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RAPID COMMUNICATION

Thermal conductivity of salvaged fused cast alumina used in the glass industry

Hsin Wang | **James G. Hemrick**

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Correspondence
Hsin Wang, Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge TN, USA
Email: wangh2@ornl.gov

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Abstract

Fused cast alumina (FCA) has been and continues to be used as a refractory material in energy intensive industries such as glass melting and chemical processing. In-service degradation due to high temperature exposure in harsh environment affects the designed furnace thermal profiles and energy consumption. Phase transformation may occur at the refractory hot face during glass melting altering the properties. Three FCA blocks recovered from industrial furnaces were investigated in this study. The as-received FCA consists primarily of a mixture of alpha (α) and beta (β) alumina that has a thermal conductivity value of 5–6 W/mK. The Hot Disk method was used to obtain thermal conductivity directly on the refractory blocks. At the hot face, a transformation from β to α alumina occurred and was confirmed by an X-ray diffraction study. Thermal conductivity measurements as a function of position also showed a clear transition from β to α alumina at both ends of a complete block with no voids. Thermal conductivity of the α alumina tripled compared to β alumina. This study provides important information of heat transfer and thermal conductivity evolution to refractory manufacturers and users.

KEYWORDS

fused cast alumina, hot disk, refractory, thermal conductivity

1 | INTRODUCTION

As the US glass industry transitions from using air-fuel to oxy-fuel for the glass melting process, the refractories used in the oxy-fuel furnace also experience higher temperature and higher alkali vapor pressure. More creep-resistant refractories such as fused cast alumina (FCA) replaced traditional silica bricks[1] as crown and super structure construction materials. These newer refractories were also found to face degradation during service. The hot and corrosive environment can cause property changes in the refractory making understanding of the refractory aging process important to the application of the refractories and the overall glass production efficiency. Thermal properties of insulating refractories can be found in recent work[2] in which specimens were extracted to obtain temperature dependency. Recent work also showed the importance of thermal properties of refractory to the glass industry.[3,4] A survey of refractory degradation test methods other than thermal conductivity has been presented before.[5]

Thermophysical properties, such as thermal conductivity, are important factors for furnace design and modeling of the glass melt. From previous postmortem studies on salvaged silica bricks,[6,7] it has been found that the thermal conductivity of silica bricks doubled after 8–10 years in service. However, thermal conductivity evolution of FCA refractory is not readily available in the literature. In this paper, we report postmortem studies on FCA refractory materials.

Microstructure changes during service are known to play a very important role in the refractory aging process.[8] In addition to microstructural degradation, high temperature exposure can promote grain growth in the refractory and, in some cases, induce phase transformation to become more thermally conducting. The consequence is the degradation of the insulating capability of refractories, which can lower the glass melt temperature or an increase of energy consumption to maintain the same temperature. To this end, X-ray diffraction and microscopy work were carried out at the University of Missouri, Rolla along with mechanical and thermal transport properties measurements conducted at the Oak Ridge National Laboratory (ORNL)[9]. Traditionally, a study on correlation between microstructure and thermal properties requires extracting many specimens for multiple measurements. This paper reports a nondestructive method on salvaged FCA blocks using a Styrofoam backed Hot Disk sensor. Thermal conductivity was measured as a function of location to correlate with microstructure and phase changes.

2 | EXPERIMENTAL

The salvaged refractory blocks, originally from Monofrax LLC, were obtained from a glass furnace as supplied by the glass manufacturer after being in service for 3 years. Three blocks were taken from (1) the charging end; (2) 2/3 from the charging end, and (3) the throat area of the float glass furnace. The surface facing the glass melt is referred to as the hot face, while the opposite surface is referred to as the cold face. The block dimensions were on the order of 7.5 cm × 15 cm × 25 cm. A thin slice was cut from each block for microscopy and X-ray diffraction measurements. Additional FCA blocks were used to establish baseline properties and conduct creep studies.

A laser flash thermal diffusivity system (Anter Flashline 5000) following ASTM E1461 and a high temperature differential scanning calorimeter (DSC) (Netzsch Pegasus 404) following ASTM E1269 were used to obtain baseline thermal conductivity data of the FCA refractory material. The diffusivity specimen was a disk 12.7 mm in diameter and 1 mm thick, and the DSC specimen was a disk 5.5 mm in diameter and 1 mm thick. Baseline thermal conductivity

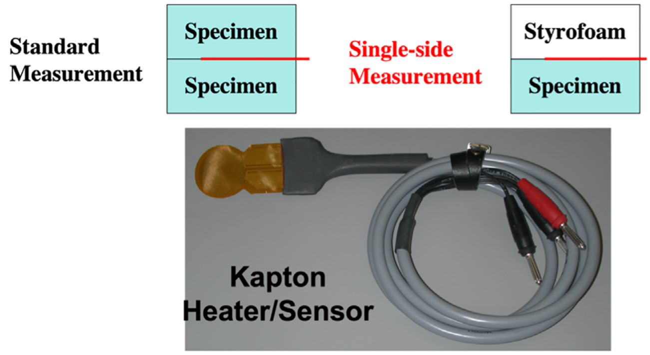

FIGURE 1 Standard and single-side method using the Hot Disk heater/sensor

of as-cast alumina block was obtained using the following equation:

$$\text{Thermal Conductivity} = \text{Density} \times \text{Specific Heat}\left(C_p\right) \times \text{Thermal Diffusivity} \quad (1)$$

We used constant density for the calculation because the volume changes due to thermal expansion only introduce errors much less than the measurement uncertainty (5%–7%).

Standard thermal conductivity measurement of refractory is traditionally carried out by the hot wire technique[10,11], in which destructive sample preparation is needed. In the present study, we used the Hot Disk method[12,13] to measure thermal conductivity directly on the refractory blocks. The standard measurement on a Hot Disk system used two identical block specimens as shown in Figure 1. The flexible sensor/heater with double-spiral nickel wire is inserted between the blocks. The radius of the sensors used ranged from 2.0 mm to 7.5 mm. A typical measurement on ceramics takes 5–20 s using a 0.1–1.0 Watt constant power. An alternative testing mode is also shown in Figure 1. By replacing the top block with a Styrofoam, the single-sided method becomes a nondestructive technique. Both test modes were used to evaluate baseline thermal conductivity of pristine, used, and postcreep FCA specimens, which were 30 mm in diameter and 25 mm thick.

For salvaged blocks, the single-sided method was used without extracting samples, the Kapton sensor was pressed against the FCA block through a piece of Styrofoam. Thermal conductivity of the Styrofoam (0.032 W/mK) was used to calculate thermal conductivity of the refractory block.

Thermal conductivity measurements were conducted as a function of location on the three salvaged FCA blocks. Blocks 1 and 2 possessed rough hot face surfaces, and a casting defect (void) was present. The hot disk sensor could not be used near these areas. Block no. 3 had the best

TABLE 1 Phase contents in each color region of the salvaged blocks identified by scanning electron microscopy and dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD)

	Block 1	Block 2	Block 3
Pink-red	α-Al_2O_3	α-Al_2O_3	α-Al_2O_3
Tan-yellow-blue	α-Al_2O_3 and β-Al_2O_3	α-Al_2O_3 and β-Al_2O_3	α-Al_2O_3 and β-Al_2O_3
White	β-Al_2O_3	β-Al_2O_3	β-Al_2O_3
Tan-yellow-blue	α-Al_2O_3 and β-Al_2O_3	α-Al_2O_3 and β-Al_2O_3	α-Al_2O_3 and β-Al_2O_3
Pink-red	α-Al_2O_3	α-Al_2O_3	α-Al_2O_3

Other detectable phases are nepheline and sodium-calcium-aluminosilicate.

surface condition. Complete measurements were carried out every 5 cm. Three tests were conducted at each location.

Chemical analysis of a pristine FCA block has 95 wt.% Al_2O_3 and 4 wt.% Na_2O, 0.5–1.0 wt.% SiO_2 and <1 wt.% other oxides: CaO, ZrO_2, TiO_2, Fe_2O_3. Mineralogically, it has 45 wt.% α-alumina and 53 wt.% β-alumina (or $NaA_{l1}1O_{17}$) and 2 wt.% vitreous phases. Scanning electron microscopy and dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD) studies identified the phases in each region.

3 | RESULTS AND DISCUSSION

Surface colors of the salvaged blocks were studied using optical microscopy. The original FCA blocks are white in color. There were five regions identified in the salvaged FCA blocks moving from the hot face to the cold face: (1) pink-red; (2) tan-yellow-blue; (3) white; (4) tan-yellow-blue, and (5) pink-red. The five regions were found in all the three blocks with the size of each area varying depending on block location in the furnace. Phase contents of the colored regions in the salvaged blocks are shown in Table 1. The colors and phase all showed symmetric distribution from the hot to the cold face.

To establish a thermal conductivity baseline of the FCA, specimens were extracted from pristine and used blacks. As shown in Figures 2A, thermal conductivity of the FCA obtained from flash diffusivity and C_p measurements, at room temperature, ranged from 5 to 6 W/mK, from 400 to 800°C, stayed constant at about 4 W/mK, and increased steadily to just over 6 W/mK at 1400°C.

Thermal conductivity of two pristine blocks was measured using the standard Hot Disk method.[13] Thermal conductivity of three measurements gave average value of 6.00 W/mK. The single-side method was used on each block and gave thermal conductivity of 5.97 W/mK and 5.99 W/mK, respectively. The single-side method has proven to give the same results as the standard method. Further, the single-side method was applied to FCA block without extracting small specimens. As shown in Figure 2B, measurements made on original surface and cut surface showed average thermal conductivity of 6.10 and 6.50 W/mK. Measurements made in an area with dendritic structure showed thermal conductivity of 5.85 W/mK. Creep testing of FCA was previously conducted at 1600°C.[14] Two pristine blocks and two postcreep cylindrical specimens were also tested with the single-side method. The results shown in Table 2 indicate no significant change in the thermal conductivity after long-term exposure under constant mechanical loading in air. Overall, room temperature thermal conductivity of mixed-phase FCA is about 6.00 ± 0.20 W/mK, even after creep testing.

The three salvaged FCA blocks were about 25 cm long. Pink zones (as referred in Table 1) were observed at both the cold face, 0 cm, and the hot face, 25 cm. Block no. 1, taken from the charging end, had a very small pink zone at the cold face (<1 cm). The hot face (20–25 cm) had a significant number of large pores, and measurements could not be made, shown in Figure 3. At the cold face, thermal conductivity was about 8 W/mK, slightly higher than the as-received values. Thermal conductivity dropped to about 6 W/mK in the white zone. Because the pink zone was very small in this sample, the Hot Disk sensor, which has a diameter of 1.5 cm, was not able to resolve transformation zones less than the sensor dimension.

Block no. 2, taken from 2/3 distance from charging end, on the other hand, had a larger pink zone, about 9 cm, at the cold face. Thermal conductivity at the cold face was 13 W/mK and dropped 10 W/mK at the transition region, as shown in Figure 4. Two measurements were made in the white zone giving thermal conductivity of 5 W/mK. The hot face of this sample was very porous. A large void formed during casting made measurements at the hot end impossible.

Block no. 3, taken from the throat end, had the best surface condition, and a total of 16 locations were measured. As shown in Figure 5, thermal conductivity as each location can be related to the local phase contents. For example, β-alumina was not detected at either the hot or the cold face ends. Thermal conductivity in the α-alumina-dominated pink region reached 15 W/mK. The

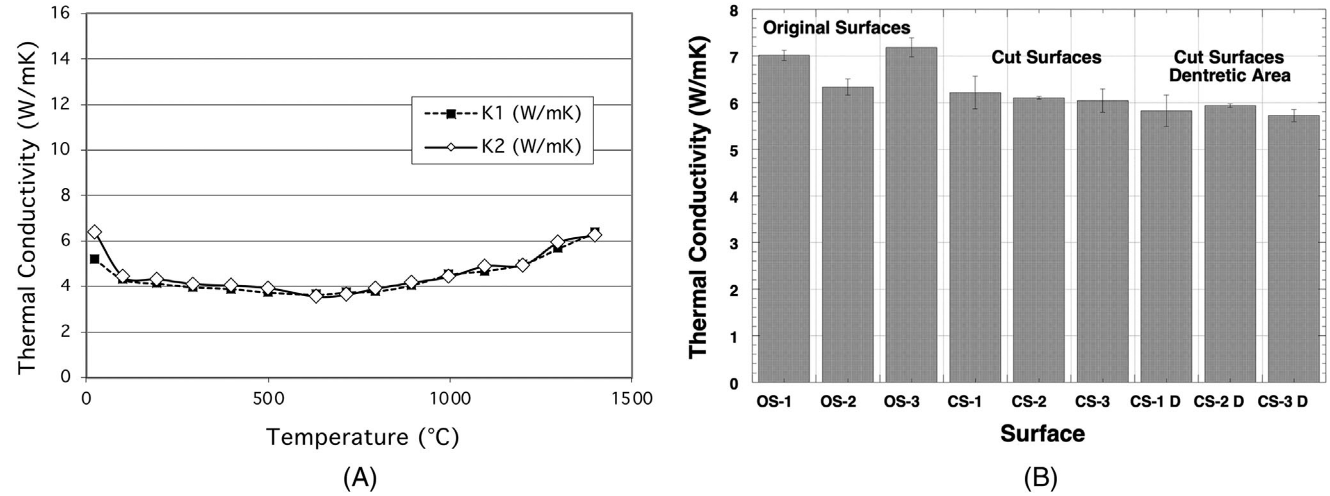

FIGURE 2 (A) Thermal conductivity of fused cast alumina (FCA) obtained from diffusivity and specific heat. (B) Thermal conductivity of FCA block using single-side method

TABLE 2 Thermal conductivity of fused cast alumina (FCA) measured by single-side Hot Disk method

Thermal conductivity (W/mK)	Pristine block 1	Pristine block 2	Postcreep block 1	Postcreep block 2
Measurement 1	5.95	6.01	5.93	6.28
Measurement 2	5.98	5.99	5.82	6.28
Measurement 3	5.97	5.96	5.88	6.00
Average	5.97	5.98	5.88	6.19

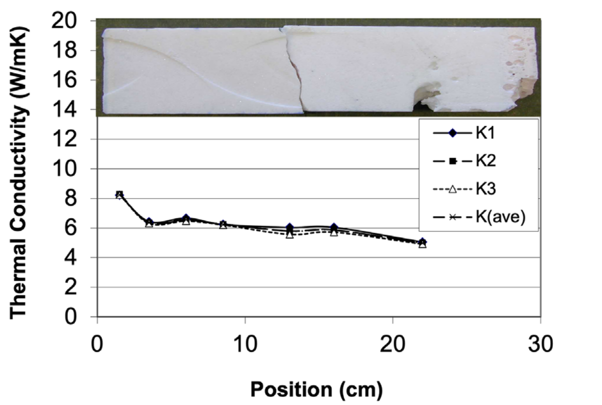

FIGURE 3 Thermal conductivity as a function of location of block no. 1 from charging end (hot face at $x = 30$ cm and cold face at $x = 1$ cm). Picture is used to show approximate locations

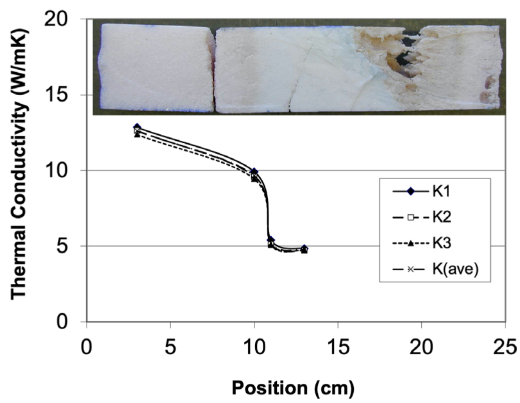

FIGURE 4 Thermal conductivity as a function of location of block no. 2 2/3 from charging end (hot face at $x = 30$ cm and cold face at $x = 1$ cm). Picture is used to show approximate location

white region, that is, between 6 cm and 22 cm, showed thermal conductivity around 5 W/mK. Two thermal conductivity measurements made at the transition regions were also consistent with the phase content.

The as-fabricated FCA blocks are a mixture of α and β alumina. Thermal conductivity of the two phases has been studied.[15,16] For pure beta phase, thermal conductivity is about 2.5 W/mK, and pure alpha phase is >25 W/mK. The large difference in thermal conductivity makes it easier to identify phase transition-related changes. The phase transformation from β-alumina to α-alumina at the hot face can be easily understood. The hot surface temperature was estimated to be 1700°C. At this temperature alkali vapor reacts with the FCA causing the β-alumina to lose sodium and results in a phase transformation to α-alumina with increased thermal conductivity of the mixture.

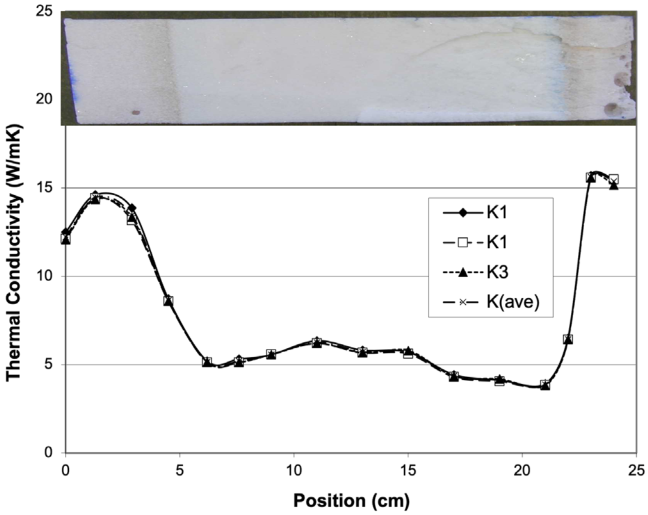

FIGURE 5 Thermal conductivity as a function of location of block no. 3 from throat end (hot face at $x = 30$ cm and cold face at $x = 1$ cm). Picture is used to show approximate location

The phase transformation at the cold face end is an interesting phenomenon. There was a temperature difference between the hot and the cold faces of about 200–300°C, thus resulting in temperature of >1400°C at the cold face. In the glass furnace, the cold face ends were backed up with thermal insulation shields, which kept the temperature very high. Due to these high temperatures, the alkali vapor in the glass furnace can migrate through the lining and attack the rear surfaces causing similar transformation. The insulation layers also reacted with the cold face surfaces resulting the transformation from β-alumina to α-alumina.

Interestingly, measurements of postcreep samples, shown in Table 2, indicate the phase transformation will not occur under normal heating in air. Therefore, it was concluded that it was the corrosive environment in the glass furnace that caused the phase transformation in FCA.

4 | SUMMARY

Thermal conductivity values of salvaged FCA refractory blocks were measured as a function of location. Phase transformation from β-alumina to α-alumina at both the hot and cold face ends due to the presence of alkali vapor resulted in significant increase in thermal conductivity. Thermal conductivity values at accessible locations of block no. 1 and 2 and all locations of block no. 3 were consistent with phase contents identified by SEM/EDS and XRD studies. The significant increases in thermal conductivity at both ends of the FCA blocks provided important insights of correlation between phase transformation and heat transfer in glass furnaces.

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ORCID

Hsin Wang https://orcid.org/0000-0003-2426-9867
James G. Hemrick https://orcid.org/0000-0002-7675-8956

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