

CVD Carbon Infiltration of a Magnesite Refractory

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It is well established that the presence of carbon in the matrix of magnesite refractories increases their life in basic oxygen steel-making applications.¹⁻⁴ The presence of carbon reduces penetration of silicate slag into the refractory matrix; however, the precise mechanism by which this occurs remains controversial. Mechanisms suggested include: carbon presenting a nonwetting interface to the slag;³ CO flowing towards the hot face retarding slag penetration;⁵ and formation of a dense zone of magnesia immediately behind the hot face.⁶ There is also speculation that this dense zone may contribute to a reduction of spalling loss. Irrespective of the specific slag resistance mechanism, carbon is a vital component in these BOF refractories, one that significantly affects their final structure, properties and performance.

Introduction of the carbon component into magnesite refractories for BOF applications is accomplished by two different techniques. One is to pitch impregnate pressed and fired bricks; normally processed magnesite refractories are evacuated, then submerged in a fluid molten pitch, which is subsequently pressurized to force the molten pitch into the pores of the refractory. In service, the carbonaceous pitch pyrolytically decomposes to leave a carbon residue in the pores of the refractory. Unfortunately, 40-60% of the pitch is lost as volatile decomposition products so that only 2-3% carbon remains in the refractory.⁷

The other process is to use a pitch or pitch/carbon mixture to actually bond the refractory grain. In this manufacturing technique, the refractory grain is mixed with the carbonaceous pitch and pressed into refractory shapes. Forming characteristics of the pitch/grain mixture limit the pitch component to $\approx 6-7\%$ so that the coked refractory contains only $\approx 4-5\%$ carbon after loss of volatiles.⁸ Another method with interesting potential as a technique for the introduction of carbon into these refractories is the chemical vapor deposition (CVD) of hydrocarbons.

Cracking of hydrocarbons has been used to infiltrate porous graphites⁹ and cellulose carbons¹⁰ with a pyrolytic carbon deposit, yielding substantially improved physical properties. This paper describes the application of CVD to the infiltration of a magnesite refractory and some of the resulting microstructural, chemical and physical property improvements. Some potential advantages of the method are discussed.

Experimental Procedure

The process of producing CVD carbon coatings or infiltrations by the CVD of carbon from a hydrocarbon gas has been reviewed in detail by Kotlensky.¹¹ In its simplest form, a hydrocarbon gas is introduced into an elevated temperature chamber containing the substrate which is to receive the pyrocarbon deposit. The gas decomposes, yielding a pyrocarbon deposit on the substrate and gaseous products including hydrogen. The actual mechanisms by which hydrocarbons decompose on surfaces into pyrocarbon and gaseous products are quite complex and remain controversial.¹²

In this study, a commercial magnesite refractory of the type used in BOF applications was obtained in the unimpregnated state. It was

The infiltration of a magnesite refractory with pyrocarbon from the chemical vapor deposition of propylene is reported. The unique microstructural, chemical and physical properties are discussed and the slag resistance compared with pitch-impregnated brick. Additional potential benefits are suggested.

diamond sawed into suitable specimens (bars $1/2$ by $1/2$ by 2 in.) for all of the observations except the slag resistance test which used specimens $1 3/4$ by $1 3/4$ by 4 in. This latter specimen size was the largest which the available infiltration equipment could accommodate. No attempt was made to establish optimum conditions for the carbon deposition; instead parameters used for another experiment¹⁰ were given minor adjustments to yield a satisfactory carbon deposit. With the exception of infiltration of three samples at 670°C, all specimens were infiltrated at 750°C using a mixture of 50% propylene-50% helium, at one atmosphere pressure and a flow rate of 0.8 ft³/h through a 3-in. diameter tube. At these particular conditions, carbon deposition can proceed for ≈ 24 h before noticeable surface deposition occurs. Increased temperatures or propylene concentrations lead to increased surface deposition and the formation of a dense surface layer which blocks infiltration of the pores.

It should be noted that nothing is special regarding the propylene/helium/750°C conditions; in theory, any hydrocarbon gas and any inert carrier gas can be used. However, it is necessary to adjust the gas ratios, flow rates and temperatures to accommodate the particular hydrocarbon cracking process. Different substrates (e.g., alumina vs magnesia) may require different conditions for successful deposition.

In addition to microstructural observations, other physical and chemical tests were performed. Apparent densities were determined from the weight and dimensions of the specimens. Open porosity was determined by the helium displacement technique and the surface area by nitrogen absorption at 77°K, BET method. Strengths were measured in 3-point bending over a $1 1/2$ -in. span using a commercial testing machine.* Carbon analyses and mercury porosimetry measurements were performed in an industrial laboratory,[†] as was the pellet-type slag test[‡] conducted at 1620°C using a CaO:SiO₂ = 1 and 30% Fe₂O₃, added as 70% wollastonite and 30% mill scale. Three pounds of slag were added as 70-g pellets at 4-6 min intervals. A pitch-impregnated magnesite was run simultaneously for a direct slag resistance comparison.

Results and Discussion

Under the previously described conditions, carbon was readily deposited throughout the magnesia refractory. Figure 1 illustrates the microstructural nature of the deposition and contrasts it with a conventional pitch-impregnated refractory (coked). Whereas the conventional pitch-impregnated refractory contains isolated carbon particles in the large pores, the CVD infiltrated carbon occurs as a uniform internal surface layer, coating the grains throughout the structure.

The mode of CVD carbon appears to be one that deposits a layer of pyrocarbon which gradually builds until the pore is blocked off or the channel leading to the internal surface is closed. Although relatively uniform deposition occurs, even throughout the $1 3/4$ -in. samples, there appears to be slightly greater buildup near the surface, particularly for long deposition times (> 16 h). This surface deposition could be reduced and probably even eliminated by further optimization of deposition parameters.

Another microstructural feature is the carbon coating of many of the very fine pores within the refractory grains (Fig. 2). This rarely occurs in pitch-impregnated refractories, where the pitch is restricted from the very fine pores by viscosity-flow considerations. This unique microstructural distribution of carbon is a consequence of the CVD method and the ability of the relatively small precursor molecules to reach fine pores.

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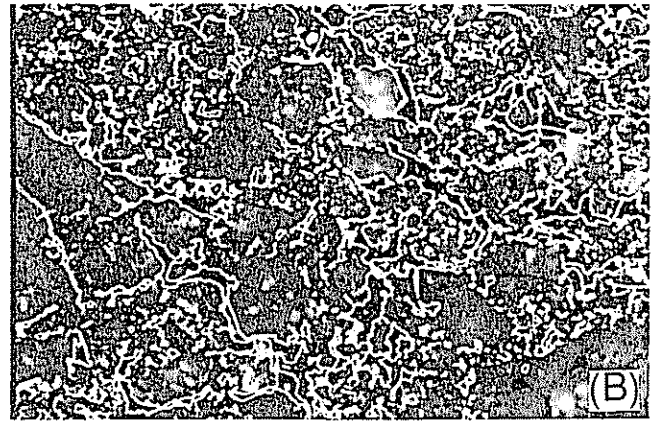
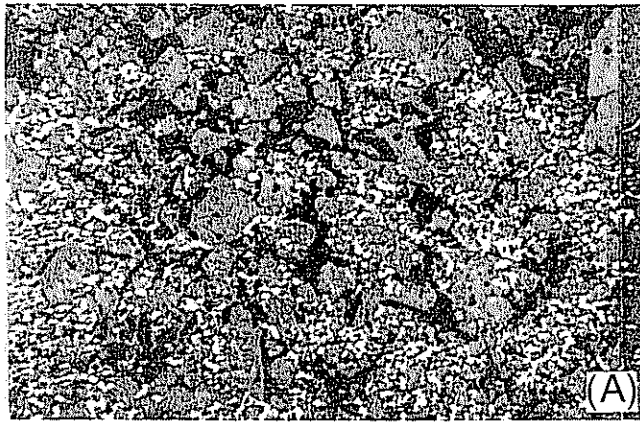


Fig. 1. Comparison of (A) pitch-impregnated and coked BOF magnesite refractory and (B) CVD carbon infiltrated brick. Carbon (white) is distinctly located in large pores of the former, but coats all internal surfaces in CVD method. (Reflected light, X70.)

Herron¹³ has observed a similar microstructural form of pyrocarbon to occur in some silica brick which have been used in coke oven linings. Presumably the volatiles from the coal contain sufficient hydrocarbons to yield pyrocarbon deposits at those portions of the refractory lining conducive to cracking and deposition within the silica brick.

Structurally, CVD carbon differs from pitch carbon, as the globules of carbon and crystallites from the coked pitch are randomly oriented. By contrast, carbon deposited from the cracking of hydrocarbons is highly oriented as the hexagonal crystal structure grows from the substrate surface in a [0001] orientation, thus exposing primarily the basal plane, (0001).¹⁴ This orientation may be chemically preferable because the basal plane of carbon crystallites is much more resistant to oxidation than are the prismatic surfaces at basal plane edges.¹⁵

Several chemical and physical characteristics of the CVD carbon-infiltrated magnesite are listed in Table I. As the deposition time increases, increased carbon content raises the density of the refractory. Carbon deposition decreases porosity open to helium at room temperature and internal surface area available to N₂ at 77°K by filling and blocking off internal pores. The inverse correlation of carbon content and open porosity suggests that for these deposition parameters, a maximum of between 7–8% carbon can be introduced into these magnesite bricks. This compares favorably with the 2–3% carbon in pitch-impregnated brick and 4–5% carbon in tar-bonded brick.

One reason for increased carbon content is the lack of volatiles associated with a CVD carbon deposit. By contrast, use of a pitch or tar yields only 40–60% carbon after pyrolysis;⁷ thus, approximately half of the precursor is lost. Another reason for increased carbon content when using the CVD process is the filling of the finer pores.



Fig. 2. Deposition of CVD carbon within very fine pores of a large grain. Similar pores never contain carbon in pitch-impregnated brick. (Reflected light, X114.)

Table I. Characteristics of CVD-Carbon-Infiltrated Magnesite

Time of infil. at 750°C (h)	Density (g/cm ³)	Open porosity (%)	Surf. area (m ² /g)	Volatiles (%)	Carbon (%)
as received	2.83	14.5	6.86		
6	2.86	10.1	2.06	0.05	3.16
11	2.90	7.3		0.05	4.31
18	3.01	3.0	1.82	0.06	5.67
20	3.03	1.6	1.19	0.06	6.69
24*				0.06	6.91

*Some surface deposition occurred in 24-h specimens.

Mercury porosimetry data (Table II) substantiate that about half the pores are filled after 11 h and there is some porosity remaining unfilled after 20 h. The slightly greater unfilled porosity, as measured by the mercury method as opposed to helium displacement, is to be expected; elevated pressures of the porosimetry technique can break open some closed pores inaccessible to the helium.

Effect of CVD carbon infiltrations on the room temperature modulus of rupture (transverse bend strength) is illustrated in Fig. 3. Strength increases linearly with CVD carbon content so that the strength is nearly tripled after a 20-h infiltration or ≈ 7% carbon weight gain. This strength behavior is typical for the filling of pores of a brittle material and has been observed for molded graphite,⁹ cellulose carbon,¹⁰ cement¹⁶ and ceramic tile bodies.¹⁷ Also of interest is the strength decrease after 24 h when there has been substantial surface deposition (carbon buildup) on the specimen surface. Apparently excessive surface deposition creates surface flaws detrimental to strength.

The slag test performed on these refractories was the Bethlehem pellet-type test.¹⁸ Two specimens each of the CVD brick and a standard pitch-impregnated brick were tested side by side. The CVD brick had 4.4% carbon and the coked pitch-impregnated

Table II. Pore Size Distribution as Determined by Mercury Porosimeter

Pore diameter (μm)	Cumulative pore volume (cm ³ /g)		
	No CVD-C (as-received)	11 h at 750°C	20 h at 750°C
80	0.0006		
50	0.0039		
30	0.0113	0.0118	
10	0.0212	0.0119	0.0057
8	0.0255	0.0160	0.0068
4	0.0302	0.0191	0.0077
1	0.0392	0.0214	0.0078
0.5	0.0396	0.0214	0.0078
0.2	0.0396	0.0214	0.0078
0.1	0.0396	0.0214	0.0078
0.04	0.0396	0.0214	0.0078



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specimens typically 2-3%. The percentages of corrosion for the two CVD specimens were 55.6 and 60.6% (58.1% average) compared to 66.3 and 74.7% (70.5% average) for the standard BOF brick (Fig. 4). This is a significant improvement in corrosion resistance, but it is difficult to assess the contributions of the CVD carbon because of the different carbon levels; the higher carbon content may also have provided increased slag resistance. Perhaps more significant are the very thin oxidized zone and reduced slag penetration ($\approx 1/5$ of that in the pitch-impregnated specimens) revealed by microscopic examination. These improvements appear particularly beneficial in terms of Barthel's proposed step-wise process of slag attack.¹⁰ Results indicate that CVD carbon-infiltrated refractories promise considerable increased slag resistance, although it has not been clearly established whether the mechanism is the carbon microstructural distribution, carbon content, or a combination of both.

Summary

Carbon can be introduced into magnesite refractories by CVD methods, specifically the cracking of propylene. The technique yields a distinct microstructure consisting of a carbon film coating

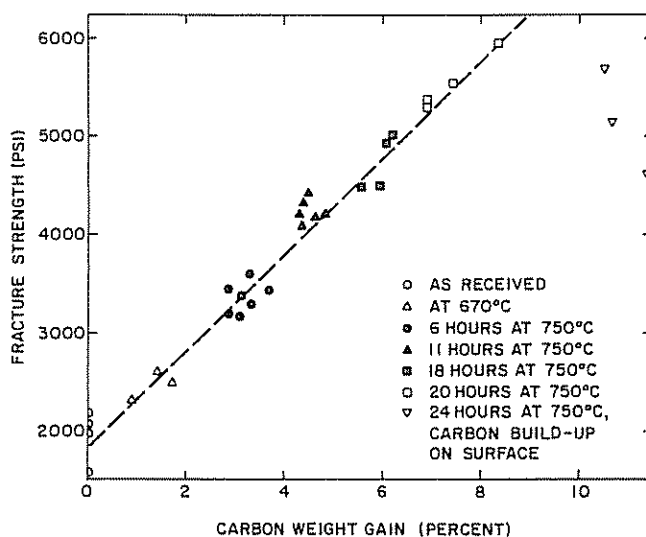


Fig. 3. Room temperature strength of CVD carbon infiltrated magnesite vs carbon content.

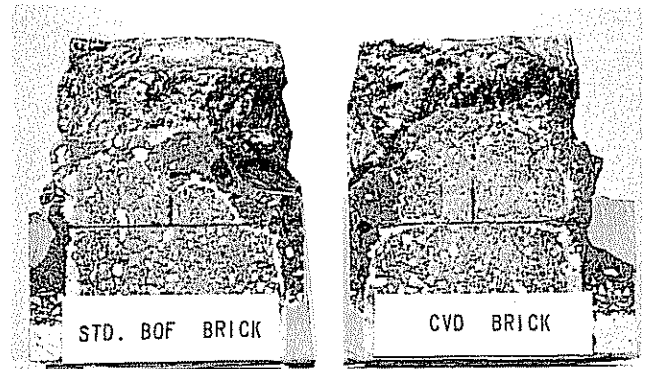


Fig. 4. Comparison of two pitch-impregnated and two CVD specimens from drip slag test. Actual specimens are above base refractory. Less of CVD carbon infiltrated refractory has corroded.

the refractory grain throughout the brick. The method permits greater carbon contents than are currently achieved by pitch impregnation or tar-bonding methods. Refractory strengths and slag resistance are improved.

However, one of the potentially most beneficial aspects has yet to be investigated. A direct result of the accessibility of the CVD method to very fine pores is the latitude of microstructural design which it permits the ceramic engineer. Whereas pitch-impregnated refractories must contain large pores that will accommodate the pitch, the use of a CVD carbon infiltration technique permits a much finer pore structure which could result in stronger refractories with substantially improved service performance.

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