

ADVANCED CERAMIC COMPOSITES FOR IMPROVED THERMAL MANAGEMENT IN MOLTEN ALUMINUM APPLICATIONS

Klaus-Markus Peters¹, Robert M. Cravens², James G. Hemrick³

¹Fireline TCON, Inc.; 300 Andrews Avenue, Youngstown, OH 44505, USA

²Rex Materials Group; 5600 East Grand River, Fowlerville, MI 48836, USA

³Oak Ridge National Laboratory; 1 Bethel Valley Road, Oak Ridge, TN 37831, USA

Keywords: Refractories, Molten Metal, Aluminum, Energy Savings

Abstract

Degradation of refractories in molten aluminum applications leads to energy inefficiencies, both in terms of increased energy consumption during use as well as due to frequent and premature production shutdowns. Therefore, the ability to enhance and extend the performance of refractory systems will improve the energy efficiency through out the service life. TCON® ceramic composite materials are being produced via a collaboration between Fireline TCON, Inc. and Rex Materials Group. These materials were found to be extremely resistant to erosion and corrosion by molten aluminum alloys during an evaluation funded by the U.S. Department of Energy and it was concluded that they positively impact the performance of refractory systems. These findings were subsequently verified by field tests. Data will be presented on how TCON shapes are used to significantly improve the thermal management of molten aluminum contact applications and extend the performance of such refractory systems.

Introduction

The production of molten aluminum creates aggressive environments for processing equipment, thereby requiring refractory materials to contain the aluminum during melting, transfer, treatment, and casting operations. Degradation of these refractories not only causes issues with reduced product quality and production yields, but also increases heat losses as the insulative properties of the refractories are compromised. Furthermore, in addition to disrupting production output, refractory failures lead to further impacts upon energy efficiency as large amounts of energy are lost during the cooling and subsequent reheating of the equipment as the refractory linings are repaired or replaced.

The need for improved refractory materials is recognized throughout the industry. A joint U.S. Department of Energy and industrial workshop held in 2000 on applications for advanced ceramics in aluminum production [1] noted that refractory materials used in melt processing equipment have many limitations. The workshop report noted that these issues may be addressed by using advanced ceramics, but new materials must be cost effective when compared to current refractory materials. Also, in 2005 the Canadian aluminum industry produced a technology roadmap [2] having the goal of identifying and bridging gaps between current technological resources in the industry and future requirements. One of the areas identified as being crucial to the future of the industry was the need for improved molten aluminum-resistant materials.

Refractory deterioration and failures can arise from several mechanisms [3,4] such as: chemical reactions between the molten aluminum and the refractory material (corrosion); mechanical degradation of the material by the process environment (erosion); and thermal stresses, leading to

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE FEB 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Advanced Ceramic Composites for Improved Thermal Management in Molten Aluminum Applications				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Fireline TCON, Inc,300 Andrews Avenue,Youngstown,OH,44505				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002300. Presented at the Minerals, Metals and Materials Annual Meeting and Exhibition (138th)(TMS 2009) Held in San Francisco, California on February 15-19, 2009. Sponsored in part by the Navy. U.S. Government or Federal Purpose Rights.					
14. ABSTRACT Degradation of refractories in molten aluminum applications leads to energy inefficiencies, both in terms of increased energy consumption during use as well as due to frequent and premature production shutdowns. Therefore, the ability to enhance and extend the performance of refractory systems will improve the energy efficiency through out the service life. TCON ceramic composite materials are being produced via a collaboration between Fireline TCON, Inc. and Rex Materials Group. These materials were found to be extremely resistant to erosion and corrosion by molten aluminum alloys during an evaluation funded by the U.S. Department of Energy and it was concluded that they positively impact the performance of refractory systems. These findings were subsequently verified by field tests. Data will be presented on how TCON shapes are used to significantly improve the thermal management of molten aluminum contact applications and extend the performance of such refractory systems.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

failure by fatigue or shock. All of these limitations reduce the energy efficiency of the process, as degraded equipment linings cause a loss of process heat (through reduced insulation) and the need for maintenance through repair or replacement of the linings.

TCON ceramic composites are newly developed materials that appear to address the issues raised by the aluminum industry workshops; they have been found to be extremely resistant to erosion, corrosion, and thermal stresses caused by molten aluminum alloys in a variety of applications. These materials are now being produced and distributed via a collaboration between Fireline TCON, Inc. (Fireline) and Rex Materials Group (RMG), with RMG marketing them under the RX-TCON trademark. As will be discussed below, these materials offer unique, cost-effective solutions to the problems that compromise the performance of refractory systems in molten aluminum processing equipment. Not only can TCON composites extend the performance life of the equipment, they can be integrated into refractory systems that outperform conventional refractories by significantly reducing the heat losses from the equipment.

TCON Composite Materials

In a classical composite, one material (the matrix or binder) surrounds and binds together a collection of particles or fibers of a different material (the aggregate or reinforcement). The different materials work together to give the composite unique properties, but within the composite the different materials can be easily discerned as discrete, dispersed, and isolated phases embedded in an otherwise homogeneous matrix material [5]. Given the well-known performance benefits of conventional composites, it can be expected that a material in which both phases form continuous networks may exhibit even better performance characteristics [5-7]. Such materials with continuous networks are called interpenetrating phase composites (IPCs) [5].

An especially interesting IPC family are co-continuous ceramic/metallic composites, as they often exhibit the attractive properties of metals such as high strength and tolerance towards thermal shock and those of ceramics such as corrosion resistance and tolerance of high temperatures without necessarily also sharing their respective undesired properties. Particularly attractive methods for their production are displacement reactions in which sacrificial oxides are reduced by a metal [8-13]. There are numerous reactions that are thermodynamically, kinetically, and mechanistically favorable [8]. Of these IPC materials produced via displacement reactions, the alumina/aluminum ($\text{Al}_2\text{O}_3/\text{Al}$) composite is the one that has been most investigated [9-13], which is produced by the reaction shown in equation 1:



This is carried out by reacting the silica (SiO_2) precursor with molten aluminum at elevated temperatures, yielding a continuous network of alumina interlaced with a continuous network of aluminum as seen in Figure 1. The aluminum network forms due to volume contractions as the silica is converted to alumina, and the silicon by-product dissolves into the aluminum. The alumina and aluminum networks typically have cross-sectional thicknesses ranging from one to a few micrometers across [8,10,11] and fine nanometer-sized grains [13]. Also, the interfaces between the alumina and aluminum phases have unique nano-scale features [14-16] that are believed to directly impact the macro-scale properties.

Inert additives that do not participate in the displacement reaction, such as silicon carbide particles, can be added to the silica precursor, yielding a multiphase composite where the inert ceramic particles are bonded together by the IPC matrix, as shown in Figure 2. These inert additives can have a significant effect on the final composite properties, such as improving the thermal shock characteristics of the material [17].

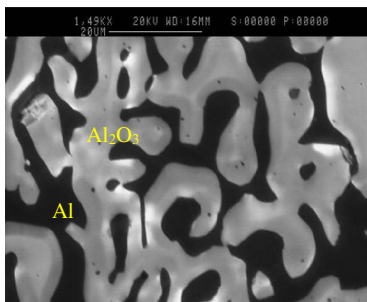


Figure 1. SEM photomicrograph of the TCON Al₂O₃-Al matrix (1,500x).

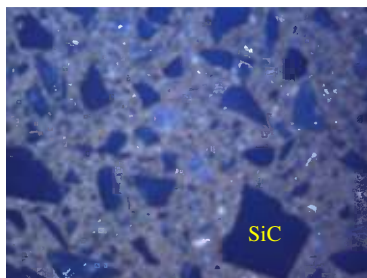


Figure 2. Optical photomicrograph of the TCON grade TC2 (50x).

The TCON process involves two basic steps: 1) Fabricating preforms of various sizes and shapes via conventional processing techniques and from readily-available precursor and inert additive materials; 2) Carrying out the displacement reaction by fully immersing the preforms in molten aluminum metal under specific processing conditions and for certain periods of time, resulting in the complete reaction of the ceramic materials and transforming them into the ceramic-metallic interpenetrating phase composites. During development of the TCON process, the following key characteristics were identified: 1) The properties of TCON materials can be tailored by varying the preform materials and process parameters. For example, the room temperature strength can be increased by a factor of up to 10 times. 2) The process is capable of producing shapes of various sizes and complexities, ranging from a few millimeters to over a meter in a single dimension. This makes the TCON process a very cost-effective method to produce net shapes with enhanced material properties.

Evaluation of TCON Materials in Molten Aluminum Applications

Laboratory Testing

A U.S. Department of Energy project entitled, “Multifunctional Metallic and Refractory Materials for Energy Efficient Handling of Molten Metals” was initiated in 2004 and one of the stated goals was to extend the life of molten-metal containment refractories by an order of magnitude through the development of new materials by the industrial collaborators. The project was supported by the Industrial Technologies Program, U.S. Department of Energy, under Grant No. DE-PS07-031D14425, and led by West Virginia University with research participation by the University of Missouri – Rolla (UMR, now called the Missouri University of Science and Technology) and Oak Ridge National Laboratory (ORNL). Fireline TCON, Inc. participated in this project as an industrial collaborator. Extensive testing by project researchers found excellent performance by the TCON materials as summarized below:

Static and Dynamic Corrosion Tests. Bars of TCON materials were immersed into molten aluminum alloys at 700°C for durations between 500 and 1,000 hours. Cross sectional samples examined by the Oak Ridge researchers using both optical and electron microscopy, revealed only minimal interaction of the TCON material with the molten aluminum [18].

Sessile Drop Testing. Static and dynamic sessile drop methods were employed for studying the wettability of TCON materials by liquid aluminum. The dynamic test more closely replicates

application conditions, with a small quantity of aluminum alloy melted by induction heating in a reducing atmosphere and dropped onto the refractory substrate. Results showed non-wetting behavior on a macroscopic scale and only slight wetting on a microscopic level [18,19].

Room and Elevated Temperature Modulus of Rupture. MOR testing was performed according to ASTM C133. Four-point bending tests gave MOR values on the order of 50-75 MPa (7-11 ksi) at room temperature (depending upon composition) and 25 MPa (3.5 ksi) at 700°C. Hemrick et al. noted that this is an extremely good strength for a refractory material, good enough for the material to be used in a structural application if desired [18].

Thermal Conductivity. Thermal conductivity was evaluated using a new method developed at ORNL, utilizing a unique High Intensity Infrared (HDIR) lamp technique [20]. The thermal conductivity of the TCON material was found to be as high as expected (about 60 W/mK) due to the presence of SiC. However, the researchers concluded that the overall insulating capability of a refractory system containing TCON material could be optimized by using thin layers of TCON backed by a highly insulating refractory [18].

Thermal Shock/Thermal Cycling. Thermal shock and thermal cycling evaluation was performed according to ASTM C1171. Strength of originally tested compositions was found to decrease due to thermal cycling/thermal shock. Testing of an optimized TCON grade (TC2), reformulated based on results from initial testing, yielded a material that showed no measurable drop off in strength (original RT MOR = 49 ± 2 MPa, RT MOR after thermal cycling = 48 ± 3 MPa) due to thermal cycling/shock.

The ORNL and UMR researchers considered the lab scale testing of TCON to be a success [18], and initiated an industrial scale test to further validate the material. As shown in Figure 3, six plates of the TCON refractory were inserted into the wall of a 325-lb melting furnace.

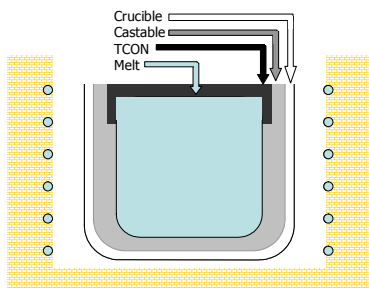


Figure 3a. Industrial scale evaluation of TCON materials - schematic



Figure 3b. Industrial scale evaluation of TCON materials - actual installation.

The melt line of the 5083 aluminum alloy was located in the center of the six inch TCON plates (i.e., three inches from the top of the furnace). The alloy was kept molten for 2,000 hours (83.3 days) and the testing included periodic (every one to three days) physical scraping off of the dross and corundum from the TCON plates to simulate refractory cleaning in industrial applications. Mg content was replenished using solid magnesium metal and the metal line was kept constant by adding additional solid 5083 alloy. Dross removal was performed in a fashion to simulate the harsh standard practices of industry described above by scraping with a metal rod. Following the test, examination of the TCON plates led the ORNL researchers to conclude that

the test was successful, as it was found that solidified aluminum present on the TCON plates was easily peeled away from the refractory and optical and electron microscopy revealed no detectable signs of aluminum penetration [18]. In addition, the researchers could find no evidence of mechanical degradation from the surface cleaning, demonstrating the excellent wear resistance of the TCON material. In summary, the ORNL and UMR researchers concluded that their testing had been successful, showing that the TCON refractory material exhibited improved corrosion and wear resistance for use with molten aluminum [18].

Field Testing

Fireline and Rex Materials Group have successfully trialed SiC-Al₂O₃-Al TCON composite materials (grades TC1, TC2, and RX1) in several different applications, as summarized below:

Hooks. The first test was in an automated production cell for casting aluminum alloy diesel pistons, where iron rings are preconditioned in molten aluminum prior to being embedded into pistons during casting. Hooks made out of TCON TC1 were used to hold iron rings during the preconditioning process, and were subsequently subjected to corrosion by molten aluminum above 700°C and erosion due to rotation of the hooks in the bath. The TCON hooks were found to last up to ten weeks, as compared with competitive hooks that typically lasted one to three days. Additionally, the TCON hooks were found to fail in a predictable and controlled manner, whereas the competitive hooks failed catastrophically and unpredictably.

Inductively Heated Channels for Holding Furnaces. Another successful evaluation was in an inductively heated channel located in the bottom of a melt holding furnace. This channel was comprised of two round, upright tubes leading into a square, horizontal tube, and an induction coil was wrapped around the square tube upon installation in the furnace. During furnace operation, cold molten aluminum traveled down into channel and was heated up by the induction field, subsequently traveling back up into the holding chamber. This tube was traditionally formed out of a castable refractory but over time there were significant issues with deposits and build up, requiring the operators to “rod” the channels and clean them out every shift. Channels made out of TCON RX-1 were evaluated and at it was found that these furnaces remained free of build up, subsequently eliminating the need for “rodding”. Life of this component went from a few weeks to about one year, saving the end user substantial dollars in maintenance costs and down time. This customer has subsequently equipped all of their furnaces with TCON channels.

Ladle Impact Pads. The second application was in a 500 lb. ladle for the transfer of molten aluminum alloy from a melting furnace to a holding furnace within a foundry. TCON TC2 was used as a melt impact pad (located in the bottom of the ladle) to reduce erosion of the refractory lining. Conventional refractory materials located in the bottom of the ladle were found to erode as the aluminum melt was poured into the ladle. This erosion led to the need to remove the ladle from service for repair as the erosion became severe. Previous maintenance practices require patching of the ladle every two to three weeks and replacement of ladles every 18-24 months adding cost and the need to have multiple ladles on hand. TCON plates were installed in the bottoms of two ladles while they were being relined. After 17 and 24 weeks of service, respectively, the pads in both ladles showed no observable corrosion or erosion. Further, during inspection the aluminum skin adhering to the TCON surface was easily peeled away indicating a lack of wetting. Based on the performance of these two ladles, the customer has added TCON plates to all of its transfer ladles.

Tap-Out Trough. In another application, a tap-out trough at a major secondary aluminum processor was retrofitted with a TCON TC2 impact pad by chiseling out a portion of the existing refractory and mortaring in a 12 x 12 x 0.75” TCON plate. This trough was connected to a reverber

furnace that was tapped two to three times a day, with approximately 250,000 lbs. of aluminum alloy being drained into the trough with each tapping. The plate lasted for over five months with no discernable effect on the TCON pad. (The trial concluded when the refractory material surrounding the TCON plate eroded away.) As a result of this positive trial, this and other molten aluminum processors will be installing TCON impact pads into tap-out troughs.

Energy Efficient Refractory Systems Utilizing TCON Composite Materials

The ability of TCON materials to mitigate erosion/corrosion issues and extend the service life of molten aluminum processing equipment indirectly results in energy savings by reducing the frequency of refractory lining repairs and replacements. However, the frequency of these intermittent energy savings is highly dependant upon the type of equipment and the severity of the environment, with months or years possibly transpiring between events. More importantly, significant and immediate energy efficiency gains can be realized by incorporating TCON shapes into refractory systems that utilize highly insulative materials. In spite of the fact that TCON materials have high thermal conductivity values, due to the significant amount of silicon carbide present, the ability to produce a variety of useful TCON shapes allows for the assembly of refractory systems that can outperform conventional refractories in terms of both longevity and energy efficiency. This is accomplished by placing relatively thin TCON shapes where needed most, namely at the hot face where it is exposed to the molten aluminum. Given the proven ability of TCON to combat erosion/corrosion, this type of refractory system allows for the use of back-up linings that are optimized for their insulative properties and less so for their resistance to molten aluminum, thereby maximizing the energy efficiency of such a system.

The benefits of this type of refractory system are illustrated in Figure 5. Cold face temperatures were calculated for the following types of refractory systems: 1) A conventional 70% alumina castable refractory; 2) 0.75" of TCON backed by Rex Material Group's FUSIO₂N™ SS fused silica; 3) A conventional 70% alumina castable refractory backed by ceramic paper (0.125" thick); 4) 0.75" of TCON backed by Rex Material Group's Fusio₂n SS fused silica plus ceramic paper; and 5) 0.75" of TCON backed by Rex Material Group's Pyrolite® 3500 ceramic fiber. Figure 5 shows how the cold face temperature is reduced as the overall thickness of each refractory system is increased. (The thickness of TCON was held at 0.75", while the thickness of the back-up materials was incrementally increased.)

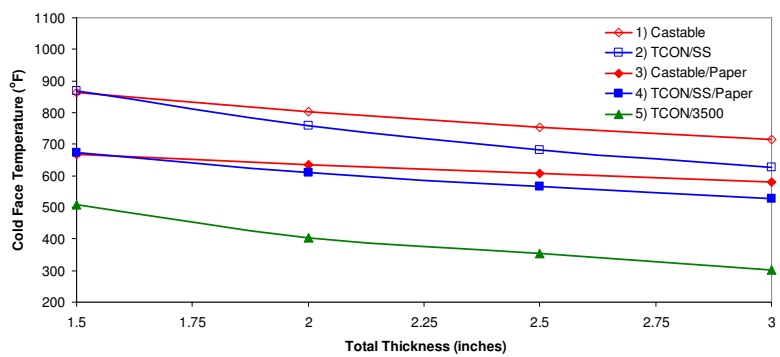


Figure 4. Cold face temperatures versus thickness of refractory system

These calculations show how a refractory system incorporating TCON at the hot face backed by an insulating refractory layer can be very effective in reducing heat losses and improving energy efficiency. At a total thickness of 3 inches, TCON backed by FUSIO₂N SS fused silica results in cold-face temperatures that are 9 to 12% lower than that achieved by a conventional 70% alumina castable refractory material (with and without ceramic paper). More significantly, 3 inches of TCON plus Pyrolite 3500 ceramic fiber achieves a cold face temperature that is 48% lower than an equivalent amount of conventional 70% alumina castable refractory material backed with ceramic paper. Therefore, the use of such a TCON/Pyrolite refractory system can achieve significant energy savings. Conversely, in the case where an aluminum cast house or foundry needs to maximize the internal dimensions of its molten aluminum processing/transfer equipment, the use of a TCON faced refractory system would be very beneficial. In such a case a 1.5 inch thick TCON/Pyrolite refractory system will be just as effective as 3 inches of conventional 70% alumina castable refractory material backed with ceramic paper.

Conclusions

TCON materials are unique refractory materials for use in molten aluminum applications and have been proven to be extremely resistant to the erosion, corrosion and thermal stresses encountered in these processing environments. Just as important to increasing the up time of processing equipment, utilizing TCON materials in the hot face of refractory systems can achieve significant energy savings throughout the operational lifetime of the equipment.

References

1. *Applications for Advanced Ceramics in Aluminum Production: Needs and Opportunities*, Proceedings of a workshop sponsored by the United States Advanced Ceramics Association, the US Department of Energy & the Aluminum Association, February 2001.
2. *Canadian Aluminum Industry Technology Roadmap*, proceedings published by Industry Canada, May 2005
3. T.W. Dunsing, "Tips on Good Refractory Practice for Aluminum-Melting Furnaces", *Industrial Heating*, April 2002, pp 27-29.
4. P. Bonadia, M.A.L. Braulia, J.B. Gallo & V.C. Pandolfelli, "Refractory Selection for Long-Distance Molten –Aluminum Delivery", *American Ceramic Society Bulletin*, Vol. 85, No. 8, p9301.
5. D.R. Clarke, "Interpenetrating Phase Composites", *J. Am. Ceram. Soc.*, 75 [4] 739-59 (1992).
6. H.X. Peng, Z. Fan, J.R.G. Evans, "Bi-Continuous Metal Matrix Composites", *Mater. Sci. Eng. A*, 303, 37-45 (2001).
7. O. Sigmund, "Composites With Extremal Thermal Expansion Coefficients", *Mech. Mater.*, Vol. 20, No. 4, 351-368 (1995).
8. W. Liu and U. Koster, "Criteria for Formation of Interpenetrating Oxide/Metal- Composites by Immersing Sacrificial Oxide Preforms in Molten Metals", *Scripta Materialia*, Vol. 35, No. 1, pp 35-40 (1996).
9. M.C. Breslin et al., "Processing, microstructure, and properties of co-continuous alumina aluminum composites", *Mater. Sci. Eng. A*, 195 (1995) 113-119.

10. W.G. Fahrenholtz et al., "Synthesis and Processing of Al₂O₃/Al Composites by In Situ Reaction of Aluminum and Mullite", *In-Situ Reactions for Synthesis of Composites, Ceramics, and Intermetallics*, pp. 99-109, ed. by E.V. Barrera et. al., The Minerals, Metals, and Materials Society, Warrendale, PA, 1995.
11. R.E. Loehman and K. Ewsuk, "Synthesis of Al₂O₃-Al Composites by Reactive Metal Penetration", *J. Am. Ceram. Soc.*, 79 [1] 27-32 (1996).
12. E. Saiz and A.P. Tomsia, "Kinetics of Metal-Ceramic Composite Formation by Reactive Penetration of Silicates with Molten Aluminum", *J. Am. Ceram. Soc.*, 81 [9] 2381-93 (1998).
13. N. Yoshikawa, A. Kikuchi, and S. Taniguchi, "Anomalous Temperature Dependence of the Growth Rate of the Reaction Layer between Silica and Molten Aluminum", *J. Am. Ceram. Soc.*, 85 [7] 1827-34 (2002).
14. J. Ringald et. al, "Scanning and transmission Electron Microscopy on Composite Materials prepared by SMP and In-Situ Displacive Reactions", *Inst. Phys. Conf. Ser. No 147*: Section 13, 1995.
15. G.S. Daehn et. al, "Elastic and Plastic Behavior of a Co-Continuous Alumina/Aluminum Composite", *Acta Materialia*, Vol. 44, No. 1, pp. 249-261(1996).
16. X.F. Zhang, G. Harley, L.C. De Jonghe, "Co-continuous Metal-Ceramic Nanocomposites", *Nano Letters*, Vol. 5, No. 6,, 1035-1037 (2005).
17. G.S. Daehn, M.C. Breslin, *JOM*, 58, 87-91 (2006).
18. J.G. Hemrick, W.L. Headrick & K-M Peters, "Development and Application of Refractory materials for Molten Aluminum", *Int. J. Appl. Ceram. Technol.*, Vol. 5, No. 3, 2008, pp 265-277
19. J. Xu, X. Liu, E. Barbero, J.G. Hemrick & K-M Peters, "Wetting Reaction Characteristics of Al₂O₃/SiC Composite Refractories by Molten Aluminum and Aluminum Alloys", *Int. J. Appl. Ceram. Technol.*, Vol. 4, No. 6, 2007, pp 514-523
20. J.G. Hemrick, R.B. Dinwiddie, and E.R. Loveland, "Technique Development for Large Sample Thermal Conductivity Measurement of Refractory Ceramics", *Proceedings of the 43rd Symposium on Refractories*, St. Louis, Missouri, March (2007).