# The Effect of Carbon Nanoparticles and Calcined Alumina on Mechanical Properties and Corrosion Resistance Behavior of the Magnesia Carbon Refractories

*E. Karamian [1]*, M. Faghih [2], M. Parastegari [3] and A.Monshi [4]*

*[1,2,3,4] Advanced Materials Research Center, Faculty of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran*

## Abstract

Nowadays, magnesia carbon refractories are very important for the iron and steel industries. It is due to their unique properties, such as low wet ability with melt iron and steel. Therefore, it is important to extend the life of the refractory. In this research, the effect of calcined alumina and nano carbon on mechanical strength and corrosion resistance against slag in magnesia carbon refractories was studied. Mechanical strength of cold crushing strength, CCS, was measured. The bulk density, BD, and apparent porosity, AP, were determined, relative to the size and weight measured, using Archimedes method standard and corrosion resistance against the slag shrub procedure. Cylindrical 50×50 mm samples were tempered at 250 °C for 3 h. The corrosion resistance of the samples cocked at 1350 °C for 2 h under reducing atmosphere (coke bed) was evaluated. XRD and SEM-EDS analyses were used for characterizations. The results showed that the combination of calcined alumina, magnesia, graphite and nano carbon produced very high strength up to 50% and density up to 12.5%, as well as very good corrosion resistance. Especially, the samples containing alumina showed better corrosion resistance, as compared with other samples, due to spinel phase.

*Keywords:* MgO-C refractory, Alumina calcined, Nano carbon, Mechanical properties, Corrosion resistance against slag.

## 1. Introduction

Magnesia carbon refractories are one of the most widely used refractory materials in the iron and steel industry. They have many applications, especially the refractory slag line [1]. Carbon oxidation, corrosion and chemical mechanical agitation of the molten slag are among the disadvantages of these materials. In this study, mechanical properties and corrosion resistance of materials were improved significantly.

Magnesia carbon refractories could have strong phases such as $MgAl_2O_4$ spinel, $Mg_2SiO_4$ forsterite, and SiC phases. Magnesia and alumina could produce spinel phase. Silicon additives, as antioxidants in the body, can cause the SiC and forsterite phases [2, 3]. Nano carbon or carbon black additives could also reduce slag penetration into the refractory by increasing density and decreasing porosity. This leads to a significant increase of the corrosion resistance. Increased refractory lifetime of the iron and steel industry is of particular importance.

After 2006, much research has been done on MgO-C refractories. For example, the development of low carbon MgO-C refractories containing a fixed 0.9 wt% of nano carbon and 1–9 wt% of flake graphite has been studied. Addition of 3 wt% of flake graphite in combination with 0.9 wt% of nano carbon black was found to be optimum, resulting in better/comparable properties, in comparison to conventional MgO-C refractory [4, 5]. The $Al_2O_3$-SiC composite can be synthesized at 1873-1973 K under argon atmosphere, with pyrophyllite and natural graphite as the raw materials, and the particle sizes of the composite synthesized at 1973 K are mainly distributed as 1-2 μm. The slag penetration and corrosion resistance of the low-carbon MgO-C refractories can be remarkably improved by adding the synthesized $Al_2O_3$-SiC composite, and the oxidation resistance is also improved to some extent. The increase of the slag viscosity and the formation of MgAl2O4 can effectively inhibit the slag penetration and corrosion for the refractories [6].

The influence of in situ spinel formation on the microstructure and strength of the MgO–C refractories containing reactive alumina can be investigated as a

* *Corresponding author*
*Email: Ekaramian@pmt.iaun.ac.ir*
*Address: Advanced Materials Research Center, Faculty of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran*
*1. Assistant Professor*
*2. M.Sc.*
*3. M.Sc.*
*4. Professor*

function of coking temperature. The improvement of refractory properties has been found to be related to the in situ spinel formation in the matrix. The microstructural evolution of the matrix is also influenced by the spinel formation from reactive alumina and MgO fine grains [7].Therefore, it is important to extend the life of these refractories. In this research, the effect of calcined alumina and nano carbon on mechanical strength and corrosion resistance against slag in magnesia carbon refractories was studied.

## 1. Experimental Procedure

Table 1 shows the raw materials used in this study. Purity of the sintered magnesia and calcined alumina was 97% and 98%, respectively. Chemical composition of the convertor steel slag is shown in Table 2. They were obtained from Azar Refractories Company.

*Table 1. Formulation of the samples (All samples contained 8 wt. % liquid resin, 0.8 wt. % HMTA and 1 wt.% Al powder).*

| Sample Code | Magnesia 2.5-4 mm | Magnesia 1.25-2.5 mm | Magnesia 0.075-1.25 mm | Magnesia <0.075 mm | Silver Graphite | Nano Carbon | Alumina Clacined |
|---|---|---|---|---|---|---|---|
| MG | 20 % | 33% | 22% | 15% | 10% | --- | --- |
| MGA | 20 % | 33% | 22% | 15% | 10% | --- | 5% |
| MGC | 20 % | 33% | 22% | 15% | 5 % | 5% | --- |
| MGCA | 20 % | 33% | 22% | 15% | 5 % | 5 % | 5 % |

*Acronyms: M: Magnesia, G: Graphite, C: Nano carbon, A: Alumina calcined*

*Table 2. Chemical composition of Isfahan Steel Company convertor steel slag (wt.%).*

| $SiO_2$ | CaO | FeO | $Fe_{total}$ | $CaO/SiO_2$ |
|---|---|---|---|---|
| 10.8% | 57.2% | 12.1% | 14.6% | 5.3 |

Materials were mixed during the four steps shown in Table 3. All raw materials were mixed at room temperature by Hobart mixer machine.

*Table 3. Steps of raw materials mixing.*

| Steps | Mixing sequence | Mixing time |
|---|---|---|
| 1 | Coarse and medium magnesia | 1 min |
| 2 | Addition of silver graphite, Al powder, HMTA and nano carbon black | 3 min |
| 3 | Addition of liquid resin | 4 min |
| 4 | Addition of fine powder magnesia (Particles size less than 0.075 mm) | 5 min |

After mixing the raw materials, bricks were shaped under 700 MPa pressure by uniaxial hydraulic pressing. Samples were shaped as cylindrical (50 mm in diameter and 50 mm in height) and tempered at 250 °C for three hours. Properties such as bulk density, apparent porosity, and cold crushing strength of tempered samples were measured. To determine the apparent porosity, the tempered samples were placed in a special container. Then, the samples were placed under vacuum vessel by an electric motor immersed in oil. After a few minutes, the samples and their apparent porosity were measured by using the Archimedes law.

In this study, CCS was used to determine the mechanical properties of materials. There were three samples for evaluating each of the three parameters of density, apparent porosity and cold crushing strength of the tempered samples.

To determine corrosion resistance, a hole had to be made in the samples and they had to be filled with slag powder. After preparation, the samples were filled with slag in an alumina crucible and placed on a bed of coke. The samples were cooked at 1350 °C for 2 h and cooled at furnace. SEM-EDS and XRD were used to characterize the samples. Also, stereoscope was used for the initial viewing.

## 3. Results and Discussion

The mean value of the results is shown in the following figures. Fig. 1 shows the results of cold crushing strength of the samples.

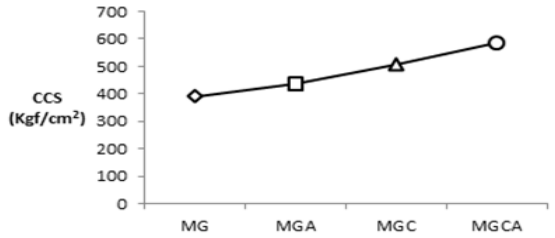



*Fig. 1. Cold crushing strength of the samples.*

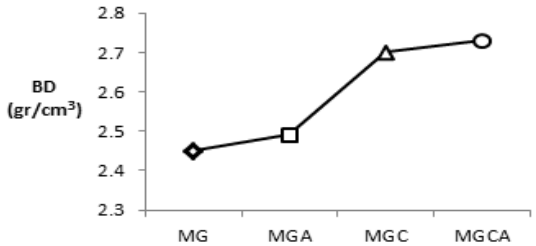



*Fig. 2. Density in different samples.*

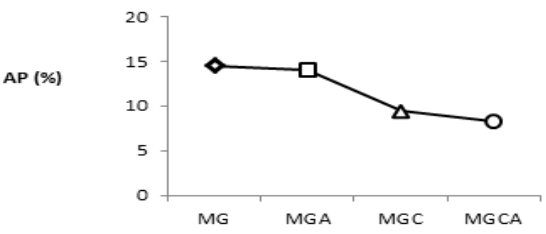



*Fig. 3. Apparent porosity of the samples.*

Cold crushing strength results showed that the addition of calcined alumina alone could increase the strength by 12%, while adding nano carbon alone could increase the strength by 25%. A very interesting result of this study was an increase of 50% of cold crushing strength due to the effect of adding calcined alumina and nano carbon.

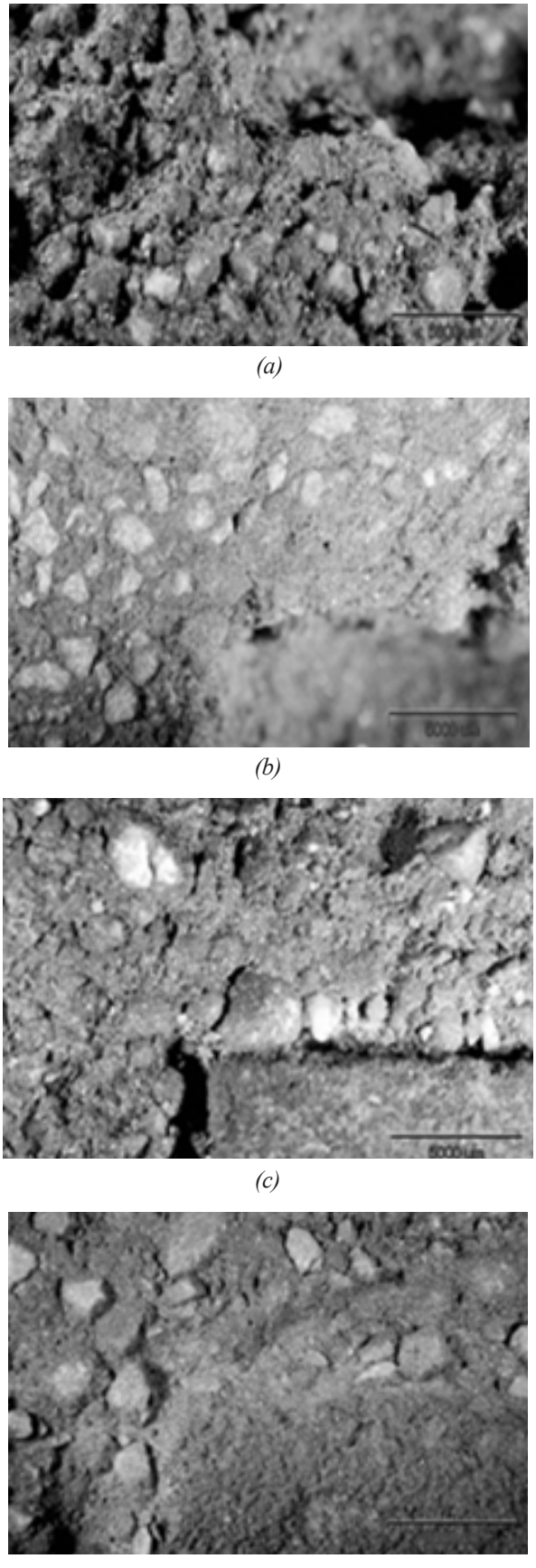
As can be seen, the density without additives had the lowest value. With the addition of 5% of calcined alumina, a slight increase in density was observed. But with the addition of 5% of calcined alumina and nano carbon, density was increased to 0.3 g/cm$^3$. In fact, density was increased up to 12.5%. The results of apparent porosity can be seen in Fig. 3. Obviously, the results were negatively correlated with the density results. As shown, apparent porosity was decreased up to 50%. Fine calcined alumina reduced porosity. However, reduced graphite particles and the rise of nano carbon could further compact the particles. Generally, both additives could improve the physical and mechanical properties and decrease porosity, while increasing density and cold crushing strength.

Fig. 4 shows the stereoscopic images of the cross section of the samples after slag resistance test. The inner hole surface of the MG sample was concaved after the test, whereas for the other samples, the inner hole surfaces were smooth. It means that additives could improve corrosion resistance.

We found an increase in corrosion resistance against slag by using additives. This was due to the presence of alumina and carbon in the refractories. The MG sample had the least corrosion resistance. The MGA sample had alumina, which increased the corrosion resistance. The main reason for the increased stability was the spinel phase. The MGC sample hads nano carbon, which could further compact the particles and increase bulk density. The MGCA sample had better corrosion resistance. The presence of both alumina and nano carbon in this sample could have contributed to an improved result.

Figs. 5 and 6 show the XRD patterns of the MGA and MGCA samples. The spinel phase appeared as an in situ form.

Figs 7, 8, and 9 show the microstructure of the MGC, MGA and MGCA samples. These micrographs show the remainder of calcined alumina and slag penetration. Based on EDS results in Fig. 7, chemical compound in A point was close to $MgAl_2O_4$ spinel phase. In fact, this, along with XRD pattern in Fig.5, confirmed the in situ formation of spinel-MA ($MgAl_2O_4$ spinel phase) in the MGA sample.



*(a)*

*(b)*

*(c)*

*(d)*

*Fig. 4. Stereoscopic image of the surface corrosion of the samples: (a) MG; (b) MGA; (c) MGC; (d) MGCA.*

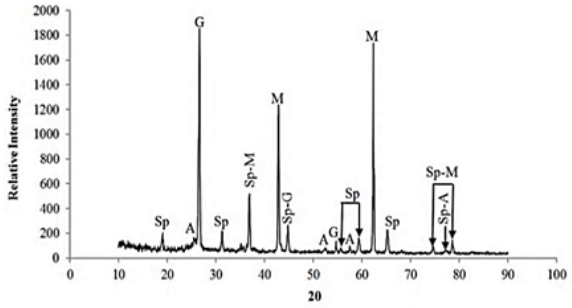



*Fig. 5. X-ray diagram of the MGA sample heated at 1350 °C.*

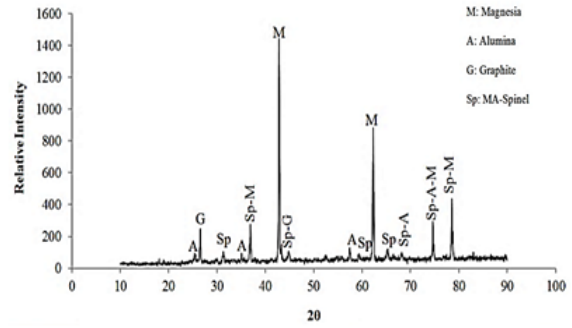
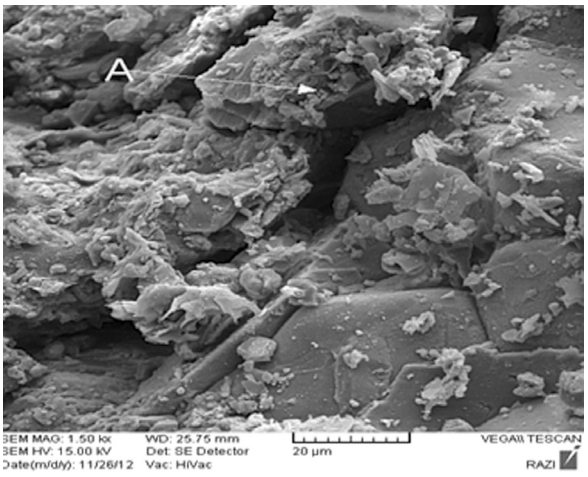



*Fig. 6. X-ray diagram of the MGCA sample heated at 1350 °C.*



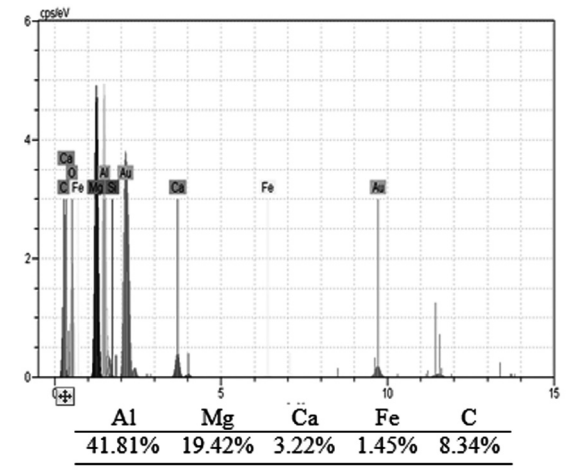




*Fig.7. SEM micrograph of the MGA sample at 1350 °C and EDS of A point observed.*

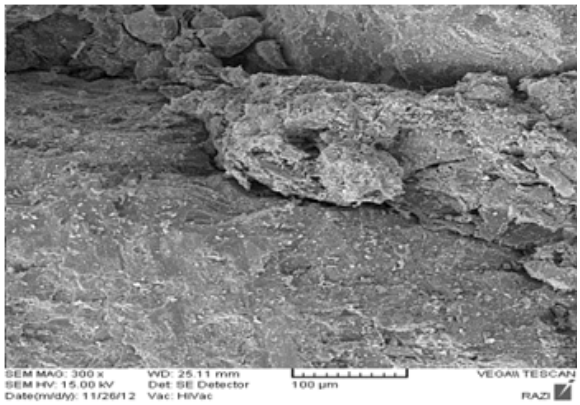
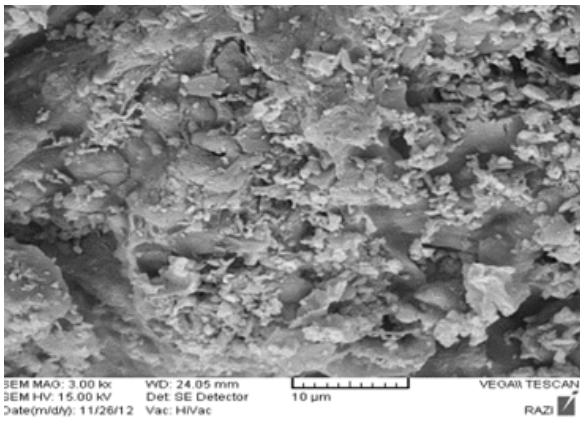
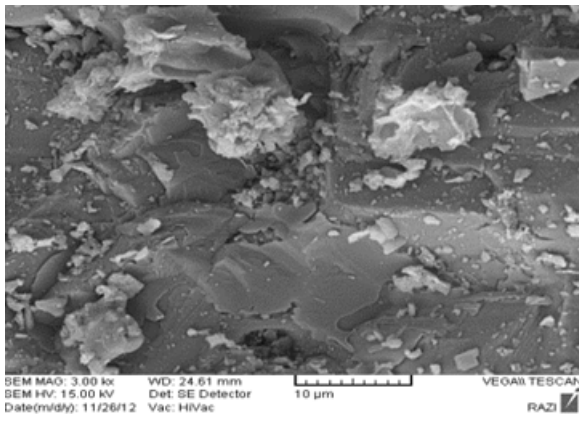



*Fig.8. SEM micrograph of the MGC sample at 1350 °C.*



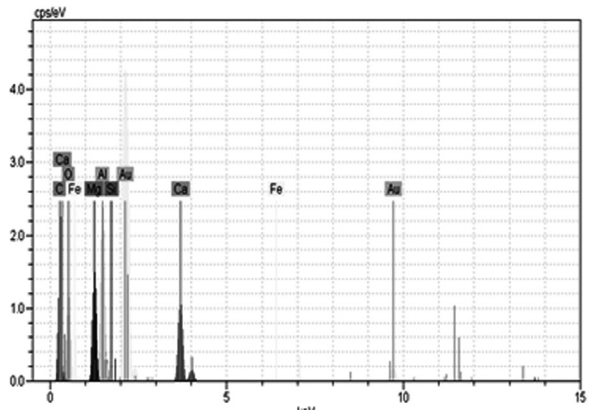




*Fig. 9. SEM micrographs of the MGCA sample at 1350 °C and EDS.*

## 4. Conclusions

• Nano carbon could increase density up to 12.5% and decrease the porosity of the body up to 50%, which ultimately increased the cold crushing strength up to 50%.
• Based on XRD patterns, spinel phase appeared as an in situ form in the samples containing alumina and alumina and nano carbon.
• Combination of calcined alumina, magnesia, graphite and nano carbon produced very high strength and good corrosion resistance.
• SEM micrographs showed high compaction in the sample containing both calcined alumina and nano carbon.
• Based on EDS results in Fig. 7, chemical compound in A point was close to $MgAl_2O_4$ spinel phase.

## References

[1] W. S. Resende, R. M. Stoll, S. M. Justus, R. M. Andrade, E. Longo, J. B. Baldo, E. R. Leite, C.A. Paskocimas, L. E. B. Soledade, J. E. Gomes, J. A. Varela: J. Eur. Ceram. Soc., 20(2000), 1419.
[2] S. Zhang, N. J. Marriott, W. E. Lee: J. Eur. Ceram. Soc.,21(2001), 1037.
[3] S. Zhang, W. E. Lee: J. Eur. Ceram. Soc., 21(2001), 2393.
[4] M. Bag, S. Adak, R. Sarkar: Ceram. Int., 38(2012), 4909.
[5] M. Bag, S. Adak, R. Sarkar: Ceram. Int., 38(2012), 2339.
[6] B. Ma, Q. Zhu, Y. Sun, J. Yu, Y. Li: J. Mater. Sci. Technol., 26(2010), 715.
[7] M. Bavand-Vandchali, F. Golestani-Fard, H. Sarpoolaky, H. R. Rezaie, C. G. Aneziris: J. Eur. Ceram. Soc., 28(2008), 563.