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# Performance of a ceramic frit anti-oxidation coating on a MgO–C refractory brick

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**Abstract**

In steel production, ladles must be preheated to minimize the heat loss of the steel melt, prevent thermal shock of refractory bricks (MgO–C), and to maximize the lining life of ladle. Partial oxidation of MgO–C bricks begins in the graphite bond during the preheating. Oxidation of graphite bond also causes a decrease in performance of the bricks because of an increase in the brick porosity. In this article, coating on a MgO–C brick surface by a ceramic film to protect against carbon oxidation was studied. Coated and un-coated bricks were heated at 1200 °C, cooled to room temperature, then the brick properties investigated. The oxidization resistance properties of brick with coating were much better than those without coating, which should lead to longer refractory service life.


*Keywords:* Anti oxidation coating; Ceramic film; MgO–C brick; Oxidation

## 1. Introduction

Carbon containing resin bonded magnesia bricks have been used in the steel industry, specifically in basic oxygen furnaces, electric arc furnaces and in ladles because of their superior thermal shock and slag wear resistance. Carbon imparts superior properties such as high thermal conductivity, low thermal expansion coefficient, high thermal shock resistance, and low wettability to molten slag, and hence better corrosion or erosion resistance. Carbon in brick has a known tendency to oxidize, which impacts their use at high temperatures. The oxidation of carbon begins at 300 °C and increases with increasing temperature [1].

Many studies have been made to prevent the oxidation of carbon/graphite. These include the coating of carbon flakes or fibers by ceramic material (SiC, silicon oxycarbide), phosphate impregnation, or the use of surface glazes [2–4]. These are expensive methods which have some limitation to application in refractory bricks [5]. Another method is the application of a thermal barrier coating on the graphite or carbon composite surface by fine particles of boron, $TiB_2$, $ZrB_2$ and SiC by vapor treatment [6–8]. As with previously mentioned techniques, these methods are not economical to use on refractory bricks. A method commonly used with brick is the addition of fine antioxidant materials such as SiC, $B_4C$, Al, Mg and/or Si to MgO–C brick formulations, preventing or limiting oxidation of carbon at high temperatures (>1400 °C) [9–11]. Again, these additions are expensive and do not completely protect against carbon oxidation at lower temperatures.

Most of the studies are related to the protection of carbon from oxidation during use at elevated temperatures (>1200 °C) in the steelmaking environment. However, in a newly installed steelmaking ladle or arc furnace lining, the resin bonded bricks must be heated to near the use temperature (≈1200 °C) to avoid heat loss, thermal shock of brick, and possible explosions when molten metal is added due to gas evolution and combustion. When a ladle is dried or preheated, surface carbon on a brick starts to oxidize, causing a porous layer on the surface of resin bonded carbon containing brick (MgO–C, $Al_2O_3$–MgO–C, SiC–C), and the quick loss of this oxidized layer during the charging of molten steel [3,12].

External coatings on the surface of composite (C–C, SiC–C) materials have been studied by several researchers [13–16]. The impregnation of aqueous solution containing silica glass, phosphate glasses, colloidal silica, and aluminum phosphate for oxidation protection of carbon is well known [13–15].

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Impregnation is not, however, a suitable technique for protection against oxidation of resin bonded refractory bricks. Surface coatings of the same materials, however, have been successfully used on to C–C or SiC–C composite materials. The behavior of this kind of coating on resin bonded magnesia carbon refractory brick, however, has not been investigated. The aim of this work is to investigate surface oxidation during preheating of MgO–C brick, and to protect against this type of oxidation using a ceramic frit coating.

## 2. Experimental procedure

Resin bonded MgO–C bricks used in this study contained 8 wt% of a natural flake graphite (min 97 wt% in purity), 88.7 wt% fused magnesia (min 97 wt% in purity) and 3.3 wt% novolac type phenol–formaldehyde resin binder. Bricks were shaped and tempered commercially (200 °C for 24 h) with the physical properties of the tempered materials listed in Table 1.

Table 1
Physical properties of MgO–C bricks used in this study.

| Material | Apparent porosity (%) | Bulk density (g/cm$^3$) | Cold crushing strength (kg/cm$^2$) |
|---|---|---|---|
| MgO–C | 4.15 | 3.03 | 460 |

The thermal analysis in tempered MgO–C brick ground to a powder form (under 100 μm) was evaluated by DTA/TG to investigate oxidizing behavior. The ceramic coating composition comprises a powder of 55 wt% vitreous borosilicate frit, 30 wt% alumina (grain size <10 μm) and 15 wt% zircon (grain size <10 μm). These materials were ball milled using corundum ball as a mixing/grinding medium. The melting behavior of the frit mix was observed using heating microscope in air on samples by Hot Stage Microscopy by Misura Instruments.

The coating solution was mixed with 60 wt% solids and 40 wt% liquid. Phosphoric acid and ethyl alcohol (30% of liquid solution) mixture were used as the liquid binder additions. External coatings on the surface of MgO–C bricks were applied by brushing to form a layer approximately 0.8 mm in thickness. The coated samples were dried at room temperature approximately for 10 min.

In normal practice, a ladle is preheated up to 1200 °C in 5 h, with longer times occasionally occurring because of the difficulties in the steel making process. The oxidation procedure used in this report was designed to characterize oxidation behavior of bricks during this type of ladle preheating. Air oxidation resistance tests were carried out on 50 mm cubic samples. Samples were placed in an electric furnace, and heated up to 1200 °C at a rate of 6.5 °C/min in air. After holding at the test temperature for 5 or 10 h, the furnace was shut off and the samples were cooled to room temperature in the test furnace at a cooling rate of 1.5 °C/min. Sample weight changes and decarburized layer thickness were determined to characterize sample oxidation resistance.

Changes in samples due to the oxidation were determined as follows:

$$\text{weight loss } (\%) = \frac{\text{weight before heating} - \text{weight after heating}}{\text{weight before heating}} \times 100\%$$

$$\text{oxidation loss } (\text{g}) = \text{weight before heating} - \text{weight after heating}$$

$$\text{oxidation index } (\%) = \frac{\text{oxidized area} - \text{original area}}{\text{original area}} \times 100\%$$

Microstructural investigations were conducted using a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) to evaluate sample changes after high temperature air exposures.

## 3. Results and discussion

In DTA/TG analyses of uncoated MgO–C brick, oxidation was found to occur in three stages. The first stage started at 200 °C and finished at 300 °C, where a 1.16 wt% mass change in treated samples occurred. This weight loss might be due to the evaporation of remaining alcohol, water, and resin in the MgO–C bricks. The second stage started at 500 °C and finished at 600 °C, where a 1.91 wt% mass change occurred. This weight loss is due to the coking and oxidation of resin. The third sage started at 650 °C and continued to approximately 1200 °C, with a 8.34 wt% mass loss. This loss was attributed to oxidation of flake graphite in the MgO–C brick, which starts at 650 °C.


Fig. 1. Hot stage microscopy images of frit mixture after heating in air at 15 °C/min.

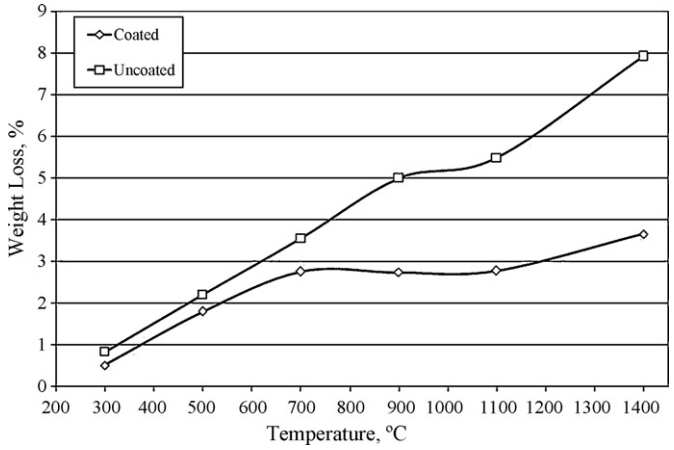


Fig. 2. Oxidation weight loss of MgO–C brick samples that were coated and uncoated when heated in air from room temperature to 1400 °C in 120 min.

A pellet (2 mm diameter and a height of 3 mm) that contained only the ceramic frit in powder form (<100 μm) was heated to 1000 °C at the rate of 15 °C/min in air using a hot stage microscope. Images taken during heating are shown in Fig. 1, which show changes in the specimen melting at different temperatures. The frit mixture was noted to start sintering at 500 °C, with a softening temperature of 652 °C. After this temperature, melting was initiated, and was completed at 952 °C, where deformation and covering the substrate surface occurred. Typical frits (boron glass, etc.) melt between 450 and 550 °C to form a high viscosity liquid that coats a brick surface. However, at the elevated temperatures (>1200 °C), the molten frit layer is not stable because of the partial evaporation of some alkalis and boron oxide contained within it [17,18]. Alumina and zircon additions increased the melting temperature of the frit glazes causing it to be more stable phase at elevated temperatures. The thermal expansion mismatch of MgO–C bricks and the frit coating were also controlled by the addition of alumina and zircon.

Oxidation properties of coated and uncoated MgO–C brick coupons were determined by measuring their weight loss in air at the temperature range from 300 °C to 1400 °C using a heating rate of 3.91 °C/min. Fig. 2 shows the weight change versus temperature dependency of coated/uncoated MgO–C bricks. It is observed in Fig. 2 that the weight losses (i.e. oxidation) start at 300 °C for coated and uncoated samples, and continue with increasing temperature. Low temperature weight losses (<300 °C) were due to the curing and oxidation of the resin binder. For coated and uncoated samples, similar weight losses up to 700 °C occurred. Beyond this temperature, melting of frit began, which covered the sample surface, limiting oxidation of the samples. At this point, the oxidation protection increases considerably in the frit covered samples, limiting weight losses through 1100 °C. Starting at 1100 °C, coated samples had limited oxidation protection through the maximum temperature evaluated (1400 °C). From the data in Fig. 2, the coated sample had a 46.15% lower weight loss than uncoated brick through 1400 °C.

After oxidation testing, the samples were wet cut to determine the oxidized area. Cross sections of coated and uncoated samples are shown in Fig. 3. The uncoated sample had a homogenous oxidation with an oxidization index of 54.62% during the 10 h of oxidation. Coking the untreated brick at 1200 °C resulted in an increase in porosity by 6–8%. Oxidation at 1200 °C occurred because of air in the furnace atmosphere, resulting in corners of the bricks being loose powder. In contrast, the coated sample had no visually oxidized area. The dense structure of the coating was found to protect bricks against oxidation at elevated temperatures for long time.

The oxidation resistance results obtained for the materials are presented in Table 2. From the data in this table, it can be concluded that frit coated samples have a higher oxidation resistance than uncoated samples. Uncoated samples had a total weight loss of 10.54% in the oxidation test after 10 h at 1200 °C. The weight loss was due to oxidation of resin and flake graphite. In contrast, coated samples had a 4.82 wt% weight

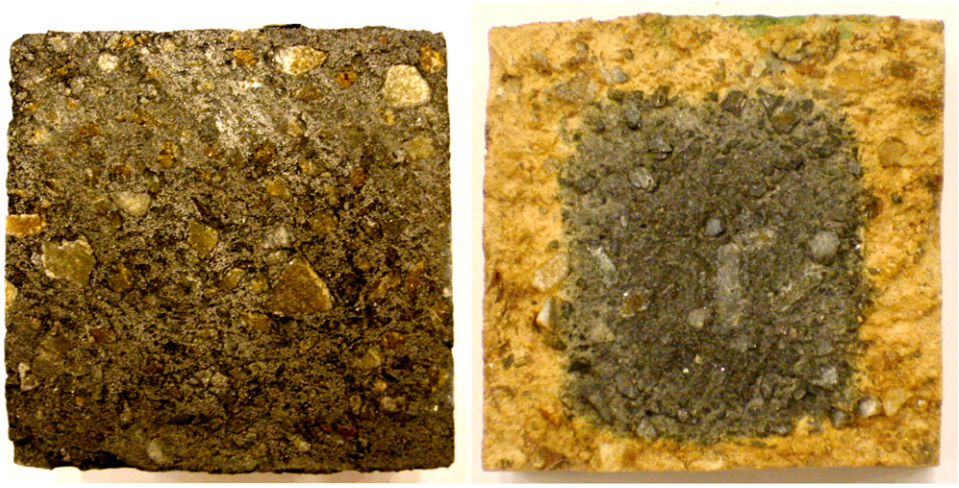


Fig. 3. Cross section view of the coated (a) and uncoated (b) samples after oxidation testing at 1200 °C for 10 h in air.

Table 2
Oxidation properties of samples after oxidation test after 5 and 10 h temperature holds at 1200 °C.

| | Coated | | Uncoated | |
|---|---|---|---|---|
| Pre heating time (h) | 5 | 10 | 5 | 10 |
| Weight loss (%) | 3.38 | 4.82 | 8.51 | 10.54 |
| Oxidation loss (g) | 23.47 | 31.64 | 60.17 | 70.65 |
| Oxidation index (%) | – | – | 39.30 | 54.62 |

loss after testing for 10 h. The applied frit coating was about 2.64 wt% of the original sample weight, so the weight loss in testing of coated samples due to the frit and resin was about 3 wt% of the original sample weight.

The cross section morphology of a coated brick oxidized at 1200 °C for 10 h was studied using SEM-BSE analysis, with the image shown in Fig. 4. The coating layer is observed to be a dense and continuous structure. The starting coating thickness applied was about 0.8 mm, which melted, forming a layer of about 110 μm in thickness. The coating and substrate have good bonding with no spalling during thermal cycling. Note, however, that some micro-cracks and pinholes in the coating exist, which might have occurred during cooling of the sample. The coating was not observed to have deeply penetrated into the brick microstructure. The thin frit coating and lack of penetration is also an advantage for refractory brick because it can be easily removed from the surface of refractory during the first charge of molten steel, resulting in minimal impact on the refractory material.

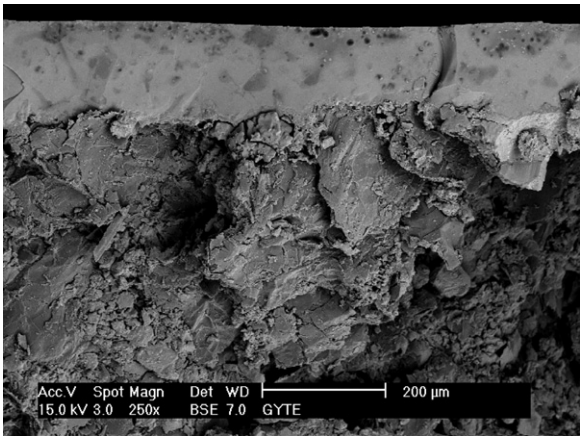


Fig. 4. SEM-BSE photographs of cross section of fractured surface of coated MgO–C brick sample oxidized at 1200 °C for 10 h in air.

Fig. 5. Photograph of frit coated MgO–C brick of working lining in steel ladle after brick installation but before use.

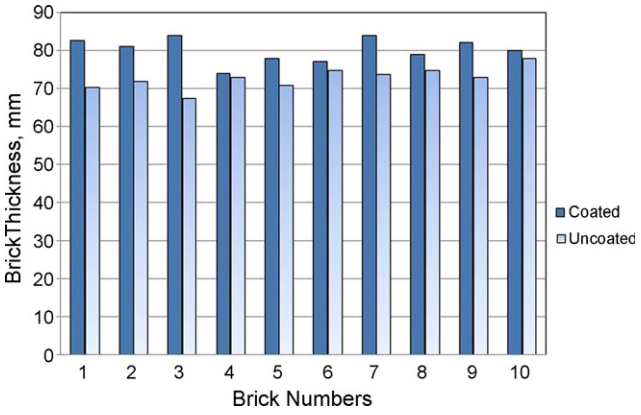


Fig. 6. MgO–C brick thickness changes of coated and uncoated materials after 96 heats in a steel ladle.

## 4. Industrial test

The results obtained during laboratory testing were the basis for an industrial test of both coated and uncoated bricks in steel ladle. Half the surface of the working line of the ladle was coated by brushing, with the other half remaining uncoated. The steel ladles were preheated and used under industrial conditions. The performances of working linings were monitored for 96 heats. Fig. 5 shows a photograph of the working lining of the steel ladle section containing coated material before use.

After 96 heats of service, the coated and uncoated bricks were removed from the ladle and the brick thickness was measured. Fig. 6 shows the change in thickness, where it is noted that the thickness of coated brick was greater than that of uncoated bricks. The average thickness of coated samples was about 80.15 mm, with a standard deviation of 2.25. In contrast, the average thickness of uncoated sample is about 72.9 mm, with a standard deviation of 2.29. The average thickness difference between coated and uncoated bricks for 10 bricks is 7.25 mm. Wear rates are calculated from the basis of original size and final size of brick. The wear rate for coated bricks was 63.1% of original brick size, while the uncoated brick was 69.02%. The coating has an advantage of 5.92% in brick thickness, which would result in a performance advantage.

## 5. Conclusions

The results of laboratory and industrial tests confirm the possibility of obtaining an increase in service life of resin bonded refractory bricks protected with a ceramic frit coating. The brick coating was composed of boron glass, zircon and alumina; and was found to improve the oxidation resistance of resin bonded magnesia carbon brick during pre-heating in a steel ladle application. It is necessary to continue industrial test

for the investigation of the variations of existing metallurgical conditions.

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