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Effects of Graphite Content on the Oxidation Resistance of MgO-C Refractory Bricks

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The effects of graphite content on the density and oxidation behavior of MgO-C refractory samples were studied. The samples were formulated with various amounts of graphite and their oxidation behavior was investigated (in an isothermal condition); using a Thermo Gravimetric system (TG), in air and at temperatures ranging from 900°C to 1450°C. The preliminary results showed that the porosity and density of tempered samples were decreased when the graphite content was increased. However, after heating the samples at higher temperatures, the decreasing rate of porosity was lowered. At the beginning of the oxidation process, the rate of weight loss was high, but was gradually decreased when the thickness of the decarburized layer increased. The overall results indicated that although the higher graphite content increased the weight loss, it reduced the thickness of the oxidized layer.

INTRODUCTION

Recently, MgO-C refractories have been used widely in steel making furnaces, such as BOF and EAF, because of their high refractoriness and excellent thermal shock and corrosion resistances, which are resulted from high thermal conductivity, low thermal expansion and wetability of graphite and the high refractoriness of MgO [1]. In this regard, much work has been done, which is available in [2-5]. Despite these advantages, graphite's oxidation is one of the main problems in MgO-C refractories, which results in an increase of porosity and a decrease in the strength and corrosion resistances of refractory. Direct oxidation (reaction of graphite with O_2) is the main mechanism at temperatures lower than 1400°C. But, at higher temperatures, indirect oxidation (reaction of graphite with MgO) becomes the main mechanism [6-9].

The main goal of this research is to investigate the effects of graphite content (5 wt% to 20 wt%) on the density and direct oxidation behavior of MgO-C refractory samples.

EXPERIMENTAL PROCEDURE

The samples were prepared using Chinese sintered magnesia (with a purity of 97% and density of 3.5 g/cm^3) and Chinese natural graphite flakes (with an ash content of 5 wt% and density of 2.26 g/cm^3). Particle size distribution of the graphite is presented in Figure 1 [10]. After mixing the raw materials and pressing, the samples were tempered at 120°C or 240°C

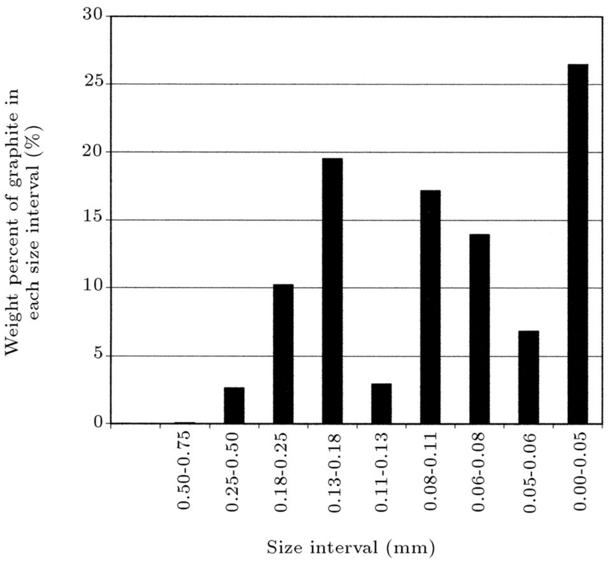

Figure 1. Particle size distribution of graphite powder.

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(depending on the resin type) for 18 h. Before oxidation tests, the samples were preheated at 600°C for 5 hrs in a coke bed, in order to remove the volatile species of resin. The bulk density and porosity of the samples were measured before and after preheating, according to ASTM C 329-88 (1999) standard.

Isothermal oxidation tests were carried out at various temperatures (900, 1100, 1300 and 1450°C) using a Thermo Gravimeter (TG) and the results were plotted as weight loss versus time. Figure 2 shows the experimental apparatus used for the oxidation test. The details of the test have been explained in [10].

RESULTS AND DISCUSSION

The effects of graphite content on porosity and density have been shown in Figures 3 and 4, respectively. An increase in graphite content improves the compaction during pressing and, therefore, decreases the porosity. The bulk density decreases, due to a lower density of graphite, in comparison with magnesia. These results are in good agreement with the results of others, such as Lubbaba et al. [2,3]. A lower rate of the decrease in the porosity of the preheated samples at 600°C must be due to the irreversible expansion of graphite during heating. More graphite content causes more irreversible expansion. This phenomenon can also explain the higher rate of decrease in the bulk density of the preheated samples at 600°C when the graphite content increases. Since all samples were preheated at 600°C before the oxidation test, the porosity and density of only preheated samples must be considered to discuss their oxidation behavior, while the compaction behavior of the samples can be understood by comparing the porosity changes in the tempered samples.

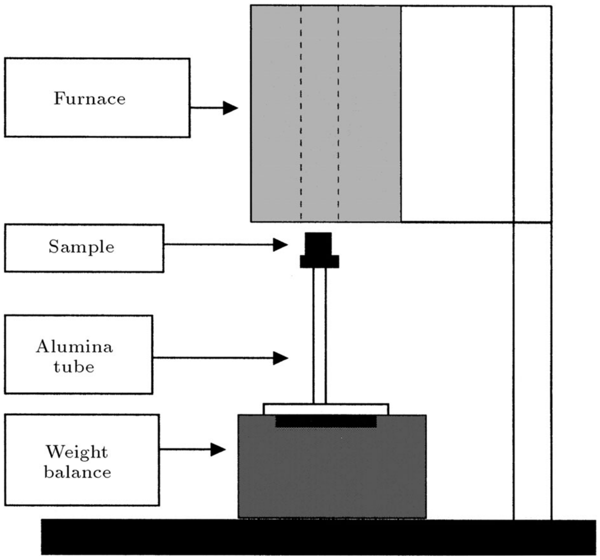


Figure 2. Schematic view of setup used for weight loss measurement.

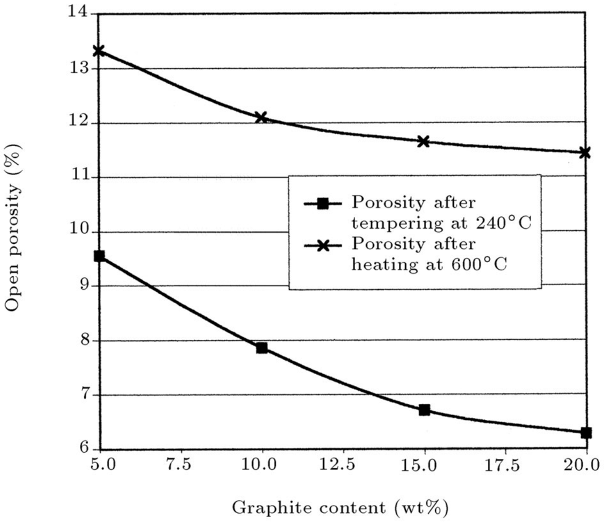


Figure 3. Changes of porosity versus graphite content.

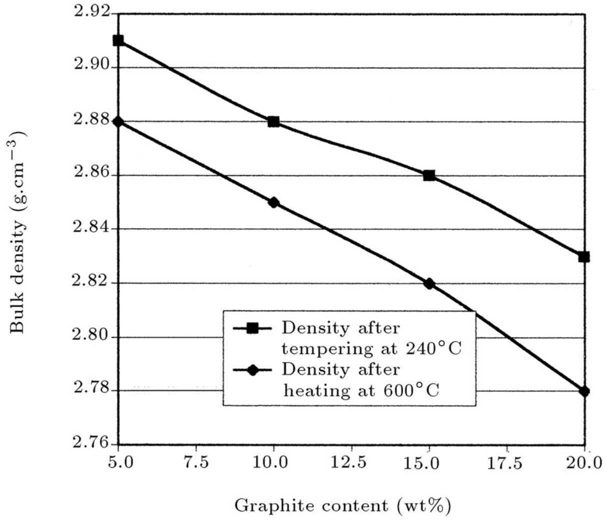


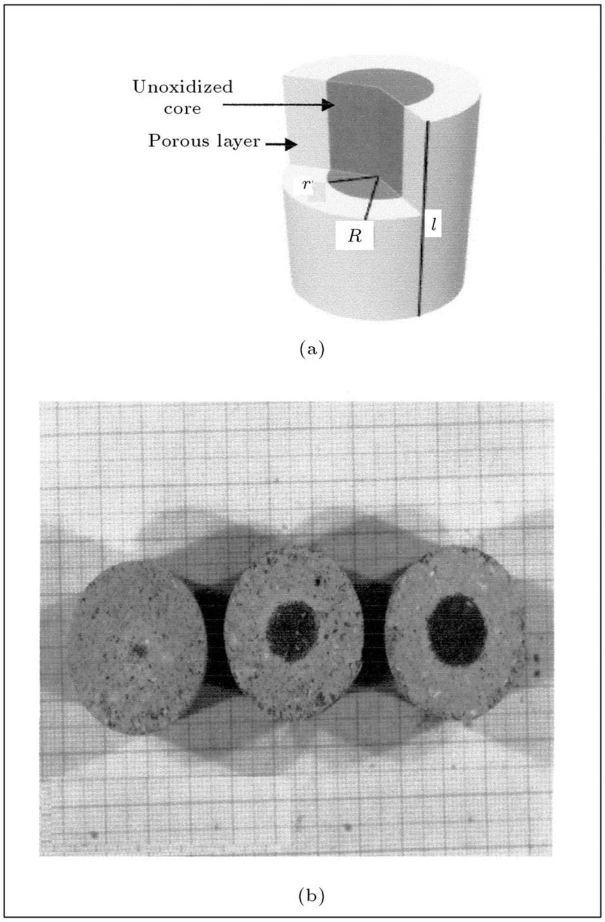
Figure 4. Changes of bulk density versus graphite content.

One of the most precise and comparable methods of presenting the oxidation behavior is based on the changes of oxidized layer thickness versus oxidation time. This method can be used by studying the cross section of each oxidized sample at various specified oxidation times and by the direct measurement of oxidized layer thickness. As shown in Figure 5, the oxidized and unoxidized regions are clearly separated with an interface, which moves inward as oxidation proceeds. Moreover, the thickness of the oxidized layer $(R-r)$ at each oxidation time can be mathematically calculated, according to TG experimental results and the following equations (referring to Figure 5a):

$$X = 1 - (r/R)^2,$$

or:

$$R - r = R[1 - (1 - X)^{0.5}]. \tag{1}$$



(a)

(b)

Figure 5. (a) Schematic view of oxidized sample; (b) Cross section of samples after oxidation at different temperatures.

In which, X is the fraction of weight loss (based on the initial graphite content) at each oxidation time, r is the radius of the unoxidized region at each oxidation time and R is the initial radius of the sample. Table 1 presents the direct measurement (experimental) and mathematical calculation results of the oxidized layer thickness at various given oxidation times. As these results show, the experimental and calculated results are almost the same.

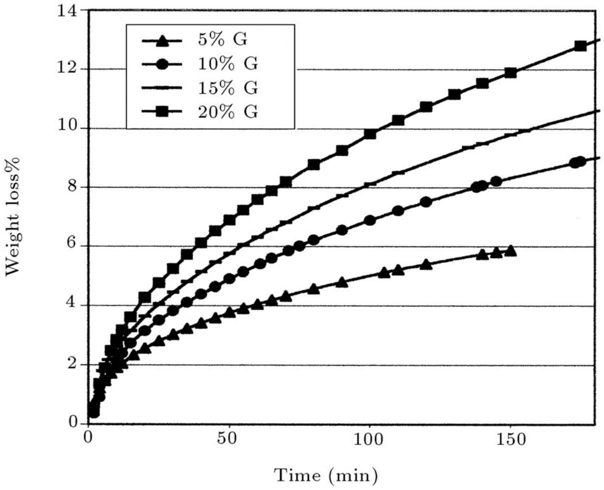


Figure 6. Weight changes of samples including various graphite contents versus oxidation time at 1100°C.

Oxidation test results of samples with various graphite content at 1100°C have been presented in Figure 6, as a percent of weight loss (based on the initial total weight of samples) versus time. As shown, at a given oxidation time, the weight loss increases when graphite content increases.

Considering the fact that the surface area of oxidation reaction interface decreases with oxidation time, the oxidation rate at each oxidation time was calculated based on weight loss per the surface area of reaction interface per time and presented in Figure 7. The surface area of the reaction interface at a given oxidation time was also calculated, based on the radius of the unreacted core in Equation 1. As Figure 7 shows, the rate of weight loss is high at the beginning, but decreases as the oxidation process goes on. In fact, in the early stage of oxidation, the overall oxidation rate is controlled by the chemical reaction rate on the surface of the sample. As oxidation proceeds, a porous

Table 1. Thickness of oxidized layer of some samples after oxidation tests.

Sample	**Percent of Graphite**	**Temperature of Test (°C)**	**Oxidation Time (min)**	**Calculated Oxidized Layer Thickness (mm)**	**Measured Oxidized Layer Thickness (mm)**	**Percent of Error**
1	20	1100	230	10.6	10.5	0.95
2	20	900	165	7.0	7.4	5.41
3	15	1100	70	5.2	5.0	4.0
4	15	900	90	5.3	5.1	3.92
5	10	1100	190	9.7	9.5	2.11
6	10	900	190	8.7	8.5	2.35
7	10	800	165	7.1	7.0	1.43

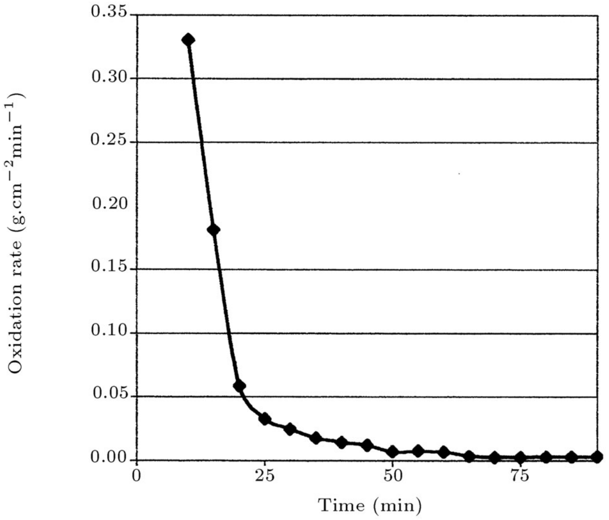


Figure 7. Oxidation rate (weight loss per reaction surface area per oxidation time) of sample, containing 15 wt% G, at 1100°C.

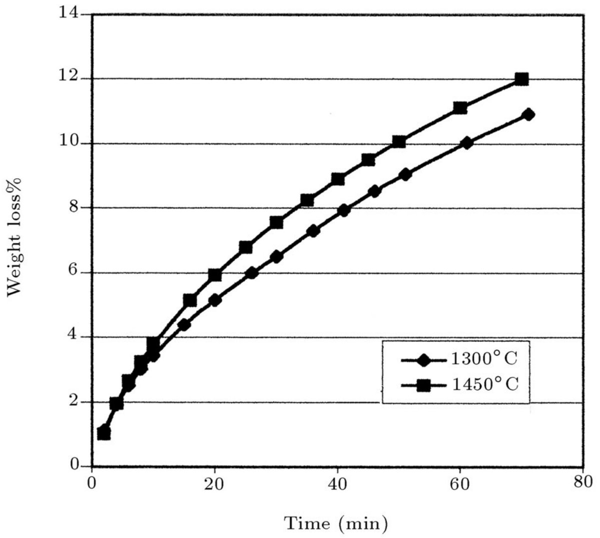


Figure 9. Weight loss of samples (15 wt% G) at 1300°C and 1450°C versus time.

oxidized layer gradually forms near the surface and the reaction interface moves inward. In this condition, gaseous oxygen must diffuse through this layer to reach the reaction interface. Therefore, the oxidation rate decreases.

The effect of temperature on the oxidation behavior of samples containing 10 wt% graphite is shown in Figure 8. As this figure shows, when the oxidation temperature rises, the oxidation rate increases, which is believed to be resulted from an increase in the chemical reaction rate constant (k_c) and the effective diffusion coefficient (D_e). The same procedure was also conducted at a higher temperature (i.e., 1450°C in Figure 9), demonstrating that the oxidation rate is still increasing. On the other hand, no dense layer has been formed or observed. Figure 8 also shows that the oxidation rate increases more rapidly at higher temperatures. The oxidation curves at 900°C and 1100°C are close to each other, but, both are far from the oxidation curve at 1300°C. Exponentially, the dependence of D_e and k_c to temperature can explain these results.

Figure 10 presents changes of oxidized layer thickness versus oxidation times at 1100°C for samples containing various graphite content. The oxidized layer thicknesses were calculated, based on Equation 1 and the experimental data in Figure 6, as mentioned above. As can be seen clearly, the thickness of the oxidized layer decreases when graphite content increases. It seems that this result is in contradiction to the previous results (in Figure 6). To explain these observations, it is necessary to consider both the effective diffusion coefficient (D_e), which mainly depends on the oxidized layer porosity, as well as the inward moving rate of

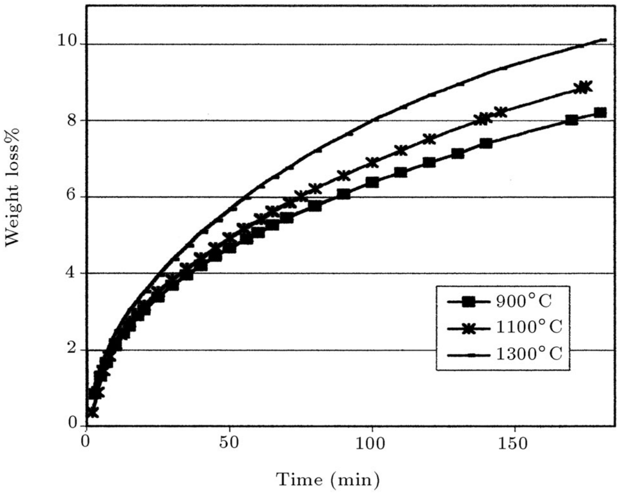


Figure 8. Weight loss of samples (10 wt%G) at various temperatures versus time.

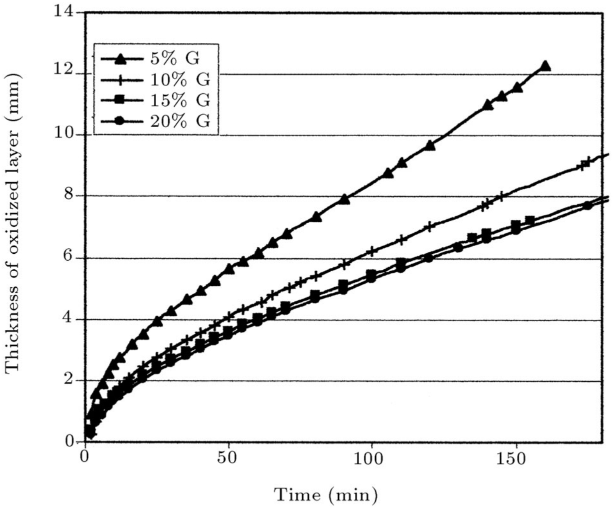


Figure 10. Changes of oxidized layer thickness of samples, including various graphite contents, at 1100°C.

the reaction interface, which mainly depends on the volume fraction of graphite in the sample. For the former consideration, D_e can be calculated according to the following equation [11], with the assumption that the oxidation is a diffusion control process [12,13]:

$$t = A[X + (1 - X)\ln(1 - X)],$$

$$A = (\rho_{mG}R^2/8\mathrm{C}_{\mathrm{O}_2}D_e). \tag{2}$$

In these equations, t is the oxidation time, X is fractional weight loss, ρ_{mG} is the molar density of graphite in the sample, R is the initial radius of the sample, $\mathrm{C}_{\mathrm{O}_2}$ is the concentration of O_2 near the surface of the sample and D_e is the effective diffusion coefficient through the oxidized layer.

In this regard, the value of the term $[X + (1 - X)\ln(1 - X)]$ was calculated at each oxidation time, according to the oxidation test results in Figure 6. Then, the constant parameter A and, consequently, D_e, were determined by adopting a linear regression method, based on Equation 2, on the obtained results (values of time versus values of $[X + (1 - X)\ln(1 - X)]$. Linear changes of $\ln(D_e)$ with $1/T$ in Figure 11 indicate the expected Arrhenious type relationship of the calculated diffusion coefficient with temperature. Figure 12 also shows the diffusion coefficient of samples containing various graphite content at 900 and 1300°C. The obtained D_e values in this work are close to the Li et al. results [14], but are half of the Faghihi et al. results [13]. According to these data, the diffusion coefficient increases when graphite content increases, which is due to an increase of porosity in the oxidized layer. This effect is partially retarded resulting from the decreasing effect of graphite content on the initial porosity of the samples (before oxidation), as mentioned in Figure 3.

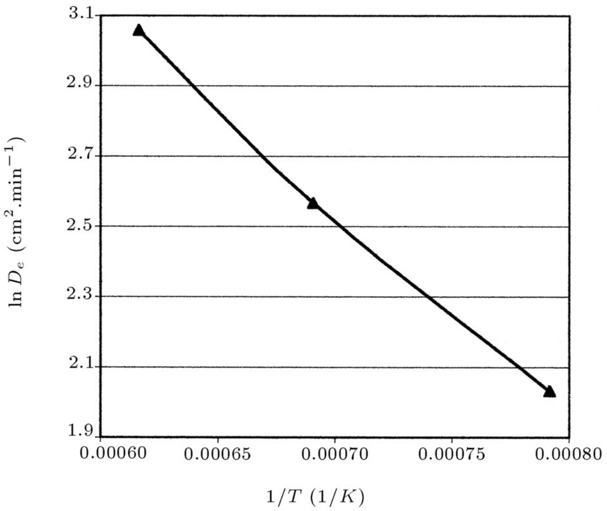


Figure 11. Arrhenious plot of D_e versus T for samples containing 10 wt% G.

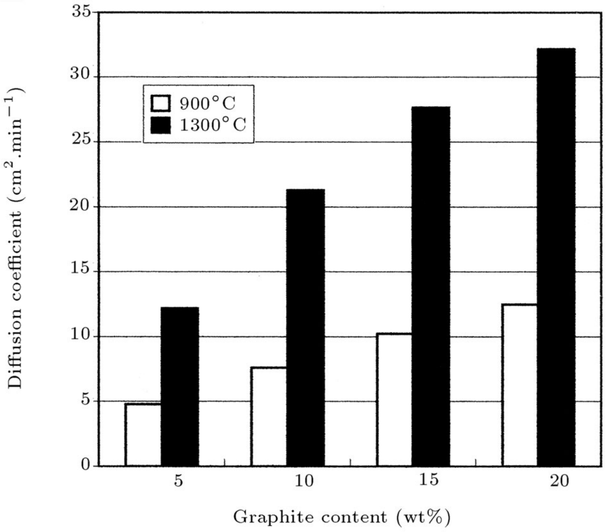


Figure 12. Diffusion coefficient changes versus graphite content.

To explain the contradictory results in Figures 6 and 10, the simultaneous effects of D_e and ρ_{mG} on oxidized layer thickness have been considered in the following equation, which was obtained by combining Equations 1 and 2:

$$t = A[1 - (r/R)^2 + 2(r/R)^2\ln(r/R)^2],$$

or:

$$t = Af(r). \tag{3}$$

For a given oxidized layer thickness $(R - r)$ or r, the oxidation time ratio of a sample containing X wt% graphite to the sample containing 5 wt% graphite can be presented by the following equation:

$$t_{X\%G}/t_{5\%G} = \Big[(\rho_{mG(X\%G)}/\rho_{mG(5\%G)}) / (D_{e(X\%G)}/D_{e(5\%G)})\Big]. \tag{4}$$

Variations of $(\rho_{mG(X\%G)}/\rho_{mG(5\%G)})$ and $(D_{e(X\%G)}/D_{e(5\%G)})$ versus graphite content $(X\%G)$ have been shown in Figure 13. As it apears, both ratios increase when graphite content increases. However, the increasing rate of the molar density ratio is higher than that of the effective diffusion coefficient ratio. Therefore, oxidation time ratio increases with an increase in graphite content. In other words, to form the same oxidized layer thickness, longer oxidation time is required for samples with higher graphite content. Although the thickness of the oxidized layer decreases with an increase in graphite content, its porosity increases. This may result in a degradation of strength and corrosion resistance. Therefore, optimum graphite content must be selected to meet the desired properties in the system.

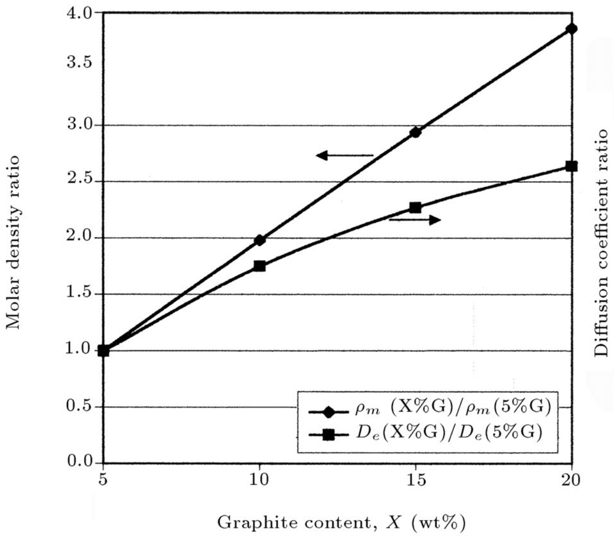


Figure 13. Changes of graphite molar density ratio and effective diffusion coefficient ratio at 1300°C versus graphite content.

CONCLUSION

In this research, the effects of graphite content on the oxidation behavior of MgO-C refractory samples were investigated.

An increase in graphite content improved compressibility during pressing and, therefore, decreased the porosity. However, this effect was retarded, due to the irreversible expansion of graphite at higher temperature.

In order to study the effect of graphite content on oxidation behavior, the changes of oxidized layer thickness were calculated, based on the weight change results in each TG test and proposed equations. With an increase in graphite content, the thickness of the oxidized layer decreased, even if the weight loss increased. These results were successfully explained by determining the changes of the effective diffusion coefficient, as well as the graphite molar density, with the changes of graphite content.

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