Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 4909–4914

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Nano carbon containing MgO-C refractory: Effect of graphite content

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 18 January 2012; received in revised form 27 February 2012; accepted 27 February 2012
Available online 5 March 2012

Abstract

Development of low carbon containing MgO-C refractories has been studied containing a fixed 0.9 wt% of nano carbon and 1–9 wt% of flake graphite. Refractory compositions were prepared and processed as per the conventional manufacturing techniques of MgO-C refractory. Properties of the different compositions were evaluated and also compared against the conventional MgO-C refractory containing 10 wt% graphite prepared under exactly similar conditions. Addition of 3 wt% of flake graphite in combination with 0.9 wt% of nano carbon black was found to be optimum and resulted in better/comparable properties to that of conventional MgO-C refractory.

Keywords: MgO-C refractories; Nano carbon; Graphite content; Properties

1. Introduction

Magnesia-carbon (MgO-C) refractories are widely used in basic oxygen furnaces, electric arc furnaces and steel ladles for their excellent corrosion resistance and other hot properties. Use of carbon mainly imparts advantages like non-wetting nature resulting in improved corrosion resistance; high thermal conductivity, low thermal expansion, low elastic modulus and thus results in superior thermal shock resistance [1].

These advantages initially attracted the refractory manufacturers to use more amount of carbon in the composition. But with time progress in knowledge and technological improvement has made it clear that higher carbon content in the brick imparts several drawbacks too [2–4], such as:

1. Greater extent of oxidation of carbon results in a highly porous poorly bonded weak brick structure, which can be easily penetrated and corroded.
2. Increase in thermal conductivity with increasing carbon content results in higher energy loss, increasing the specific energy consumption per unit of steel produced.
3. Increase in shell temperature leading to damage and deformation.
4. Increased chances of carbon pick-up by molten metal.
5. Generation of higher extent of CO_x gases.

Hence MgO-C refractory with reduced carbon content without compromising with the beneficial properties is a challenge to the refractory technologists. A number of researchers [4–6] has reduced the total carbon content in MgO-C compositions by addition of nanometer sized particles. These nano sized particles, as additives or as carbon source, fill up the interior pores and gaps between the various sized grains of the refractory composition. Thus results reduced porosity, improved density, strength and other refractory characteristics. Nano carbon containing magnesia carbon refractories are important as they can improve the refractory properties along with the reduction in total carbon content, thereby reducing the chances of heat loss from the metallurgical process, reduced risk of carbon pick-up by metal and producing more eco-friendly refractories.

Literature study shows that MgO-rimmed MgO-C refractory [7] having nano structured matrix with less than 5% of total carbon resulted in superior thermal shock resistance and oxidation resistance. Use of hybrid graphite black (HGB) in MgO-C brick improved [8] thermal shock resistance, corrosion resistance, oxidation resistance and resulted in excellent performances in RH degassers. Formation of nano structured matrix in MgO-C refractory [9] using nano carbon black and

---

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

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2012.02.082

hybrid graphite also resulted in improved spalling resistance and excellent high-temperature oxidation resistance. Use [10] of nano carbon black also reduces the total carbon content and thus resulted in reduced in heat loss and thermal stress to the steel shell. Addition of nano carbon black was also reported [11] to improve the properties of low-carbon containing MgO-C refractories, like crushing and bending strengths both before and after coking, oxidation resistance and thermal shock resistance. Again due to fineness and higher volume, distributions of nano carbon particles are much better in the refractory matrix [12,13] and they reduce/suppress the sintering of MgO grains, resulting in lower elastic modulus and accordingly improved thermal spalling characteristics. The present authors also found [14] that addition of nano carbon has produced uniform dispersion of carbon particles in the matrix and better filling of the tiny spaces, pores/gaps amongst the coarse, medium and fine particles and thus reduces porosity, increases densification, strength, corrosion resistance, etc.

Though the literature shows that use of nano carbon replacing graphite in MgO-C refractories has shown tremendous improvement in quality, but still it cannot completely replace the flake graphite. Nano carbon, mostly used as amorphous carbon black, has inferior oxidation resistance and thermal conductivity compared to graphite flakes, which are also primary requirement for MgO-C refractory. Hence the amount of graphite in combination with nano carbon content remains an important parameter. But extensive literature search does not provide much information on the variation of graphite content in nano carbon containing magnesia carbon refractory. And so the present work aims to study the same. Effect of increasing amount of flake graphite content in the presence of nano carbon on the properties of MgO-C refractory is studied. Compositions are also compared with conventional MgO-C refractory (without any nano carbon) processed under exactly similar conditions.

2. Materials and methods

The raw materials, additives and binders used in the present study are exactly similar to those used in the previous work [14]. 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. The physico-chemical properties of fused MgO and details of flake graphite, nano carbon black, pitch powder and liquid resin used in the present study are provided in Tables 1 and 2 respectively. Aluminium metal powder (98% pure and finer than 100 μm) and boron carbide powder (95% pure, total B = 77 wt%, total C = 21 wt % and finer than 150 μm) were used as additive in the system. Different compositions of MgO-C refractories were formulated by varying graphite content between 1 and 9 wt% with fixed nano carbon content of 0.9 wt%, as found optimum from the previous work [14]. Conventionally used MgO-C refractory (Batch TC), containing 10 wt% of flake graphite as carbon source, has also been prepared under similar conditions, characterized and compared for each of the properties measured. Details of all the batch compositions are given in Table 3.

All the raw materials, additives and binders were mixed as per the batch composition and processed through mixing, aging, pressing, tempering, etc., as detailed in the previous study [14]. 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 a single data point and discussed in Section 4.

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

Table 1
Physico-chemical properties of fused magnesia.

Chemical analysis (oxide content, wt%)							Physical properties		
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Alkalis	Bulk density	App. porosity	Crystal size
0.40	0.07	0.50	Traces	1.40	97.35	0.50	3.3 g/cc	3.8%	800 μm

Table 2
Physico-chemical properties of flake graphite, nano carbon black, pitch powder and liquid resin.

Raw materials	Flake graphite	Nano carbon black	Pitch powder	Liquid resin
Fixed carbon (%)	94.1	98.03	52	47.85
Volatile matter (%)	0.80	1.42	47	
Ash (%)	5.08	0.39	1.4	
Surface area ($m^2 g^{-1}$)	6.37	116.5		
Softening point (°C)			135	
Specific gravity at 25 °C				1.23
Viscosity (CPS) at 25 °C				8500–9000
Moisture				~4.0

Table 3
Batch composition.

Raw materials	T-1	T-2	T-3	T-4	T-5	T-C
Fused MgO	97.1	95.1	93.1	91.1	89.1	89
Flake graphite	1	3	5	7	9	10
Nano carbon	0.9	0.9	0.9	0.9	0.9	0
Resin	2.75	2.75	2.75	2.75	2.75	2.75
Pitch	1	1	1	1	1	1
Al metal powder	0.5	0.5	0.5	0.5	0.5	0.5
Boron carbide powder	0.5	0.5	0.5	0.5	0.5	0.5

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, 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 atmospheric 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. Modulus of elasticity (MOE) was measured by the ultrasonic pulse velocity testing (UPVT) method (as used in IS:13311 (Part 1) – 1992 for concrete structures), in which velocity of ultrasonic pulse/wave was measured along the length of tempered samples of 150 mm × 25 mm × 25 mm. The test equipment (PUNDIT sonic test machine, make CNS Electronics Ltd., UK) has provisions for generating ultrasonic pulse, transmitting it through the sample, receiving and amplifying the pulse and measuring and displaying the pulse travel time. Elemental mapping analysis of carbon for understanding the distribution of carbon particles in the refractory matrix of different batches was done using a scanning electron microscope (model JSM 6480 LV, make JEOL, Japan).

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 (AP)

Increase in graphite content from 1 to 3 wt% has decreased the porosity sharply (Fig. 1). This is due to increased extent of voids filling amongst various sized MgO grains by graphite powders. Fine 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 and reducing the porosity [4–6,14,15]. But further increase of graphite content to 5 wt% or above has shown an increase in porosity values. The presence of nano carbon particles, having nanometer sizes and very high volume along with graphite powders might have covered the voids present and further increase in graphite content only increases the volume, resulting in a relatively porous structure. This is similar in observation to the previous study [14] where such increased porosity was observed with increasing amount of nano carbon beyond a certain level. For conventional MgO-C refractory composition, TC, inter-granular voids are not filled as there are no nano carbon particles (having very high volume to weight ratio) in the composition.

3.2. Bulk density (BD)

The variation of BD (Fig. 2) grossly supports the AP character. Higher extent of pore filling has resulted in better packing effect and a sharp risein BD value, from 3.05 g/cc to 3.12 g/cc with the increase of graphite content from 1 to 3 wt%. But further increase of graphite content results in a continuous decrease in BD values. This may be related to the overall increase in volume of the sample with increasing amount of

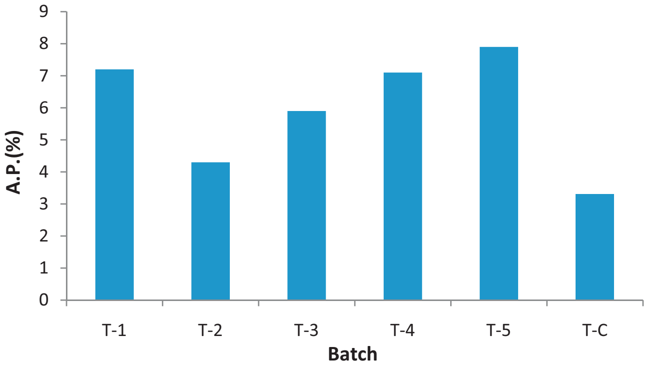

Fig. 1. Plot of apparent porosity with the variation of graphite content.

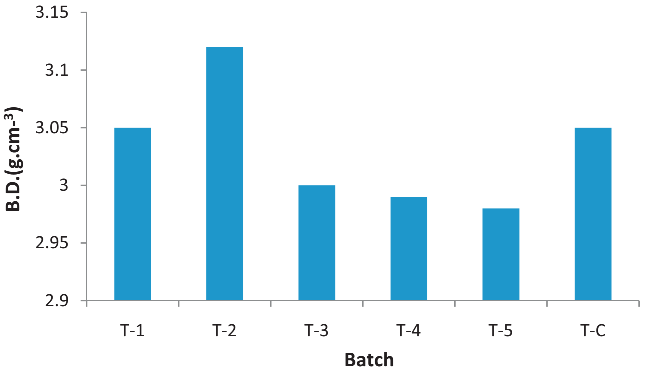

Fig. 2. Plot of bulk density with the variation of graphite content.

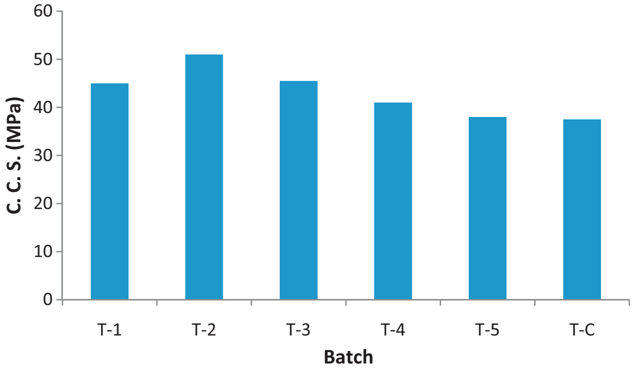

Fig. 3. Plot of cold crushing strength with the variation of graphite content.

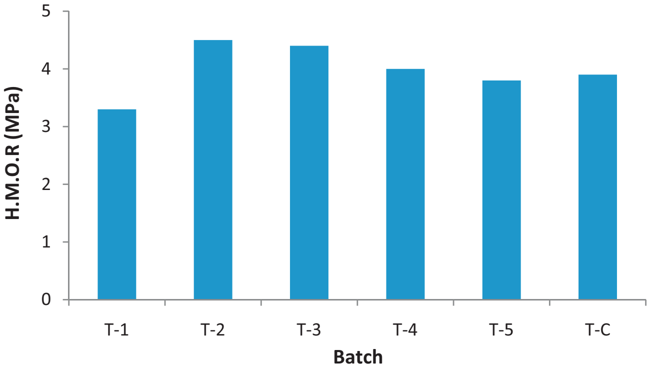

Fig. 4. Plot of hot modulus of rupture with the variation of graphite content.

graphite, as also observed in AP study. Also increase in graphite content results in the decrease in MgO aggregate content (having higher density values) of the batch (Table 3), which also lowers the density values.

3.3. Cold crushing strength (CCS)

Higher extent of pore filling with the increasing amount of graphite content from 1 to 3 wt% has resulted in an increase in CCS value (Fig. 3). But further increase of graphite content shows a steady and continuous decrease in the CCS values. This may be due to the increased porosity level and decreased density values associated with the increased bulk volume of the sample at higher percent of graphite content.

3.4. Hot modulus of rupture (HMOR)

HMOR value is found to increase with the increase in the graphite content from 1 to 3 wt% (Fig. 4). This increase is associated with the increased packing effect (filling of voids by finer graphite particles) and carbide formation due to reaction between carbon and aluminium metal (antioxidant additive) at the high temperatures. Carbide formation results in better bonding and increased strength. But above 3 wt% of graphite no further betterment is achieved. Higher amount of graphite has resulted in no further pore filling effect. Again at higher graphite content it is not entirely in the voids of aggregate structure. Hence it has an increased chance of oxidation. Carbide formation is limited due to the fixed amount of Al-metal powder present in the batch compositions but increased amount of graphite results in higher extent of oxidation at high temperatures. And oxidation produces a porous structure and deteriorates the hot strength properties.

3.5. Oxidation resistance

Fig. 5 shows the cut cross section of the oxidized cylindrical samples of different batch compositions. Visual observation shows that increasing amount of total carbon content in the batches increases the oxidation, resulting in a poor oxidation resistance with higher amount of total carbon content. Variation in oxidation percentage (measured by dimensional method) with the increase in graphite content is shown in Fig. 6. Carbon oxidizes at high temperature in oxidizing atmosphere and higher the carbon content, higher is the extent of oxidation. Again the total carbon content in T-5 and T-C are almost similar but the oxidation percentage of T-5 is marginally higher than that of T-C, 39.8% and 37% respectively. This is due to the presence of nano carbon in Batch T-5, which is much finer and active and gets oxidized faster.

3.6. Modulus of elasticity (MOE)

Variation of MOE values against increasing amount of graphite content is shown in Fig. 7. Increase in graphite and decrease in MgO content results in a continuous and gradual decrease in the MOE values. Graphite, having a lower MOE value replaces MgO of high MOE, produces a continuous decrease in the MOE values. Also better dispersion of finer graphite particles hinders the sintering of MgO particles and

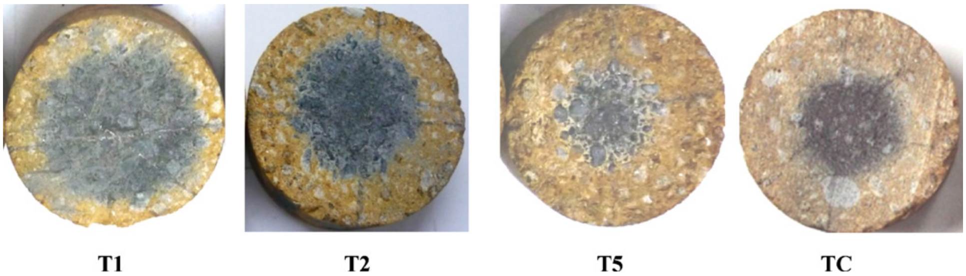

Fig. 5. Different batches after oxidation test and cutting.

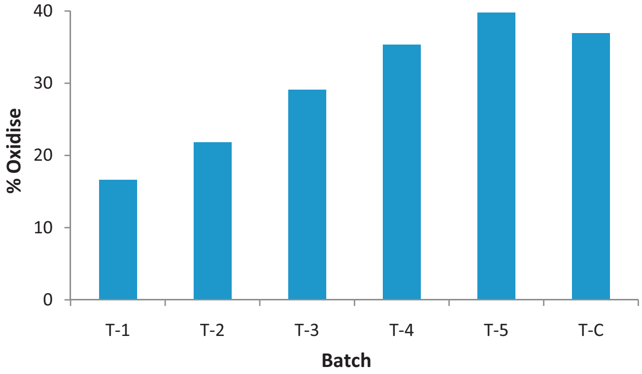

Fig. 6. Plot of oxidation with the variation of graphite content.

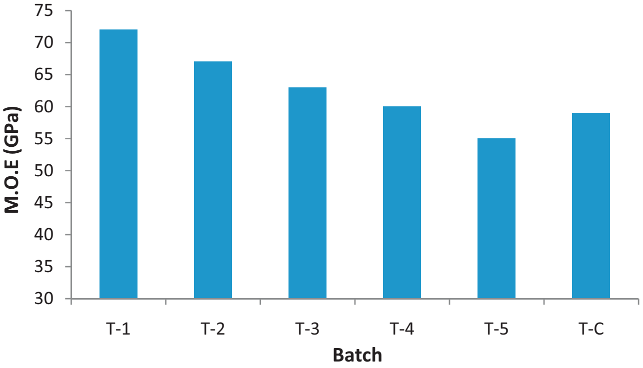

Fig. 7. Plot of modulus of elasticity with the variation of graphite content.

thereby reduces the modulus of elasticity of the batches [12,13]. Batch T-5, containing 9 wt% graphite and 0.9 wt% nano carbon, shows little lower MOE value than that of T-C batch containing 10 wt% of graphite (55 GPa and 59 GPa respectively), due to higher extent of distribution of carbon particles which is associated with the finer size of nano carbon.

3.7. Distribution of carbon

Distribution of carbon particles in the different batch compositions was characterized through elemental mapping of carbon, as shown in Fig. 8A–D. 1 wt% graphite containing composition shows (Fig. 8A) relatively less distribution of carbon particles, can be observed as white dots/spots in the figure. It is due to lesser extent carbon particles present in the composition. Increasing amount of graphite content shows much higher concentration and better distribution of carbon particles, observed in Fig. 8B and C, containing 3 and 9 wt% of graphite respectively. Much higher concentration of carbon particles in the T5 batch results in poor oxidation resistances. Conventional MgO-C refractory, containing 10 wt% graphite, also shows (Fig. 8D) uniform distribution of carbon particles but the concentration/distribution of carbon particles in this batch appears to be lesser than that of the T2 and T5 batches (Fig. 8B and C). This difference may be due to the absence of nano carbon particles in TC batch. Nano carbon particles, being

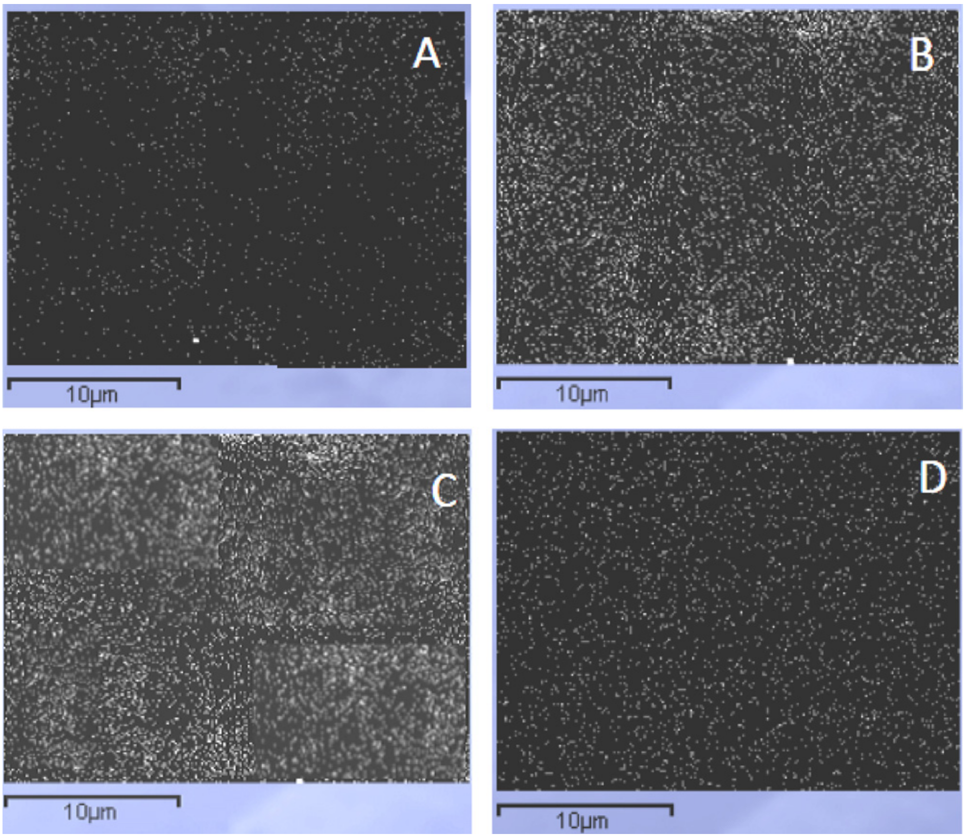

Fig. 8. Elemental mapping of carbon/distribution of carbon particles in different batches, (A) Batch T-1, (B) Batch T-2, (C) Batch T-5 and (D) Batch T-C.

very fine in size and having very high volume, result much higher distribution of carbon particles even when the total carbon content in the batch is much lower [14].

4. Conclusion

Nano carbon containing magnesia carbon refractories is developed varying graphite content between 1 and 9 wt% with a fixed nano carbon content of 0.9 wt%. Addition of 3 wt% graphite was found to be optimum. Increasing amount of graphite content up to 3 wt% has resulted uniform dispersion carbon particles in the matrix phase, thereby filling the inter-granular voids in a better way. This reduces porosity, increases densification, strength and hot strength, etc. Higher amount of graphite in the presence of nano carbon has not filled the voids further and results in inferior properties. Higher concentration of carbon particles is observed in the carbon mapping analysis for the samples T2, containing 3 wt% of graphite and 0.9 wt% of nano carbon, compared to TC batch, containing 10 wt% graphite, due to the presence of nano carbon particles in T2 batch.

Acknowledgements

The authors thankfully acknowledge the support and help of the staff of NIT, Rourkela and TKRL, Belpahar during different processing, experimentation and characterization part of the work.

References

[1] E. Mohoamed, M. Ewais, Carbon based refractories, Journal of the Ceramic Society of Japan 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: Proceeding of the 8th UNITECR-03, 19–22nd October, Osaka, Japan, (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, 19–22nd October, Osaka, Japan, (2003), pp. 521–524.

[6] T. Ochiai, The development of refractories by applying nano-technology, Refractories (Tokyo) 56 (4) (2004) 152–159.

[7] S. Takanaga, Y. Fujiwara, M. Hatta, Nano-Tech. refractories – 3. Development of MgO-rimmed MgO-C brick, in: Proceedings of the 9th UNITECR-2005, November 8–11, Orlando, FL, USA, 2005.

[8] T. Matsui, T. Goto, Y. Yamada, N. Taki, Characteristics and applications of nano tech magnesia carbon bricks, in: Proceedings of the 9th UNITECR-2005, November 8–11, Orlando, FL, USA, 2005.

[9] Y. Fujiwara, K. Namba, S. Takanaga, Development of nano tech MgO-C brick. Pt.1. Application of nano technology to matrix, Journal of Technical Association of Refractories Japan 24 (3) (2004) 210.

[10] M. Hatta, K. Namba, S. Takanaga, Development of nano tech MgO-C brick. Pt.3. MgO-C brick with nano structural matrix, Journal of Technical Association of Refractories Japan 24 (3) (2004) 212.

[11] 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, Journal of Iron and Steel Research International 17 (10) (2010) 75–78.

[12] Y. Xuejun, Q. Zheming, H. Liangquan, The influence of nanometer carbon black on the mechanical properties of phenolic resin, Processing of Aircraft Materials 33 (4) (2003) 34–38.

[13] L. Xianhui, W. Chifei, The optimization of characterization and preparation on nanometer carbon blacks, Processing Technology of Nanometer Materials 2 (5) (2005) 47–49.

[14] M. Bag, S. Adak, R. Sarkar, Study on low carbon containing MgO-C refractory: use of nano carbon, Ceramics International 38 (2012) 2339–2346.

[15] T. Ochiai, Development of refractories by applying nano technology, Journal of Technical Association of Refractories Japan 25 (1) (2005) 4–11.