Formation of Mg_2C_3 phase in N220 nanocarbon containing low carbon MgO-C composition

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Abstract. This paper reports a non-conventional microstructure with sequecarbide (Mg_2C_3) formation in N220 nanocarbon containing low carbon magnesia carbon composition having magnesium metal powder as antioxidant. 5 wt% graphite containing MgO-C refractory with and without 1 wt% N220 nanocarbon is studied and 2 wt% magnesium metal powder is used as the lone antioxidant. The compositions were mixed with powder and liquid resin binder, pressed uniaxially at 150 MPa and cured at 220°C. Cured samples were coked at 1000°C for 2 h. Matrix of the coked samples was studied in detail for microstructural analysis phase content and formation of nail-shaped sequecarbide was found in the nanocarbon containing compositions. The *in-situ* sequecarbide formation has resulted in the strength of the batch.

Keywords. Sequecarbide; matrix phase; *in-situ* ceramic phase.

1. Introduction

MgO-C refractory is a composite material containing fused and sintered magnesia, graphite (as carbon source) and bonded by high carbon containing pitch and resin, with metallic powders as antioxidants to protect the carbon. MgO-C refractories have dominated the steel converter lining and slag line of ladles for decades as they possess superior resistances against slag corrosion and penetration because of the non-wetting properties of carbon (graphite) and excellent thermal shock resistance at elevated temperature due to high thermal conductivity, low thermal expansion co-efficient and low elastic modulus properties of graphite [1].

However, conventional MgO-C refractories have several drawbacks like, oxidation of carbon at high temperatures resulting in a porous weak structure, higher energy loss from the process due to higher thermal conductivity of graphite, chance of carbon pickup by molten steel, etc [2–4]. To minimize these drawbacks, researchers are trying to develop low carbon containing MgO-C refractory, by introducing new class of carbon materials like, N220 carbon black, graphene oxide, carbon nano tubes, etc [5–8]. These new class of MgO-C refractories with much reduced carbon content are likely to have physical, mechanical, thermal, thermomechanical and chemical properties similar or better than that of the conventional MgO-C refractory. In a previous study, it was found that 1 wt% of N220 nanocarbon black along with 3–5 wt% of graphite showed similar properties as that of 16 wt% graphite content conventional refractory [5–7]. The reasons for showing similar refractory properties even with lower

carbon content are as follows:

1. Better filling of pores and resulting in a more compact structure by fine nanocarbon particles,
2. Higher efficiency to coat magnesia grains at lower amount of carbon level which results in better non-wetting properties in refractory
3. Greater extent of *in-situ* ceramic phase formation due to higher surface of nanocarbon, resulting in better mechanical properties.
4. In addition to these advantages, formation of graphitic nature of carbon from the resins at high temperature also improves the refractory properties [3].

Carbon in magnesia carbon refractory is oxidized in two ways, i.e., (a) direct oxidation and (b) indirect oxidation. Direct oxidation occurs at lower temperature (reaction 1) when carbon is directly oxidized by oxygen from the environment [9].

Indirect oxidation that happens at or above 1400°C, when carbon oxidized by oxygen from the MgO, i.e., (reaction 2) and Mg (g) evolves.

Taffin and Poirier [10] studied the antioxidation properties of magnesia carbon refractory by adding magnesium metal powder as antioxidants. The magnesium metal powder starts to evaporate at relatively low temperature, i.e., 400–500°C [10].

Table 1. Physiochemical properties of raw materials.

Raw materials	MgO	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	Na ₂ O
Fused Magnesia	97.35	0.07	0.40	1.40	0.22	0.26
Raw materials	Carbon (%)	Volatile matter (%)	Ash (%)	Surface area (m ² g ⁻¹)		
Flake graphite	94.1	0.80	5.08	5.7		
Raw materials	Carbon (%)	Volatile matter (%)	Ash (%)	Surface area (m ² g ⁻¹)		
Nanocarbon black (N220)	98.29	1.3	0.19	120.1

The resulting Mg gas, from the reactions 2 and 3, starts to react with carbon to form MgC₂ at about 400–500°C (reaction 4) [11].

In this study, Mg metal powder is added to magnesia carbon refractory. The specimens are prepared as per the conventional method and coked at 1400°C for 4 h. Phase and microstructure of the coked sample is investigated.

In this report, nail-type sequicarbide (Mg₂C₃) appeared in magnesia carbon refractory. Besides that, with reference to the literature, crystallized graphite can be obtained from magnesium carbide at relatively low temperature, which reflects in our hot strength and corrosion resistance study.

2. Materials and methods

Raw materials used for the study are fused magnesia (from Chinese supplier, Magus Marketing, India) with size fractions 3.0–1.0 mm, 1.0–0.075 mm and <75 micron; flaky graphite (Agarwal Graphite Industries, India), magnesium metal powder as antioxidant (>98% pure and finer than 100 micron) and nanocarbon black (N 220 variety, Birla Carbon, India). The Chemical composition of fused magnesia, flaky graphite and N220 nanocarbon are given in table 1. Phenolic resin, both powder and liquid variety, were used as a binder. Five wt% graphite and 1 wt% nanocarbon containing the composition was selected for this experiment from our previous study [5,6]. The raw materials listed in table 2 were used for the preparation of experimental desired shape of refractory. First magnesia grains with different grain size were mixed with nanocarbon black for about 5 min in a mechanical mixture for better coating of magnesia grains by carbon black. Then the liquid resol-type resin were added to the magnesia-carbon mixes and stirred for 10 min. After that all fines including magnesia fines were added to magnesia-carbon-resin mixture and mixed it for 30 min. Total mixing time was 45 min, after which the mixture was uniaxially pressed in a hydraulic

Table 2. Batch composition details.

Raw materials	1	2
Fused magnesia	92	93
Flaky graphite	5	5
Nanocarbon black N220	1	0
Mg metal powder	2	2
Powder resin	1	1
Liquid resol resin	3.75	3.75

press machine at 1500 kg cm⁻² to form shapes of dimensions 50 mm × 50 mm × 50 mm and 125 mm × 25 mm × 25 mm, respectively. All the different shapes were then cured at 220°C for 12 h. Cured samples were then characterized for various refractory properties, as detailed below.

Hot strength, as modulus of rupture (HMOR) was measured in air at 1400°C as per ASTM C133-7 standards, using 125 mm × 25 mm × 25 mm sized samples in a HMOR furnace apparatus (Bysakh, India). Coked (coking was done by reducing the atmosphere at 1000°C for 4 h) strength was measured as cold crushing strength (CCS) as per the standard IS: 1528, Part-4 (2002). Phase analysis by X-ray diffraction technique (RIGAKU, Japan) and micro-structural development in the matrix phase of the coked samples by scanning electron microscope (FEI, USA) were also studied. Slag corrosion test by static cup method was done at 1600°C for 2 h using a 50 mm cube sample with a drilled hole of dimension 20 mm diameter and 25 mm height at the centre. Steel converter slag was used for corrosion and its chemical composition is given in table 3. Samples after corrosion test were cut along the vertical axis into two halves and the sections were then measured for corrosion and penetration. To understand the wear mechanism of magnesia carbon refractory, slag refractory interface was taken for the microstructure study.

3. Result and discussion

3.1 Phase analysis and microstructural study

Phase analysis of the coke samples show (figures 1 and 2) that both the batches are containing the constituent phases,

Table 3. Chemical composition steel converter slag (wt%).

CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	MnO	CaO+MgO+MnO/SiO ₂
37.5	16.48	6.08	6.95	26.45	3.99	3.00

namely prime constituent magnesia and graphite. Other than these two phases, there are small peaks of sequicarbide phase in the batch 1 composition (figure 1), but it is absent in batch 2 (figure 2). The presence of nanocarbon in batch 1 helped to form the sequicarbide phase as proposed by D Osetzky [11]. Nanocarbon has reacted faster with MgO forming Mg (g) and it reacts to a greater extent in the formation of the sequicarbide phase as well. This does not happen in the case of graphite.

Figure 1. XRD of batch composition 1. **Figure 2.** XRD of batch composition 2.

At about 1400°C, carbon is oxidized to carbon monoxide by taking the oxygen from the MgO and leaving the Mg (g) vapours.

The antioxidant Mg metal starts to evaporate at 400–500°C. Nanocarbon, having higher surface area and higher reactivity, starts to react with the antioxidant Mg metal and forms magnesium carbide.

The FESEM micrographs of the batch compositions 1 and 2 are shown in figure 3a–d and figure 4, respectively. Figure 3a–d reveals that a greater extent of nail-type microstructure was found in magnesia carbon refractory. In addition, the EDS data of figure 3d shows that only magnesium and carbon are present on the nail-type microstructure. This *in-situ* ceramic phase is detected on and beside the magnesia grains. From the above results it may be concluded that the nail-type features found is magnesium sequicarbide. The EDS also shows the same for the batch composition 1. Figure 2a shows that a higher amount of nail-type magnesium carbide phases are present in the matrix phase beside the magnesia grains. For better recognition, higher resolution micrographs are shown in figure 2b–d. However, in case of batch composition 2 where nanocarbon is absent, no such type of microstructure is observed in the matrix phase (figure 4).

3.2 Strength study

The coked and hot strength of batch compositions 1 and 2 are shown in figure 5. Strength development of the refractory samples is dependent on the microstructural development and *in-situ* ceramic phase formation. The microstructure and phase analysis evidence shows that there is a formation of nail-type *in-situ* sequicarbide in batch composition 1. The strength values of composition 1 are considerably higher than that of composition 2. The presence of nanocarbon in composition 1 and formation of nail-structured magnesium carbide phases in the composition is responsible for such enhancement of strength properties, which are absent in composition 2. In addition, the coked strengths of both the compositions are higher compared to the hot strength values; this may be due to the oxidation of carbon during hot strength measurement at high temperature resulting in a porous refractory.

Figure 3. (a–c) Micrographs of batch composition 1 (1 wt% NC), nail-like structure formation in the matrix phases and (d) larger view of the nail structure and its EDS study.

Figure 4. Micrographs of batch composition 2.

Figure 5. Coked and hot strength of two different batch compositions.

Figure 6. Corrosion resistance of batches.

Figure 7. (a) Low resolution micrographs of slag corrosion wall (slag-refractory interface). (b) High resolution of marked portion of figure a.

3.3 Corrosion resistance

Corrosion resistance in terms of slag penetration into refractory wall is shown in figure 6, represented as penetration depth. Nanocarbon might have shown its graphitic nature at elevated temperature. Composition 1, containing 1 wt% nanocarbon, shows better corrosion resistance compared to composition 2. This is due to the formation of graphitic nature of nanocarbon [3] and *in-situ* ceramic phase, sequicarbide formation at higher temperatures. Moreover, as per Osetzky [11], crystallized graphite is formed from magnesium carbide at relatively low temperature i.e., 950–1200°C. Both the graphitic nature of nanocarbon at high temperatures and crystallized graphite formation from sequicarbide at low temperatures has helped in improving the corrosion resistance of composition 1. Some typical microstructure of slag refractory face is shown in figure 7a and b.

The nail-type magnesium sequicarbide, which was formed in batch composition 1, is showing better refractory properties in terms of strength (hot and coked) and corrosion

resistance than batch composition 2. This is because of the nail-type structure, which helps to bind the matrix phase properly. However, magnesium metal powder is relatively less efficient than aluminium metal powder because addition of aluminium metal powder helps three-dimensional rod-type networks along with octahedral magnesium aluminate spinel, which holds the matrix phase in a better way than the nail-type Mg_2C_3 [5,6].

4. Conclusion

Nail-type microstructures were obtained in low carbon magnesia carbon refractory, where magnesium metal powder was acting as an antioxidant. Formation of such a type of microstructure helps to achieve better strength at higher temperature and also shows better corrosion resistance. This is due to the formation of sequicarbide at a higher temperature, which was confirmed by FESEM, XRD and EDS.

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