the energy requirements. Evidently, the very low thermal conductivity of the fibrous insulation allows the near-surface temperature to increase rapidly enough to bond the coatings to the underlying insulation.

Visual examination of the bonded coatings on the aluminosilicate showed that the applied coatings had reacted with the fibrous insulation to form a dense coating that was much thicker than the amount of rare earth powder initially applied (Figs. 4.39 and 4.40). This observation was the same for all of the rare earth coatings. X-ray diffraction results showed reaction products between the rare earths and the SiO₂ and Al₂O₃ in the insulation. Some cracking of the dense coating was observed.

In the case of the zirconia-based fiber insulation, the HDI-treated coatings were adherent, but not dense enough to "seal" the surface like the aluminosilicates. The fibrous nature of the insulation was intact, indicating the higher refractoriness of the zirconia (Fig. 4.41). Very little interaction between the coatings and the zirconia was observed. All of the rare earths, however, can go into solid solution with ZrO₂, and thus, such an interaction would be difficult to determine. The emittance in the visual spectrum, measured at 540°C, is shown in Figs. 4.42 and 4.43. The data indicate some changes are occurring in the rare-earth-based coatings.



Fig. 4.39. Surface of HDI-treated aluminosilicate fiber insulation with a Nd_2O_3 coating. The coating is formed by reaction of the rare earth powder and the underlying insulation material.



Fig. 4.40. Cross section of HDI-treated aluminosilicate fiber insulation with a Nd₂O₃ coating.



Fig. 4.41. Cross section of HDI-treated zirconia fiber insulation with a Nd_2O_3 coating. The coating is formed by reaction of the rare earth powder and the underlying insulation material. The fibrous nature of the insulation remained.

UMR measured the change in emission of the coated fibrous insulating ceramics with and without various coatings. A top-loading electric-resistance-heated furnace heated the samples to 1450°C. After the sample reached 1450°C, a cold probe with a fiber optic probe coaxially mounted was inserted in the furnace. The element power was then switched off, and the total emission was measured every 50°C until the sample reached 750°C. Initial experiments showed that the spectrometer picked up emission from the elements and the furnace chamber. A mullite muffle tube partially improved this, eliminating the band peaks in the emission spectra due to the moly-disilicide elements. However, emission from the mullite tube varied as a function of furnace power or amperage. This variable emission could not be held stable. Because the emission was a function of furnace power, all spectra were captured with the element power off during the entire cooling to eliminate the spectra from the heating elements.



Fig. 4.42. Visual spectrum emittance from aluminosilicate (51% SiO₂-48% Al₂O₃) insulation: (a) as-received and (b) with HID-treated neodymia coating. Tests were performed at 540°C.



Fig. 4.43. Visual spectrum emittance from zirconia (ZrO_2 -8% Y_2O_3 -3% SiO₂) insulation: (a) as-received and (b) with HDI-treated neodymia coating. Tests were performed at 540°C.

The samples after testing are shown in Fig. 4.44. The coating delaminated from the surface of the sample for the CeO₂, Nd₂O₃, and rare-earth-mixture coatings. The delamination of the coating could be due to thermal expansion mismatch or partial sintering of the coatings at 1450°C. The delamination held approximately 2 mm of the underlying fibrous ceramic. This would indicate that the interface between the coating and the fibrous ceramic is stronger than the fibrous ceramic. The shape of the laminated area is indicative of cooling or heating delamination, depending upon the thermal expansion coefficient differences.



Fig. 4.44. Samples after emittance testing.

The emitted radiation of all of the samples showed that the emission intensities varied greatly between the coatings. However, samples with the same coating on different substrates had similar intensity values, as shown in Fig. 4.45. Thus, the intensity of emission is more dependent on the coating than the substrate. The aluminosilicate control had the lowest emission intensity (9.6 mW/cm²nm), while the zirconia-based control had the second highest emission intensity (52.5 mW/cm²nm). The emission increased from ~10 mW/cm²nm for the aluminosilicate with no coating; to ~30 mW/cm²nm for the samples coated with Nd₂O₃, CeO₂ and La mixture; to ~40 mW/cm²nm for the Y₂O₃ and La₂O₃ coatings and the uncoated zirconia-based sample. Additional evidence that the emitted intensity is more dependent on the coating than the substrate is shown by the fact that the coated zirconia-based samples have a higher intensity than the coated aluminosilicate samples approximately half the time (60%).

Additional tests showed that the emitted intensity of the uncoated control samples follow the emission spectra of a graybody. The Nd_2O_3 and rare-earth-mixture coatings were not gray bodies. That is, the intensity did not increase as defined by Planck's law, as a function of wavelength. There were distinct peaks in the emission at 640, 720, 780 and 860 nm. These peaks are due to the band absorption and reradiation characteristics of neodymium, which makes this element popular in lasers. Emission of all of the samples followed Planck's law with regard to temperature where the emission increased as temperature increased. The emissions from Nd_2O_3 and rare earth-mixture samples also followed Planck's law with respect to temperature.

4.3.2 Summary

Surface coatings were used to alter the emissivity of fibrous ceramic. Reducing the emissivity reduces the absoprtion of energy by the fibrous ceramic, leading to a reduction in heat transfer. Currently, most fibrous ceramics used for insulation have an emissivity of about 0.9 when measured from 0 (perfect reflector) to 1 (perfect blackbody). It was shown that the Nd₂O₃ and rare-earth-mixture coatings caused the wavelength of emission to be changed, while the other coatings (CeO₂, La₂O₃, and Y₂O₃) altered only the graybody emissivity. The coating dominated the change in emissivity. No difference could be found between emissivity of the coatings on zirconia-based and aluminosilicate fibrous ceramics, even with the large differences in emission between the uncoated aluminosilicate (9.6 mW/cm²nm) and zirconia-based (46 mW/cm²nm). The emission increased from aluminosilicate (~10 mW/cm²nm) with no coating; to the samples coated with Nd₂O₃, CeO₂ and a La mixture (~30 mW/cm²nm); to the Y₂O₃ and La₂O₃ coatings and the uncoated zirconia-based sample (~40 mW/cm²nm). All of the samples followed Planck's law with respect to temperature.



Fig. 4.45. Average intensity from 550 to 1100 nm of samples at 1250°C.

4.4 Cost Estimate

As with every industrial process, cost is a major concern in the application of the technology. Many of the expenses associated with the HDI process are uncertain because experience with the technology is limited. Capital costs are on the order of >\$150,000 for the equipment, depending on the complexity of the system. However, amortization of these costs over the lifetime of the equipment is unknown. As more experience is gained with the HDI system, these costs will become better understood. The operating costs can be estimated more quantitatively. The lamps used in the process have a lifetime of ~1200 h and cost about \$500. Electricity costs (assuming 5¢/kWh and using 80% power and a scan speed of 1 cm/s) translate into a cost of ~0.25¢/in.² (0.04¢/cm²), or about 34¢/ft². As with any new technology, the costs should be reduced as the technology matures and production volumes increase.

5. Accomplishments

This project has met the technical, technology transfer, and commercialization goals. Each of the accomplishments is described below.

5.1 Technical Accomplishments

The goals of the project were to (1) reduce open surface porosity on commercially available refractories and demonstrate improved penetration resistance; (2) fabricate corrosion-resistant surface layers on refractories by selective sintering of secondary layers and show improved corrosion behavior; and (3) produce noncontact refractories with high-emissivity surface coatings. Each of these goals was met.

During the first year of the project, the HDI treatment of commercial refractories to reduce surface porosity (by essentially sealing the surface to prevent liquid penetration) showed that the surface properties can be altered. Surface melting was plainly evident on the refractories at moderate power levels (\geq 1375 W/cm²). During solidification of the surface melted region on aluminosilicate materials, the mullite grains that formed were highly oriented with the *c*-axis perpendicular to the surface. Corrosion testing showed that the HDI treatment was effective in reducing penetration by molten copper.

Work during the second year of the project showed that surface chemistry changes could be performed by bonding an adherent coating onto the underlying refractory and that this coating would inhibit wetting and/or corrosion. It was demonstrated that zirconia-rich coatings could be formed on the surfaces of alumina zirconia silicate (AZS) refractories using HDI thermal treatments. During high-temperature processing, the surfaces are melted and mixing occurs between the applied zirconia coating and the underlying refractory. The coatings are characterized by the formation of fine dendritic ZrO₂ grains and some porosity. Corrosion testing in a container glass–NaCO₃ mixture at 1400°C showed that the coatings help form boundary layers on the surfaces and reduce dissolution of the refractory.

During the final year of the project, high-emissivity coatings were produced on noncontact refractories by bonding rare earth oxides onto fibrous materials using the HDI system. These types of coatings are used extensively in heat-treating furnaces. The results showed that the surface coatings could alter the emissivity of fibrous ceramics. Reducing the emissivity reduces the energy absorbed by the fibrous ceramic, leading to a reduction in heat transfer. The coatings dominated the change in emissivity. No difference could be found between the emissivity of the coatings on zirconia-based and aluminosilicate fibrous ceramics, even with the large differences in emission between the uncoated base materials. All of the samples (uncoated and coated) followed Planck's law with respect to temperature.

5.2 Technology Transfer

The project included several industrial partners: Allied Mineral, Inc. (Columbus, Ohio); Emhart Glass Co. (Owensville, Mo.); Magneco-Metrel, Inc. (Addison, Ill.); Allvac, Inc. (Monroe, N.C.); and Albany Research Center (Albany, Ore.). These companies provided refractory samples used in the HDI processing and testing. They were involved in the project from the standpoint of being informed of the results for their products and being able to give their input on the results and the methods used in testing the samples after HDI processing.

In addition, several other companies were contacted and visited during the course of the project to introduce them to the technology and solicit their viewpoints. These companies were St. Gobain/Norton (Buckhannon, W.Va.) and Minteq, Inc. (Slippery Rock, Pa.).

5.3 Publications, Presentations, and Patents

Below is a list of publications (Sect. 5.3.1) and presentations (Sect. 5.3.2) that grew out of this project. A patent disclosure (Sect. 5.3.3) was submitted but later rejected.

5.3.1 Publications

- 1. T. N. Tiegs, J. O. Kiggans, FC Montgomery, C. A. Blue, and M. Velez, "HDI Surface Treatment of Ceramics," *Am. Ceram. Soc. Bull.* 82, no. 2 (2003) 49–53.
- T. N. Tiegs, J. O. Kiggans, F. C. Montgomery, and C. A. Blue, "High-Density Infrared Surface Treatment of Ceramics," *Ceram. Trans.* 135, 239–246, American Ceramics Society, Westerville, Ohio, 2002.
- 3. T. N. Tiegs, J. O. Kiggans, F. C. Montgomery, D. C. Harper, and C. A. Blue, "Surface Modification of Ceramics by High-Density Infrared Heating," *Ceram. Eng. Sci. Proc.* **24**, no. 3, 477–482, American Ceramics Society, Westerville, Ohio, 2003.
- T. N. Tiegs, F. C. Montgomery, D. C. Harper, C. A. Blue, M. Velez, M. Karakus, and R. E. Moore, "Surface Treatment of AZS Refractories Using High-Density Infrared Heating," pp. 3–12 in *Proc.* 64th Conference on Glass Problems, American Ceramics Society, Westerville, Ohio, 2004.
- 5. T. N. Tiegs and C. A. Blue, "High-Density Infrared Surface Treatments of Refractories," *Refractories Applications and News*, University of Missouri, Rolla, 2002.
- T. N. Tiegs, F. C. Montgomery, C. A. Blue, and M. Velez, "High-Density Infrared Surface Treatment of Refractories," pp. 93–100 in *Refractories: Trends in Research and Applications*, ed. P. Vincenzini and G. Aliprandi, Proceedings of the International Symposium B2 "Refractories: Trends in Research and Applications" of the 10th International Ceramics Congress, CIMTEC 2002, Florence, Italy, July 14–18, 2002,vol. 35 of Advances in Science and Technology, 2003.

5.3.2 Presentations

- 1. "High-Density Infrared Surface Treatment of Ceramics," American Ceramic Society Annual Meeting, St. Louis, Mo., April 29–May 1, 2002.
- 2. "Surface Treatment of Refractories by High Intensity Infrared Heating," American Ceramic Society Pacific Coast Meeting, Seattle, Wash., Oct. 1–4, 2002.
- 3. "Surface Modification of Ceramics By High-Density Infrared Heating," American Ceramic Society Meeting on Advanced Materials, Cocoa Beach, Fla., Jan. 27–31, 2003.
- 4. "Surface Treatment of AZS Refractories Using High-Density Infrared Heating," 64th Conference on Glass Problems, Urbana, Ill., Oct. 28, 2003.
- 5. "Surface Treatment of Refractories for Glass Contact Applications," 35th Symposium of the Society for Glass Science and Practices, Wheeling, W.Va., May 6, 2004.
- 6. "Ceramic Coatings on Refractories Produced by High Intensity Infrared Heating," American Ceramic Society Annual Meeting, Indianapolis, Ind., April 20, 2004.
- 7. "High-Density Infrared Surface Treatment of Refractories," 10th International Ceramics Congress, Florence, Italy, July 14–18, 2002.

5.3.3 Patent Disclosure

An invention disclosure pertaining to the treatment of refractories using HDI was submitted to the ORNL Patent Office. UT-Battelle decided not to file a patent application with the U.S. Patent Office.

5.4 Commercialization

This project was exploratatory in nature to determine the feasibility of various surface modifications of refractories. Technology transfer activities are presented in Section 1.2, above.

6. Conclusions

The HDI system offers a unique method for surface treatment of ceramics. It is characterized by the extremely high heating and cooling rates that are possible with the technique. The surface treatment of commercial refractories has shown that surface properties can be altered and porosity reduced. With refractories, surface melting was plainly evident at moderate power levels (\geq 1375 W/cm²). During solidification of the surface melted region on aluminosilicate materials, the mullite grains that formed were highly oriented with the *c*-axis perpendicular to the surface. Corrosion testing showed that HDI treatment was effective in reducing penetration by molten copper.

Examination of the use of HDI heating to produce coatings demonstrated that zirconia-rich coatings can be formed on the surfaces of AZS refractories. During high-temperature processing, the coated surfaces are melted and mixing occurs between the applied zirconia coating and the underlying refractory. The coatings are characterized by fine dendritic ZrO₂ grains and some porosity. Corrosion testing in a container glass-NaCO₃ mixture at 1400°C showed that the coatings help form boundary layers on the surfaces; these boundary layers inhibit penetration by the molten glass.

Finally, surface coatings were used to alter the emissivity of fibrous ceramics. Reducing emissivity reduces the energy absorbed by the fibrous ceramic, leading to a reduction in heat transfer. Currently, most fibrous ceramics used for insulation have an emissivity of ~0.9 when measured from 0 (perfect reflector) to 1 (perfect blackbody). It was shown that the Nd₂O₃ and rare earth mixture coatings caused the wavelength of emission to be changed, while other coatings (CeO₂, La₂O₃, and Y₂O₃) altered only the graybody emissivity. The type of coating dominated the change in emissivity. No difference could be found between emissivity of the coatings on zirconia-based and aluminosilicate fibrous ceramics even with the large differences in emission between the uncoated aluminosilicate and zirconia-based materials.

7. Recommendations

The HDI technologies developed in this project demonstrated improved refractory performance by surface treating with HDI heating. The results were of interest to several refractory, glass, and metal melting industries. However, several hurdles currently prevent commercial implementation of the technologies. The most significant is cost. Capital costs are high, especially for a relatively new technology, such as HDI heating. As the use of HDI increases in several other areas, the capital costs will decrease, and the technology will become more available for use in treating refractories. Capital costs are more of an issue with small to medium companies with a smaller number of plants. Operating costs are also an issue, mainly because refractories are a commodity product, and the profit margins in their manufacture and sale are small. The small margins are offset by the large volumes of materials used. Thus, any increase in manufacturing has a significant impact on the profitability of the materials. There was also reluctance by the refractory companies to develop technologies that would result in lower refractory volume.

Before HDI surface treatment technologies are implemented by industry, larger-scale testing is necessary. The current project achieved only small-scale testing. An additional two years of R&D work would be needed to develop the technology and test scale-up in order to allow commercial testing.

8. References

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- 3. S. Bourban et al., "Solidification Microstructure of Laser Remelted Al₂O₃-ZrO₂ Eutectic," *Acta Mater.* 45, no. 12 (1997) 5069–5075.
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- 5. L. Bradley et al., "Surface Modification of Alumina-Based Refractory Materials Using a Xenon Arc Lamp," *Appl. Surf. Sci.* **154-155** (2000) 675–681.
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- 8. X. Xin et al., "High-Emissivity Refractory Coating Improves Furnace Output in China," *Industrial Heating*, 49–50 (June 1999).
- 9. M. Dunkl et al., "Formation of Boundary Layers on Different Refractories in Glass Melts," Proceedings of 62nd Conference on Glass Problems, *Ceram. Soc. Eng. Sci. Proc.* 24, no. 1, 211–223, American Ceramics Society, Westerville, Ohio, 2003.

Appendix A: Posters

- A.1 Surface Treatment of Refractories Using High-Density Infrared Heating
- A.2 Surface Treatment of Refractories Using High-Density Infrared Heating
- A.3 Surface Treatment of Refractories Using High-Density Infrared Heating



A.1. Surface Treatment of Refractories Using High-Density Infrared Heating

A.2. Surface Treatment of Refractories Using High-Density Infrared Heating

Surface Treatment of Refractories Using High Density Infrared Heating

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Mariano Velez, Bill Headrick, Bob Moore, and Musa Karakus University of Missouri-Rolla, Rolla, MO

Introduction

·Refractories play crucial role in IMF industries •Major degradation mechanism has been penetration and corrosion by molten metals or glass •Methods to reduce penetration, wetting, and corrosive chemistry would improve refractory life

> High Density Infrared Lamp Can Be Used To Surface Treat Refractories





ORNL Plasma Infrared Processing Facility

Approach and Objective ·Early IR work concentrated on metals processing

•Project started in October 2001 and had three tasks •Reduce surface porosity to improve penetration resistance ·Change surface chemistry with coatings to improve corrosion resistance

Current activities examining methods to increase emissivity of non-contact refractories

Industrial Collaborators

•Emhart Glass •Allied Mineral Magneco-Metrel

Advantages of Using High Density IR Heating

•Compared to laser, can cover large areas Short wavelength irradiation •Fast heating and cooling rates •Very high temperatures attainable •Potential for continuous processing

Cost Estimates for IR Surface Treatments

•Capital Cost Uncertain •~\$250 K for equipment •Amortization over lifetime unknown

Annottation over interme unknown
Annottation over interme unknown
Costs
-Tube life -1200 hours at \$500/tube
Electricity (assuming 54/we'n tusing full power and
san speed of 1 cm/sec)
-0.3\$/square inch (0.05¢/square centimeter)
-43\$/square foot

Publications 1. T. N. Tiegs, J. O. Kiggans, F. C. Montgomery, C. A. Blue, and M. Velez, 'HOI Surface Treatment of Ceramics," Am. Ceram. Soc. Bull 82 [2] 49-53 (2003).

2. T. N. Tiegs, J. O. Kiggans, F. C. Montgomery, C. A. Blue, "High Density infrared Surface Treatment of Ceramics," Ceram. Transactions, Vol. 135, 239-246, Am. Ceram. Soc., Westerville, O Density Transa (2002) rulle, OH

T. N. Tiegs, J. O. Kiggans, F. C. Montgomery, D. C. Herper, an C. A. Blue, "Surface Modification of Ceramics By High Density Infrared Healing," Ceram. Eng. Sci. Proceed., 24[3] 477-482, Am. Ceram. Soc., Westerville, OH (2003).

T. N. Tiegs, F. C. Montgomery, D. C. Harper, C. A. Blue, M. Velez, M. Karakus, and R. E. Moore, "Surface Treatment of AZS Refractorise Suring High Density Infrared Healing", pp. 3-12 in Proceed. of 64th Conference on Glass Problems, Am. Ceram. Soc., Westerville, OH (2004).

Presentations 1. Presentation made at the American Ceramic Society Annual Meeting in St. Louis, MO. April 29-May 1, 2002 entitled, "High Density Infrared Surface Treatment of Ceramics."

2. Presentation made at the American Ceramic Society Pacific Coast Meeting in Seattle, WA Oct. 1-4, 2002 entitled," Surface Treatment of Refractories By High Intensity Infrared Heating."

3. Presentation made at the American Ceramic Society ... researcher made at the American Ceramic Society Meeting on Advanced Materials in Cocoa Beach, FL, Jan, 27-31, 2003 entitled," Surface Modification of Ceramics By High Density Infrared Heating."

4. Presentation made at the 64th Conference on Glas Problems in Urbana, IL, Oct. 28, 2003, entitled "Surface Treatment of AZS Refractories Using High Density Infrared Heating."

Presentation made at the 35th Symposium of the Society for Glass Science and Practices on May 6, 2004 in Wheeling, WV, entitled "Surface Treatment of Refractories For Glass Contact Applications."

6. Presentation mude at the American Ceramic Society Annual Meeting in Indianapolis, IN, April 20, 2004 entitled, "Ceramic Coatings on Refractories Produced by High Intensity Infrared Heating."

Initial Results - Changing Surface Emissivity of Refractories

Refractories with High Emissivity Should Reduce Energy Consumption During Heat-Treating Operations

•Non-contact fiber insulation used extensively in heattreating furnaces •Two commercial fiber insulation tested

•Alumino-silicate (51% SiO2-48% Al2O3) with density of 0.32 g/cc and a maximum use temperature of

1400°C •Zirconia (ZrO₂-8% Y_2O_3 -3% SiO₂) with a density of 0.48 g/cc and a maximum use temperature of 1700°C

Fiber Insulation with Rare Earth-based Coatings Bonded with IR Treatment



UT-BATTELLE







A.3. Surface Treatment of Refractories Using High-Density Infrared Heating