Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2339–2346

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Study on low carbon containing MgO-C refractory: Use of nano carbon

Mousom Bag [a], Sukumar Adak [b], Ritwik Sarkar [a,*]

[a] Department of Ceramic Engineering, National Institute of Technology, Rourkela, India
[b] TRL Krosaki Refractories Ltd., Belpahar, India

Received 19 September 2011; received in revised form 28 October 2011; accepted 31 October 2011
Available online 6 November 2011

Abstract

Development of nano carbon containing magnesia carbon refractories has been studied to reduce the total carbon content, thereby reducing the heat loss from the metallurgical process and producing more eco-friendly refractories. The carbon contamination from refractory to liquid metal will be minimized using low amount of nano carbon. Different percentages of nano carbon are used in combination with graphite as carbon source and the total carbon is maintained below the half of the total carbon of the conventional MgO-C refractories. The compositions were processed as per the conventional manufacturing techniques and the properties were evaluated and compared against the conventional refractory prepared under exactly similar conditions. Also elemental mapping of carbon was done to study the distribution of the nano carbon in the matrix.

Keywords: MgO-C refractories; Nano carbon; Properties

1. Introduction

Magnesia-carbon (MgO-C) refractories are widely used in basic oxygen furnaces, electric arc furnaces and steel ladles and these refractories contain about 12–18% total carbon. The primary source of carbon in magnesia-carbon refractories is graphite, which offers many advantages in refractory applications [1]. It has a high melting point and improves the corrosion resistance of the refractory, mainly due to its lower wettability by metal and slag. Thermal shock resistance of the refractory is also improved due to the low thermal expansion, high thermal conductivity and low modulus of elasticity promoted by the graphite addition. Due to these advantages initially there was a tendency to use more carbon in the brick to have better corrosion resistance and thermal shock resistance. But with the progress in technology and knowledge it has become clear that higher carbon content in the brick imparts several drawbacks too [2–4], such as:

1. Carbon has the inherent drawback of oxidation and gets oxidized during use in steel making process, associated with oxygen lancing, at high temperatures. Oxidized refractory has a highly porous structure with nearly no bonding and strength and easily penetrated and corroded by steel making slags. Use of antioxidants restricts and delays the oxidation of carbon, but it cannot be stopped totally.
2. Higher energy loss due to increased conductivity of refractory, causing higher energy consumption per unit of steel produced.
3. Increase in shell temperature leading to damage and deformation of the shell/metallurgical vessel.
4. Chances of carbon pick-up from refractory become high, where as steel making is basically a decarburization process and user industries are very stringent about the purity of steel.
5. Releases more amount of the carbon dioxide or carbon monoxide gases to the atmosphere.

Hence it is the demand of the day to produce magnesia carbon refractory with reduced carbon content to avoid all such drawbacks of the conventional carbon containing refractories. Research have already been started to develop a new kind of MgO-C refractory with low carbon content [2–4]. However, this may lead to decline in corrosion and thermal shock resistances of the refractory. A number of researchers [4–6] have obtained MgO-C compositions with excellent properties by adding nanometer sized particles, as additives or carbon which play a role by filling up the interior pores and gaps between the various particles. 1.5% nano carbon containing

* Corresponding author.
E-mail address: ritwiksarkar@rediffmail.com (R. Sarkar).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.10.086

MgO-C refractories showed [6] thermal spalling resistance equivalent to that of conventional refractories containing 18% graphite. Some other studies [7,8] on use of nano carbon in MgO-C refractories showed improved spalling resistance as nano carbon suppresses the sintering of MgO and gradual improvement in mechanical properties with the increasing amount of nano carbon. MgO-rimmed MgO-C bricks were produced [9] by applying nano structured matrix with less than 5% of carbon and found that thermal shock resistance and oxidation resistance of developed brick was remarkably superior rather than the conventional one whereas corrosion resistance was almost on a level. Nano-tech magnesia carbon bricks, utilizing the nano compound graphitized black (hybrid graphite black; HGB) having outstanding features like high thermal shock resistance, corrosion resistance, oxidation resistance were reported [10] to provide excellent durability in RH degassers. Addition of nano sized carbon black and hybrid graphite black in MgO-C brick resulted [11] improved spalling resistance due to the formation of a nano-structured matrix and excellent high-temperature oxidation resistance. MgO-C bricks containing both nano sized carbon black and flake graphite were found [12] to reduce the total carbon content with reduction in heat loss and thermal stress on the steel shell. Addition of nanometer carbon black was also reported [13] to improve the crushing and bending strengths before and after coking, oxidation resistance and thermal shock resistance of the low-carbon MgO-C composites.

In the present study effect of increasing amount of nano carbon on the properties of MgO-C refractory is studied keeping total carbon content below half of that of the conventional MgO-C refractories. Composition with optimum nano carbon addition is also compared with conventional composition processed under exactly similar conditions.

2. Materials and methods

Commercially available high purity fused magnesia (Chinese magnesite, supplied by Magus Marketing, India), natural flake graphite (Agarwal Graphite Industries, India) and nano carbon black (Birla carbon, India) were used as starting materials and the details of these are provided in Table 1. Pitch and resin were used as binder and the details of them are provided in Table 2. Aluminium metal powder (98% pure and finer than 100 μm) and boron carbide powder (95% pure, total boron = 77 wt%, total carbon = 21 wt% and finer than 150 μm) were used as additive in the system. Different compositions of MgO-C refractories were formulated by varying nano carbon content between 0 and 1.5 wt% with fixed graphite content of 3 wt%. Conventionally used MgO-C refractory (Batch TC) has also been prepared under similar conditions for comparison purpose and details of all the batches are provided in Table 3.

All the raw materials, additives and binders were thoroughly mixed in a pan mixer as per the batch composition and following the mixing sequences, as mentioned in Table 4, to obtain a homogeneous mixture. Mixed batches were aged for 2 h and compacted to brick shape of dimension 220 mm × 110 mm × 75 mm by uniaxial hydraulic pressing in a steel mould. Bricks were pressed at the maximum specific pressure of 200 MPa using hydraulic press (SACMI, Italy) with 12 strokes. Pressed shapes were then tempered at 200 °C for 12 h in a tempering kiln, which removes volatiles, polymerizes the organic binders and imparts strength to the shapes. Different physical, mechanical and thermo-mechanical properties of the tempered shapes were evaluated. An average of five different individual test results is represented here in different plots as data point and discussed in the results and discussion portion.

Apparent porosity (AP), bulk density (BD), and cold crushing strength (CCS) were measured as per the standard of IS: 1528, Part-8 (2002), IS: 1528, Part-12 (2002) and IS: 1528, Part-4 (2002) respectively. Hot modulus of rupture (HMOR) was determined by three-point bending test at 1400 °C in air with a soaking time of 30 min, conforming to ASTM C133-7, using 125 mm × 25 mm × 25 mm sized samples cut from the tempered shapes in a HMOR testing apparatus (Netzsch 422,

Table 1A
Physico-chemical properties of fused magnesia.

Oxide content (wt%)	
SiO_2	0.40
Al_2O_3	0.07
Fe_2O_3	0.50
TiO_2	Traces
CaO	1.40
MgO	97.35
Alkalis	0.50
Physical properties	
Bulk density	3.3 g/cm^3
Apparent porosity	3.8%
Crystal size (average)	800 μm

Table 1B
Physico-chemical properties of flake graphite and nano carbon black.

Raw materials	Flake graphite	Nano carbon black
Carbon (%)	94.1	98.03
Volatile matter (%)	0.80	1.42
Ash (%)	5.08	0.39
Surface area ($m^2\ g^{-1}$)	6.37	116.5

Table 2A
Physico-chemical properties of pitch powder.

Carbon (%)	52
Volatile material (%)	47
Ash (%)	1.4
Softening point (°C)	135

Table 2B
Physico-chemical properties of liquid resin.

Specific gravity at 25 °C	1.23
Viscosity (CPS) at 25 °C	8500–9000
FixedCarbon (%)	47.85
Non-volatile matter (%)	80.10
Moisture (%)	~4.0

Table 3
Batch composition.

Raw materials/batch	T-1	T-2	T-3	T-4	T-5	T-6	T-C
MgO (0–6 mm)	96	95.7	95.4	95.1	94.8	94.5	89
Flake graphite	3	3	3	3	3	3	10
Nano carbon	0	0.3	0.6	0.9	1.2	1.5	0
Al metal powder	0.5	0.5	0.5	0.5	0.5	0.5	0.5
B4C powder	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Liquid resin	2.75	2.75	2.75	2.75	2.75	2.75	2.75
Pitch powder	1	1	1	1	1	1	1

Germany). For oxidation resistance test, cylindrical samples (height = 50 mm, diameter = 50 mm) were cut from the tempered bricks and placed in an electrically heated furnace (heating rate of 5 °C/min) under ambient condition at 1250 °C for 5 h. Cooled samples were cut horizontally into two pieces and oxidation was measured diametrically by dimensional measurement using a vernier calipers. Slag corrosion test by static crucible method was done for all the different compositions using a shape of 75 mm cube, with a drilled hole of dimension 40 mm diameter and 40 mm height, at 1650 °C for 4 h using steel converter slag. The slag composition is provided in Table 5. Corroded samples were cut horizontally into two pieces and the sections were visually compared and corrode dimensions were used for comparison. Thermal shock resistance of the different batches was tested on cut samples of dimension 30 mm × 40 mm × 40 mm. These samples were heated in oxidizing atmosphere at 1400 °C for 10 min and then cooled in air for 10 min. The number of such heating and cooling cycles that a sample can withstand before any crack formation was noted as the spalling resistance. Samples were also studied for pore size distribution using mercury intrusion porosimeter (Micrometrics, US make) up to a intrusion pressure of 33 kpsi and distribution of carbon was checked by elemental mapping of carbon using a scanning electron microscope (model JSM 6480 LV JEOL, Japan).

Table 4
Mixing sequence of MgO-C bricks.

Steps	Mixing sequence	Mixing time (min)
1	Coarse and medium MgO	1.0
2	Addition of graphite, aluminium metal powder, pitch powder and nano carbon black	4.0
3	Addition of liquid resin	8.0
4	Addition of fine MgO powder	12.0

Table 5
Details of steel converter slag.

Oxide content (wt%)	
SiO_2	12.48
Al_2O_3	2.08
Total iron as Fe_2O_3	36.00
TiO_2	Traces
CaO	39.5
MgO	6.95
MnO	0.99
Basicity	~3.0

3. Results and discussion

Physico-chemical properties of the starting materials show (Table 1) that fused MgO is more than 97% pure with high CaO/SiO_2 ratio and large crystal size. Sources of carbon are also highly pure and nano carbon black used has a very high surface area, indicating the particles in nano meter size range.

3.1. Apparent porosity, bulk density and cold crushing strength

The change in AP with the increase in nano carbon content is shown in Fig. 1. Increasing nano carbon content reduces the AP value up to 0.9 wt% of nano carbon. This is due to increased filling of the inter-particle spaces of the refractory by much finer nano particles. Nano particles can disperse evenly in a better way among the tiny spaces between coarse, medium and fine magnesia particles thereby filling of interior pores and gaps (4–6, 14). But further increase in nano carbon content increases the AP value. The value of AP is even greater compared to the batch without nano carbon (T1). This may be due to excess amount of nano particles that do not enter into the inter-particle voids and remains as free. These very fine excess particles increase the porosity of the brick.

Bulk density values, plotted in Fig. 2 supports exactly the trend as observed for AP. The BD without the nano carbon is 3.06 g/cm^3, which increases with the increase in nano carbon content for better pore filling and reaches a value of 3.12 g/cm^3 for 0.9% nano carbon. Further increase in the nano carbon content does not result in further filling of the pore volume, but

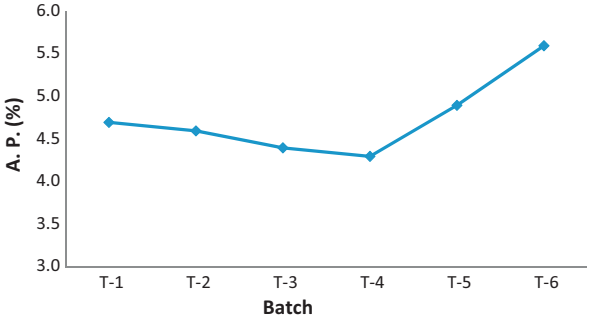

Fig. 1. Plot of apparent porosity with the variation of nano carbon contents.

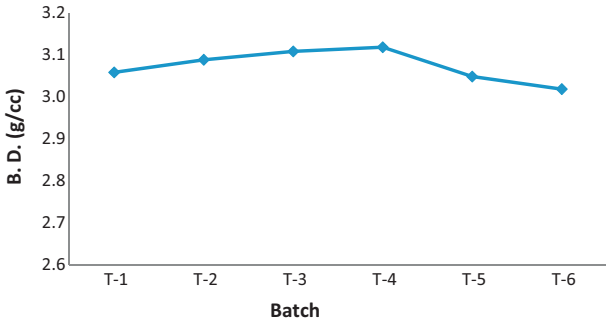

Fig. 2. Plot of bulk density with the variation of nano carbon contents.

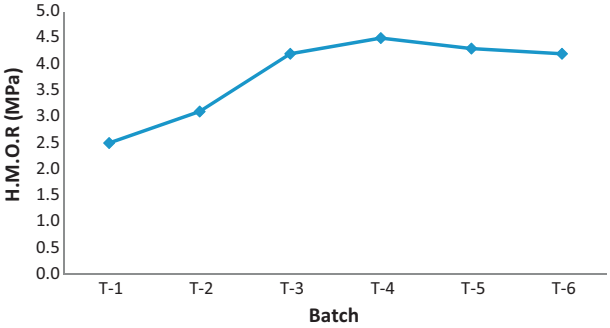

Fig. 4. Plot of hot modulus of rupture with the variation of nano carbon contents.

the bulk volume has increased due to the excess amount of finer particles present, thereby reducing he BD values.

The variation of CCS of the batches with the variation in nano carbon content is shown in Fig. 3. CCS increases with the nano carbon percentage, from 32 MPa for T-1 batch to more than 1.5 times greater value of 51 MPa for T-4 batch, containing 0.9% nano carbon. This is because of the increased filling of pores, resulting in an increase in compaction and densification and higher strength values. But further increase in nano carbon content resulted nearly the similar CCS values. This may be explained as pore filling is achieved nearly the optimum for 0.9% nano carbon and further increase in nano carbon does not affect the filling and also the strength behavior.

3.2. Hot modulus of rupture

Fig. 4 shows the variation of HMOR values among the different batches studied. HMOR values are found to increase with the nano carbon content from 2.5 MPa at zero nano carbon content to 4.5 MPa at 0.9 wt% and remain almost constant on further increase in nano carbon. With the increase of nano carbon content better filling as well as better compaction has occurred, resulting in a better strength. Again, nano carbon, being very reactive as carbon source, forms carbide on reaction with metal additives at a higher rate especially at the high temperatures. Carbide formation results better bonding and increased strength. Increasing amount of nano carbon increases the extent of carbide formation and accordingly the strength too. But above 0.9% nano carbon no further betterment is achieved. It may be associated with the increased oxidation of nano carbon when present at higher percentages, producing a porous structure and nullifying the beneficial effect of increased extent carbide formation.

3.3. Oxidation resistance

The oxidation resistance values of the batches are shown in Fig. 5. Increase of nano carbon in the batches shows an increase in the oxidation resistance (reduced extent of oxidation). Diameter-wise oxidation has been reduced from 25.56% for zero nano carbon containing composition to 21.82% for 0.9 wt% containing one. Nano carbon being very reactive in nature produces faster and greater extent of carbide on reaction with the metal additive. As carbides are having better oxidation resistance than free carbon and it coats the surfaces of the carbon particles, carbide formation increases the oxidation resistance. But above 0.9% nano carbon content oxidation increases, it may be associated with no further carbide formation (due to fixed amount of metal additive, 1 wt% Al powder) or higher oxidation for higher amount of nano carbon, as also observed in the case of HMOR.

3.4. Static slag corrosion

Fig. 6 shows the cross section of the refractory containing without and with nano carbon after slag corrosion test. Incorporation of nano carbon is observed to significantly inhibit the slag corrosion and penetration. The effect of carbon is more

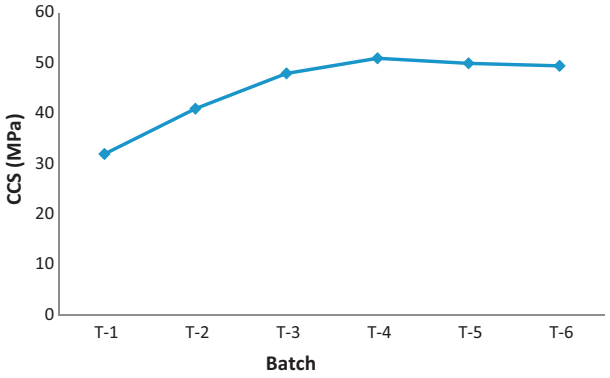

Fig. 3. Plot of cold crushing strength with the variation of nano carbon contents.

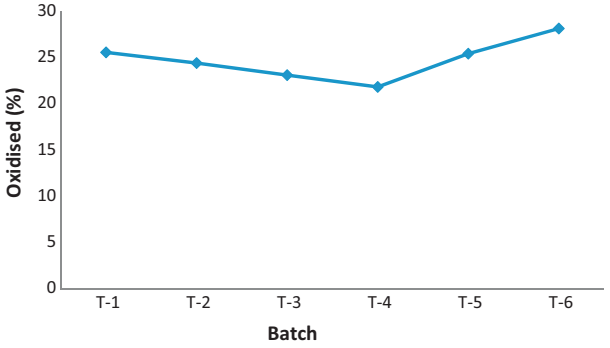

Fig. 5. Plot of oxidation resistance with the variation of nano carbon contents.

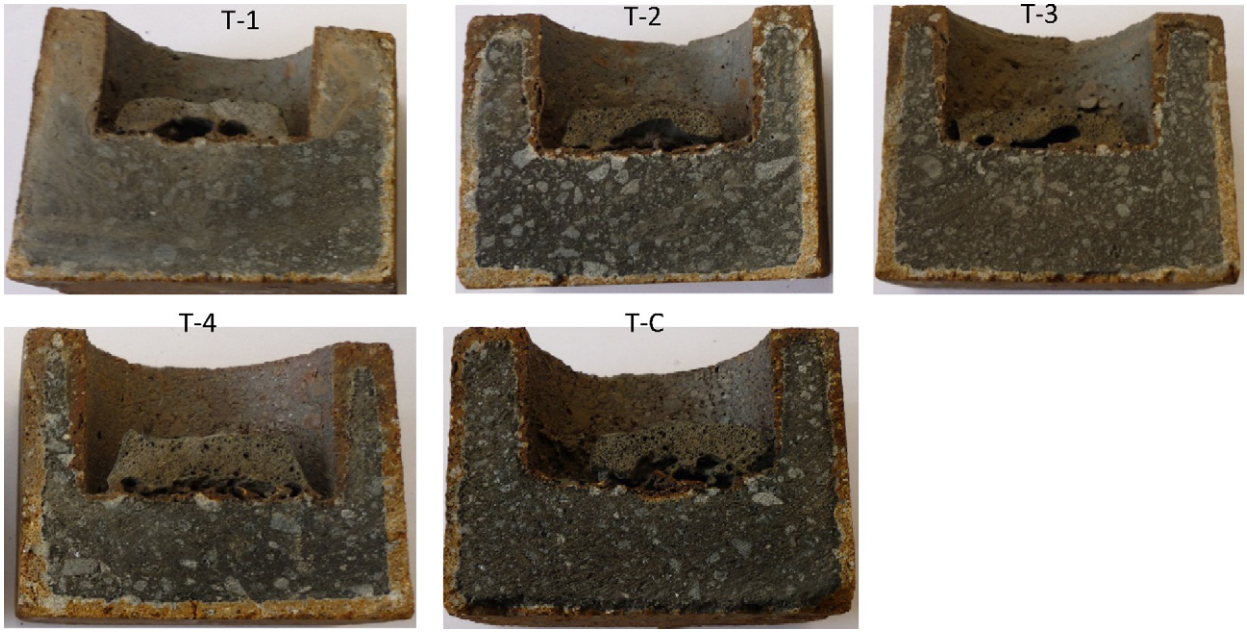

Fig. 6. Different corroded samples after cutting.

prominent when the particle size of carbon decreases to nano level as the reactivity, surface area and surface volume increases by many folds. Thus nano carbon prevents the corrosion of the matrix by forming a coating of carbon particles on the surface. Hence addition of nano carbon in MgO-C refractory exhibits better slag corrosion and penetration resistance, as also observed by Matsui et al. [10] and Ochiai [14] due to its high surface to volume ratio.

Fig. 7 shows the variation in penetration depth (mm) as a function of nano carbon content. Increase in nano carbon greatly reduces the penetration depth. Higher amount of nano carbon increases the distribution of carbon particles throughout the matrix and reduces the penetration depth of the slag. Nano carbon being very fine and very reactive imparts the beneficial characteristics of carbon to a great extent even at a very low amount and improves the corrosion and penetration resistances.

3.5. Thermal shock resistance

Thermal shock resistance, as number of cycles for different compositions is plotted in Fig. 8. Increase in nano carbon content greatly improves the distribution of carbon particles in the entire matrix due to much finer size (corresponding high surface area and high volume of nano carbon), results in a better thermal shock resistance. Nano materials not only absorb and relieve the stress due to thermal expansion and shrinkage of refractory particles but also reduce mal-distribution of thermal stress in the interior portion of refractories [6,14] thus improves thermal shock resistance. Also better dispersion of very fine nano carbon particles hinders the sintering of MgO particles and thereby reduces the modulus of elasticity and improves spalling resistance [7,8].

3.6. Distribution of carbon

Distribution of carbon was checked by elemental carbon mapping for different compositions as shown in Fig. 9A–D. 0.3 wt% nano carbon containing composition shows (Fig. 9A) relatively less uniform distribution of carbon particles in the carbon mapping plot. It is due to fewer amounts of nano carbon present in the composition. Increasing nano carbon to 0.6 wt% (T-3) showed (Fig. 9B) uniform distribution of carbon particles

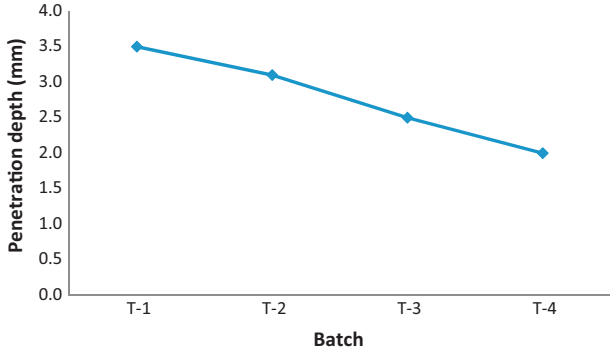

Fig. 7. Plot of penetration depth of different batches after slag corrosion test.

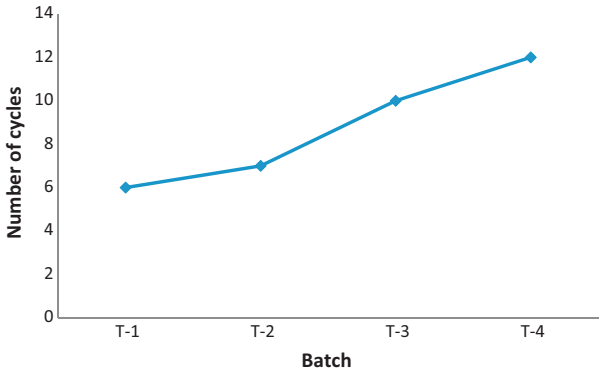

Fig. 8. Plot of thermal shock resistance of different batches.

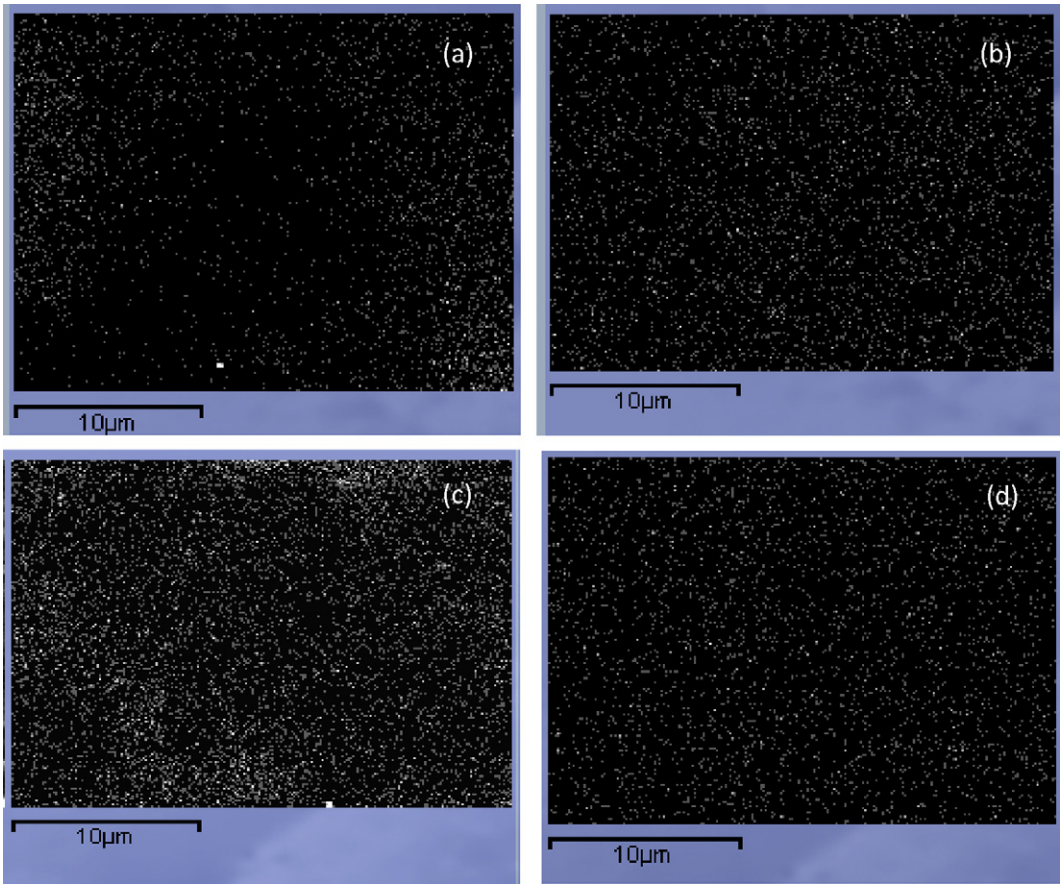

Fig. 9. Distribution of carbon by elemental mapping, (a) Batch T-2, (b) Batch T-3, (c) Batch T-4 and (d) Batch T-C.

in carbon mapping and further increase to 0.9 wt% (T-4) showed (Fig. 9C) uniform distribution with much higher concentration of carbon particles all through the matrix. This uniform distribution and higher concentration of carbon particles improved the overall properties. Again the conventional MgO-C refractory, containing 10 wt% graphite, also shows (Fig. 9D) uniform distribution of carbon particles.

3.7. Pore size distribution

Mercury intrusion porosimetry shows (Fig. 10A–D) that pores are present in two major size ranges, one in coarser side with a pore concentration around 100 μm and the other one is relatively in finer range between 10 and 1 μm. Also it is found that with the increase in nano carbon content the volume of coarse pore decreases from about 0.0022 mL/g for 0.3 wt% nano carbon (Fig. 10A) to 0.0012 mL/g for 0.9 wt% nano carbon (Fig. 10C) containing batch. It is due to the filling up of the spaces/voids between different macro refractory particles by the nano carbon. The similar effect of reduction in pore volume is also observed for the finer group of pores but the effect is much reduced. Again at higher nano carbon content (0.9 wt%), pores are also formed in the nano size range, around 10 nm, which may be related with the inter-particle voids between the nano meter sized carbon particles. Conventional MgO-C refractory shows (Fig. 10D) a pore distribution pattern which similar to 0.3 wt% nano carbon containing batch (Fig. 10A).

3.8. Property comparison with conventional; MgO-C refractories (containing 10 wt% graphite)

The above study shows that batch T-4, containing 0.9 wt% of nano carbon has the optimum properties. Properties of this batch is compared (Table 6) against a conventional composition of MgO-C refractory made using the same raw materials and additives, containing 10 wt% graphite, processed under exactly the similar conditions. Porosity value of T-4 batch is marginally higher as it contains lesser extent of fine carbon particles compared to conventional MgO-C but has higher density value as it has about 7% higher MgO content, having higher density compared to graphite (carbon). Addition of nano carbon has shown much higher cold crushing strength compared to that of the conventional one. This may be associated with the occurrence of microcracks between the nano carbon black particles and matrix and these micro cracks absorb energy, which result in obvious improvement of mechanical properties for nano carbon containing compositions, as reported and explained by Lin et al. [15]. HMOR value and oxidation resistance of T-4 batch were found to be much improved as compared to that of conventional one. This improvement is due to the increased formation of carbide phases formed by reaction between metal powder and highly reactive carbon source, nano carbon. Again slag penetration and thermal shock resistance were found to be very competitive one. Elemental mapping of carbon (Fig. 9) shows uniform distribution of carbon in both the

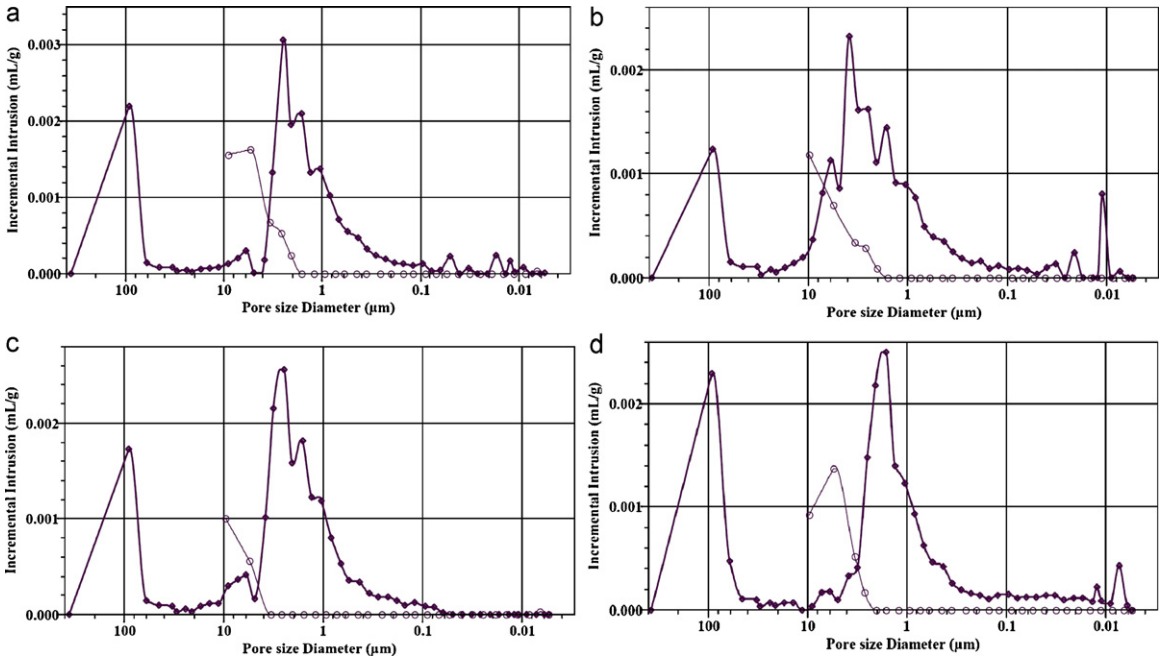

Fig. 10. Mercury intrusion porosimetry study of different samples, (a) Batch T-2, (b) Batch T-3, (c) Batch T-4 and (d) Batch T-C.

Table 6
Property comparison of batch T-4 and conventional MgO-C refractory.

Property	Batch T-4	Batch T-C
Apparent porosity (%)	4.3	3.8
Bulk density (g/cm^3)	3.12	3.05
Cold crushing strength (MPa)	51	37.5
HMOR (MPa)	4.5	3.9
Oxidation loss (%)	21.82	36.95
Slag penetration depth (mm)	2.01	1.98
Thermal shock resistance (cycle)	12	12

samples but higher concentration of carbon for T-4 batch, due to higher volume of nano carbon materials, though total carbon is lesser than half the amount of carbon present in conventional MgO-C refractories. Hence similar or better properties were achieved for MgO-C refractories by reducing total carbon by more than 50% using 0.9% nano carbon and 3% graphite.

4. Conclusions

New types of magnesia carbon refractories with total carbon less than half of the conventional refractories have been developed by conventional manufacturing technique using exactly the similar raw materials and addition of nano carbon. Variation of nano carbon content has shown variation in properties and the addition of 0.9 wt% of nano carbon in combination with 3 wt% graphite as the carbon source was found to be optimum content to obtain the best properties in the refractories. Addition of nano carbon has resulted more evenly disperse of the matrix phase, thereby filling in a better way among the tiny spaces between coarse, medium and fine particles of starting materials and filling of interior pores and gaps. This reduces porosity, increases densification, strength, corrosion resistance, etc. Again nano carbon also absorbs and relieves the stress due to thermal expansion and shrinkage of the refractory particles, thereby reduces the mal-distribution of thermal stress in the interior portion of refractories and improves thermal shock resistance. Thus a MgO-C refractory with much reduced carbon content but superior properties compared to conventional MgO-C refractories is obtained.

Acknowledgements

The authors thankfully acknowledge the support of different scientific and technical personnel of NIT, Rourkela and TKRL, Belpahar during the processing and characterization part of the study.

References

[1] E. Mohoamed, M. Ewais, Carbon based refractories, J. Ceram. Soc. Jpn. 112 (10) (2004) 517–532.
[2] X. Peng, L. LI, D. Peng, The progress of low-carbon MgO-C composite study, Refractories 37 (6) (2003) 355–357.
[3] Z. Boquan, Z. Wenjie, Y. Yashuang, Current situation and development of low-carbon magnesia-carbon materials research, Refractories 40 (1) (2006) 90–95.
[4] S. Tamura, T. Ochiai, S. Takanaga, T. Kanai, H. Nakamura, Nano-tech refractories-1: the development of nano structured matrix, in: Proceedings of the 8th UNITECR-03, Osaka, Japan, 19–22 October, (2003), pp. 517–520.
[5] S. Tamura, T. Ochiai, S. Takanaga, T. Kanai, H. Nakamura, Nano-tech refractories 2: the development of the nano structural matrix to MgO-C bricks, in: Proceedings of the 8th UNITECR-03, Osaka, Japan, 19–22 October, (2003), pp. 521–524.
[6] T. Ochiai, The development of refractories by applying nano-technology, Refractories (Tokyo) 56 (4) (2004) 152–159.
[7] Y. Xuejun, Q. Zheming, H. Liangquan, The influence of nanometer carbon black on the mechanical properties of phenolic resin, Process. Aircraft Mater. 33 (4) (2003) 34–38.

[8] L. Xianhui, W. Chifei, The optimization of characterization and preparation on nanometer carbon blacks, Process. Technol. Nano. Mater. 2 (5) (2005) 47–49.
[9] S. Takanaga, Y. Fujiwara, M. Hatta, Nano-Tech. refractories-3: development of MgO-rimmed MgO-C brick, in: Proceedings of the 9th UNITECR-2005, Orlando, FL, USA, November 8–11, 2005.
[10] T. Matsui, T. Goto, Y. Yamada, N. Taki, Characteristics and applications of nano tech magnesia carbon bricks, in: Proceedings of the 9th UNITECR-2005, Orlando, FL, USA, November 8–11, 2005.
[11] Y. Fujiwara, K. Namba, S. Takanaga, Development of nano tech MgO-C brick. Pt.1. Application of nano technology to matrix, J. Tech. Assoc. Refract. Jpn. 24 (3) (2004) 210.
[12] M. Hatta, K. Namba, S. Takanaga, Development of nano tech MgO-C brick. Pt.3. MgO-C brick with nano structural matrix, J. Tech. Assoc. Refract. Jpn. 24 (3) (2004) 212.
[13] B. Liu, J. Sun, G. TANG, K. Liu, L. Li, L. Liu, Effects of nanometer carbon black on performance of low-carbon MgO-C composites, J. Iron Steel Res. Int. 17 (10) (2010) 75–78.
[14] T. Ochiai, Development of refractories by applying nano technology, J. Tech. Assoc. Refract. Jpn. 25 (1) (2005) 4–11.
[15] L. Lin, T. Guangsheng, H. Zhiyong, L. Kaiqi, P. Xiaoyan, Effects of dispersion and content of nanometer carbon on mechanical performance of low carbon MgO-C materials, in: Proceedings of the 11th UNITECR-09, Salvador, Brazil, October 13–16, 2009.