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Effect of MgO and ZrO_2 additions on the properties of magnesite-chrome composite refractory

A. Ghosh *, M.K. Haldar, S.K. Das

Refractories Division, Central Glass & Ceramic Research Institute, Kolkata 700 032, India

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Abstract

Magnesite-chrome aggregates have been prepared from friable chrome ore and magnesia of different reactivity in the presence of an additive, ZrO_2. Two types of batch compositions using sintered magnesia, caustic magnesia and chrome ore have been selected for preparing mag-chrome composites. The batch consisting of sintered magnesia and friable chrome ore (SMC) was vibromilled for 8 h, whereas caustic magnesia compositions were added directly to a vibromilled chrome ore (CMC) and mixed in a fluidized bed mixer. Additions of 1–5 wt.% ZrO_2 were made to the batches. Firings were carried out between 1700 and 1750 °C with 2 h soaking. Aggregates were characterized by evaluating densification, hot modulus of rupture and microstructure. The reactivity of magnesia was found to play an important role in the final properties of samples. Introducing less reactive sintered magnesia improved all the properties of the aggregates. ZrO_2 was found to be a good sintering aid in the magnesite-chrome composites.

Keywords: A. Sintering; B. Composites; B. Microstructures; C. Mechanical properties; D. MgO; D. Spinel

1. Introduction

Basic steel making furnaces use a considerable tonnage of refractory grade chrome ore for making magnesite-chrome refractories. These refractories are usually produced from magnesia and different varieties of chrome ore. The pure mineral chromite has the formula $FeCr_2O_4$ (32.14% FeO and 67.8% Cr_2O_3) and is rarely found in nature. Naturally occurring chrome ore is a solid solution of simple spinels with the composition ($Fe^{2+}Mg^{2+}$) ($Cr^{3+}Al^{3+}Fe^{3+}$)$_2$O$_4$ [1,2]. Because chrome ore in massive form is now being depleted, the lower quality friable grade chrome ore has been used as an alternate material to meet the demand of basic refractories for various applications in steel and cement industries. It is often mixed with fine magnesia to form an intermediate, prereacted grain on calcinations. These grains or aggregates are the main raw materials for brick making, possessing similar properties to a fine-grained, fused material. In magnesite-chrome refractories, when the chrome component in the mixture is predominantly made of fine particles, the formation of a periclase-chromite-spinel direct bond is enhanced. As the size of the chromite particle increases, it has been found that the sintering temperature needs to be raised up to 2000 °C. Earlier studies have suggested that fine grinding of chromite ore is required to decrease the sintering temperature below 1900 °C [3–5]. Different authors have studied the performance of highly fired magnesite-chrome bricks and interpreted their result using relevant quaternary phase diagram [6–9]. Increasing the chromite ore content in the mixture decreases the densification, which is related to the poor sintering tendency of chromium oxide [10]. Increasing the sintering temperature also enhances the tendency of chromium oxide to crystallize in the chromite ore [11]. The addition of unstabilized ZrO_2 in $MgCr_2O_4$ causes the fracture surface energy of the resulting $MgCr_2O_4$–ZrO_2 composition to depend on the agglomerate particle size, particle size distribution and volume fraction of ZrO_2 [12].

In the present study, an attempt has been made to develop magnesite-chrome aggregates from friable chrome ore and magnesia of different reactivity in the presence of an additive, ZrO_2. The sintered variety of magnesia is high temperature fired (>1900 °C) and is less reactive; while the caustic variety is lightly calcined (1100 °C), and is highly reactive.

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* Corresponding author. Tel.: +91 33 4838084; fax: +91 33 2473 0957.
E-mail address: arup@cgcri.res.in (A. Ghosh).

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2. Experimental

Caustic magnesia, sintered magnesia (source of magnesia is NedMag Industries in The Netherland) and friable chrome ore from India were used as raw materials in this study. The batches comprising magnesia and chrome ore were weighed so that the end product contains 18% Cr_2O_3. The batch consisting of sintered magnesia and friable chrome ore (SMC) was vibromilled separately for 8 h, while caustic magnesia was added directly to the vibromilled chrome ore (CMC). ZrO_2 additives from 1 to 5 wt.% were added to the batches. Five percent polyvinyl alcohol solution was added to each batch as binder; they were then mixed in a fluidized bed mixer, sieved through a 20 mesh BS sieve and briquetted using a uniaxial press at a pressure of 100 MPa. The briquettes with a size of 12 mm (diameter) × 12 mm (height) were initially air dried and subsequently oven dried at 110 ± 5 °C for 24 h. Firing (heating rate from RT up to 1000 °C—5 °C/min and from 1000 to 1700/1750 °C—3 °C/min) of the briquettes was carried out in a programmed electric muffle furnace, with 2 h soaking at the sintering temperature. The physical properties of aggregates and the bulk density and apparent porosity of these sintered briquettes were evaluated by standard liquid displacement method using Archimedes' principle. The hot flexural strength of the test samples at elevated temperature was determined by an instrument fabricated at Central Glass & Ceramic Research Institute, Calcutta, India. The test was carried out by three-point bending on 60 mm × 6 mm × 6 mm samples. The rate of temperature increase was at 5 °C/min with a soaking time of 30 min at each test temperature. The test load was applied at a rate of 50 kg/min. Crystalline phases of the sintered mag-chrome test samples were identified by X-ray diffraction using a Ni-filtered Cu Kα radiation with a scanning speed of 2° (2θ) per minute on a PHILIPS PW (1790) X-ray diffractometer. The microstructure of sintered mag-chrome test samples was observed using an optical microscope under reflected light.

2.1. Raw material characterization

The raw materials were characterized for chemical, physical and mineralogical properties. The chemical analysis of raw materials (Table 1) indicated that caustic magnesia contained 94.8% MgO while the sintered magnesia was 95.9% MgO. SiO_2 content of both the MgO varieties was between 1 and 2%. Because the CaO content is low, the amount of low melting phase forming (monticellite or merwinite) is low. The higher L.O.I. of 5.8% in the caustic magnesia is due to presence of magnesium hydroxide, which decomposes above 300 °C as indicated by the differential thermal analysis (DTA) (Fig. 1 and Table 3). The specific gravity of caustic magnesia (Table 2) is lower than that of sintered magnesia because it contains some low-density magnesium hydroxide. The caustic MgO powder is extremely fine in particle size, with a specific surface area of 13.5 m^2/gm. The chrome ore consists of 61.9% Cr_2O_3, which is reasonably high. A Fe_2O_3 content of 12.3% is due to the presence of iron spinel in the chrome ore, while a low SiO_2 content (around 0.4%) will result in the formation of a small amount of detrimental silicate phase in the matrix. The physical properties show a high specific gravity of 4.34 g/cm^3 and a fineness in a narrow range, with 51% in between −150 + 240 BS mesh (Table 2).

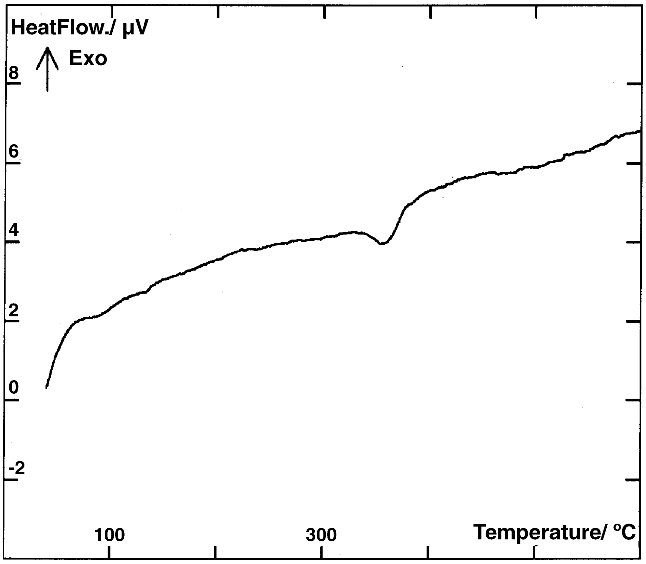


Fig. 1. Differential thermal analysis of caustic magnesia.

Table 1
Chemical analysis of raw materials

Constituents	Sintered MgO (NedMag Industries, The Netherland) (wt.%)	Caustic MgO (NedMag Industries, The Netherland) (wt.%)	Chrome ore (Indian Origin) (wt.%)
SiO_2	2.0	1.30	0.4
Al_2O_3	0.6	0.2	9.8
Fe_2O_3	0.3	1.8	12.3
CaO	0.6	1.2	0.4
MgO	95.9	94.8	14.5
K_2O	0.1	0.3	0.01
Na_2O	0.2	0.4	0.02
B_2O_3	0.01	0.01	–
L.O.I.	1.1	5.8	–
Cr_2O_3	–	–	61.9

Table 2
Physical properties of raw materials

Properties	Sintered MgO (vibromilled)	Caustic MgO (as received)	Chrome ore (as received)
Specific gravity	3.57	3.37	4.34
Surface area (m^2/gm)	1.0	13.5	–
Sieve analysis (wt.%)			
(−18 + 36)	N/A	N/A	0.1
(−36 + 60)	–	–	0.4
(−60 + 72)	–	–	0.1
(−72 + 100)	–	–	1.2
(−100 + 150)	–	–	32.0
(−150 + 240)	–	–	51.0
(−240)	–	–	15.2

N/A: not analyzed.

Table 3
Mineralogical properties of raw materials

Properties	Sintered MgO (vibromilled)	Caustic MgO (as received)	Chrome ore (as received)
XRD (major phase)	MgO	MgO	Chrome spinel
DTA endothermic peak (°C)	–	350	300

3. Results and discussions

3.1. *Densification*

The bulk density and apparent porosity of different mag-chrome aggregates are shown in Fig. 2(a) and (b). The SMC batch shows higher bulk density than that developed with caustic magnesia (CMC). The sintering process is accompanied by spinel formation along with the densification. Samples containing caustic magnesia (higher surface area) favours spinel formation, which delays the densification process [13]. However, in the sintered magnesia and chrome compacts (SMC), the larger crystallite size of MgO lowers the reaction rate of mag-chrome spinel formation and favours aggregate consolidation. In both sintered and caustic magnesia, zirconia proves to be an effective sintering aid. The bulk density increases in both cases with an increase in the amount of ZrO_2 additive. The mechanism by which ZrO_2 additives influence the reaction sintering of mag-chrome refractories was described in earlier work [14]. ZrO_2 alters the grain boundary between assemblage and the morphology of the grains, changing the dihedral angle (φ). The lowering of the dihedral angle means γ_{ss} will be smaller, which will facilitate grain-to-grain contact and ultimately direct bond formation. This tendency increases the

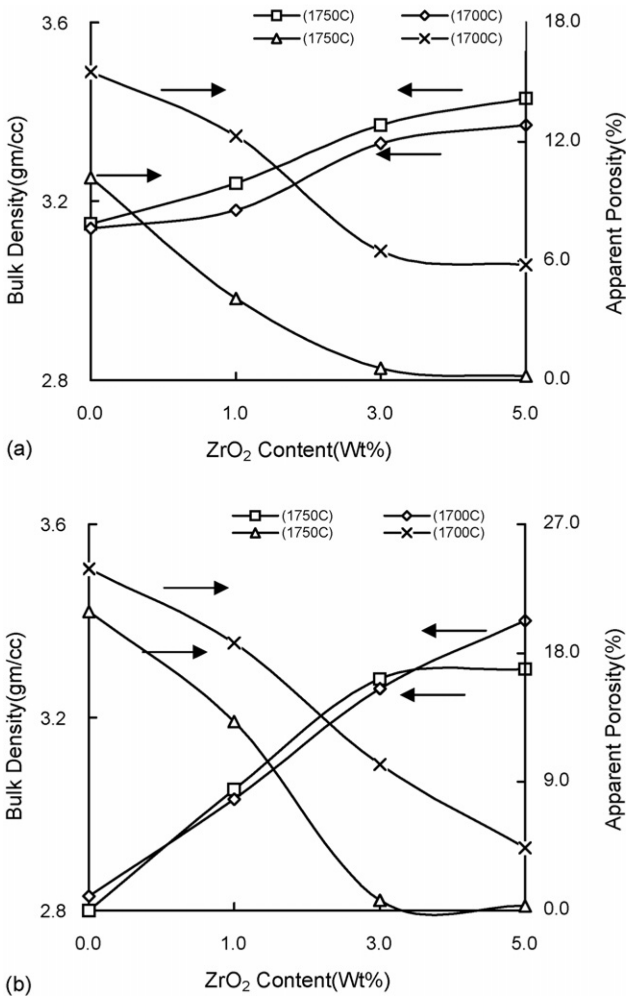


Fig. 2. Bulk density and apparent porosity of magnesite-chrome aggregates developed from (a) sintered magnesia and (b) caustic magnesia.

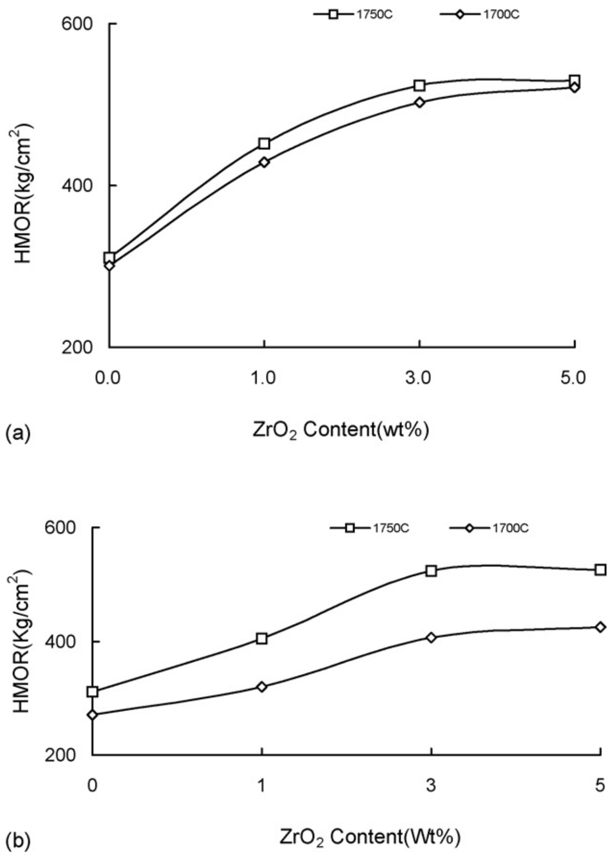


Fig. 3. Hot modulus of rupture of magnesite-chrome aggregates developed from (a) sintered magnesia and (b) caustic magnesia.

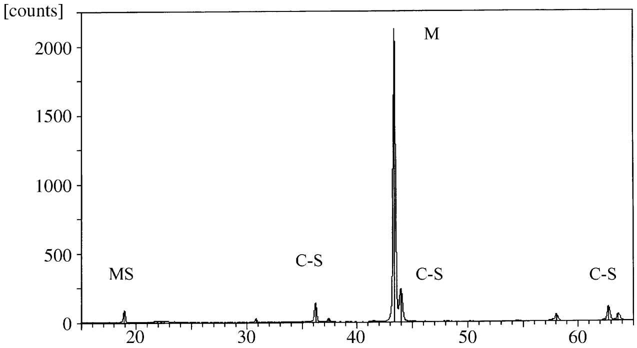
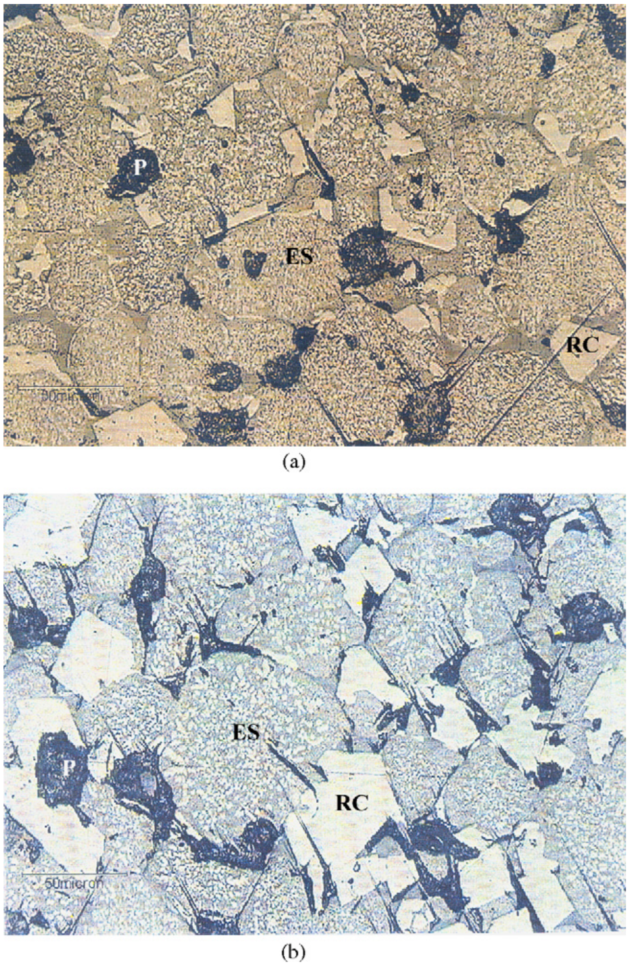


Fig. 4. XRD analysis of magnesite-chrome aggregates sintered at 1750 °C. M = MgO; C-S = chrome spinel; MS = $MgSiO_4$.

densification and improves the high temperature modulus of rupture strength as shown in Fig. 3(a) and (b).

3.2. High temperature strength

The hot modulus of rupture at 1300 °C of the mag-chrome aggregates is shown in Fig. 3(a) and (b), and improves with an increase in the ZrO_2 concentration present in the compacts. Higher amount of ZrO_2 additive increases the densification as well as grain-to-grain bonding, which is responsible for the improved high temperature strength. Apart from the effect of ZrO_2 additives, the presence of a homogeneously distributed composite phase of chrome spinel and magnesia in the samples is also responsible for improving the hot strength. When the load is increased, the initial crack formation in the first phase is arrested in the second dissimilar phase, resulting in delayed fracture of the refractory aggregates [15].



(a)

(b)

Fig. 5. Optical photomicrographs of magnesite-chrome composite fired at 1750 °C: (a) sintered magnesia and friable chrome ore and (b) caustic magnesia and friable chrome ore. Phases: ES, exsolved spinel over magnesia; RC, remnant chrome grain; P, pores.

3.3. Mineralogical phases and microstructure

The mineralogical phases of the sintered magnesia-chrome composite with no ZrO_2 determined by X-ray analysis is shown in Fig. 4 and indicates that the fired product contains magnesia, chrome spinel and minor amount of magnesium silicate.

The optical photomicrographs of mag-chrome aggregates sintered at 1750 °C are shown in Fig. 5(a) and (b). The microstructure of the aggregates consists of magnesia grains, exsolved chrome spinel over MgO, remnant chrome and porosity. In the case of sintered magnesia and chrome ore (SMC) compact (Fig. 5a), a significant amount of exsolved spinel (white dots) are observed over the MgO grains. In these aggregates, substantial direct bonding is visible between the magnesia grains and remnant chrome ore (light grey). In contrast, in the CMC batch (Fig. 5b), exaggerated grain growth of magnesia is visible along with a higher amount of remnant chrome ore. This leads to higher porosity, with less compact grains.

4. Conclusion

(a) The reactivity of magnesia plays a significant role in the physical and microstructural properties of magnesite-chrome composite refractories.
(b) The less reactive sintered magnesia, with a bigger crystal size and a lower reactivity, improves the bulk density and the direct bonding of chrome grains, causing a decrease in the remnant chrome ore in the microstructure.
(c) ZrO_2 incorporation improves the physical and thermo-mechanical properties of magnesite-chrome composite refractories.

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