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Effect of compositional variation on the synthesis of magnesite–chrome composite refractory

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Abstract

Magnesite–chrome composites have been prepared by utilizing sintered magnesite and friable chrome ore in presence of titania as additive. Three types of batch compositions containing 5% Cr_2O_3, 18% Cr_2O_3 and 30% Cr_2O_3 have been selected for developing mag–chrome composites. The aggregates were developed by first vibro milling the raw materials and then additives were incorporated in wt.% along with 5% PVA solution as binder to the different batches. It was then properly mixed by fluidized bed mixer and after sieving in 20-mesh BS sieve briquettes were formed uniaxially at a pressure of 100 MPa. The briquettes were first air dried and subsequently oven dried at $110 \pm 5\,^{\circ}C$ for 24 h. Finally, the green briquettes were fired at 1700 and 1750 °C in electrically program controlled muffle furnace. The physical properties as well as thermo-mechanical properties and microstructural studies of the sintered aggregates have been evaluated. The common feature observed in the microstructures is the exsolution of spinel phase in magnesia grains. The hot properties of the composites are superior when the Cr_2O_3 content is increased to 30%. Additives played a significant role in improving the bulk density and strength.

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

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1. Introduction

Magnesite–chrome refractories, which are mainly used in steel, cement and copper industry is useful owing to its high refractoriness, high temperature stability, moderately low thermal expansion and resistance to slag. The Cr_2O_3 content of the refractory varies depending upon the application areas. The main application areas are LD converters, Ladles, VOD/AOD vessels, EAF, copper furnace, cement rotary kiln, etc. These refractories are commonly used in secondary steel making because of their high resistance to wide varieties of slags and their stability at high temperature. Till recently, the mag–chrome refractories were produced from a mixture of magnesia and massive variety of chrome ore. However, massive chromes ore being depleted throughout the world, an alternate friable chrome ore has become popular.

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 chromite is a solid solution of the simple spinels with the composition $(Fe^{2+}Mg^{2+})(Cr^{3+}Al^{3+}Fe^{3+})_2O_4$. Therefore, it can be regarded as a solid solution of different spinels [1,2]. The unstabilized ZrO_2 inclusion in $MgCr_2O_4$ shows, fracture surface energy of $MgCr_2O_4$–ZrO_2 composition depends on the agglomerate particle size, distribution and volume fraction of ZrO_2 [3]. Different authors studied the petrology of high fired magnesia chrome bricks and interprets their result in the light of relevant quaternary phase diagram [4–7]. Effect of chemical composition was studied on microstructure and mineral composition of three kinds of fused magnesia–chrome grain [8]. It has been reported [9] that the distribution of the silicate phase in magnesia–chrome bricks changes with increase in firing temperature.

In these refractories the silicates began to melt around 1380 °C and as the molten silicate increases, both magnesia and spinel were taken into solution. On cooling, large portion of this dissolved periclase and spinel were reprecipitated, the latter on the surface of both existing periclase and chrome grains and spinel were reprecipitated, the latter on the surface of both existing periclase and chrome grains. The matrix of magnesite–chrome brick is influenced by brick manufacturing conditions and steel making and con-

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stitutes a factor of deterioration such as structural spalling [10]. The characteristics of fine powders and its sintering behavior control the microstructure of these bricks.

In magnesite–chrome refractories when the chrome component in the mixture is predominantly made of fine particles, the formation of periclase-chromite-spinel direct bond is enhanced. Besides, as the size of the chromite particle increases the sintering temperature raises up to 2000 °C. Earlier studies suggested that fine grinding of chromite is required to decrease the sintering temperature below 1900 °C [11–13].

Increasing the chromite content in the mixture decreases its ability to densify, which is related to poor sintering tendency of chromium oxide [14]. However, increasing the sintering temperature enhances the tendency of chromium oxides to crystallize [15].

In the present study, an attempt has been made to prepare magnesite–chrome composite by utilizing Chinese sintered magnesite and Indian friable chrome ore in presence of titania as additive. Three types of batch compositions containing 5% Cr_2O_3, 18% Cr_2O_3 and 30% Cr_2O_3 have been selected for developing mag–chrome composites.

2. Experimental

Sintered magnesite of Chinese origin and Indian friable chromite of Orissa region were used as raw materials in this study. The raw materials were vibro-milled separately for 24 h. Additives were incorporated in wt.% along with 5% PVA solution to the different batches. It was then properly mixed by fluidized bed mixer and after sieving in 20 mesh BS Sieve, briquettes of dimension 25 mm (ϕ) × 25 mm (h) were formed at a pressure of 100 MPa. The briquettes were first air dried and subsequently oven dried at 110 ± 5 °C for 24 h. Firing was carried out by program controlled electric muffle furnace at 1700 and 1750 °C with 2-h soaking.

The physical properties of aggregates were evaluated by bulk density and apparent porosity by standard liquid displacement method using Archimedes' Principle. The flexural strength of the aggregates at elevated temperature was determined by an instrument fabricated at Central Glass & Ceramic Research Institute, Calcutta, India. The test carried out by three point bending method of sample having dimension 50 mm × 5 mm × 4 mm. The rate of rising of temperature was maintained at 5 °C/min with a soaking time of 30 min at the test temperature. A load was then applied at the rate of 50 kg/min. Thermal shock resistance of the samples was studied by measuring the flexural strength retention on multiple air quenching cycles from 1000 °C to ambient air. For this purpose, the rectangular bars having dimensions 50 mm × 5 mm × 4 mm were heated to 1000 °C in an electric furnace with a soaking period of 30 min, then the samples were quenched in ambient air, cooled for 10 min followed by reheating at 1000 °C for 10 min. This cycle was repeated and retained flexural strength was measured after second and fifth cycles. Flexural strength was determined by standard three point bending method in INSTRON apparatus. Identification of different crystalline phases were carried out by X-ray powder diffraction studies using a nickel filtered Cu-K_α radiation with a scanning speed of 2° (2θ) per minute. Experiments were carried out using a PHILIPS PW (1790) X-RAY DIFFRACTOMETER. The microstructures of mag–chrome aggregates were observed under optical microscope. The samples were polished and viewed under reflected light.

3. Results and discussions

3.1. Raw material characterization

The chemical analysis of both magnesite and friable chrome ores has been given in Table 1. The sintered magnesia contains around 95.9% MgO. As the CaO content is low, the probability of low melting phase formation is less. The specific gravity is 3.57 which reaches the theoretical value. Surface area of sintered magnesia is 1.0. The specific surface area was measured by the instrument of Carlo Erba Strumentazione, Italy, Model 1750 Sorpty which is based on BET principle. XRD analysis shows that the major phase is MgO. The chemical analysis of chrome ore has shown 62% Cr_2O_3 which is considered to be reasonably high. Fe_2O_3 content of 12.3% reveals the presence of some iron spinel in the ore. Low silica content of around 0.4% will form minimum silicate phase in the matrix. Physical properties of chrome ore show high specific gravity of 4.34 and fineness in the narrow range with 51% in between $-150 + 240$ BS mesh. Mineralogical property through XRD study shows major phase is spinel and SiO_2 rich gangue is minor. However, the different spinels (e.g. $FeCr_2O_4$, $MgCr_2O_4$, $MgAl_2O_4$, $FeFe_2O_4$, $MgFe_2O_4$, etc.) cannot be distinguished, as their peaks are overlapping. A differential thermal analysis shows a minor endothermic peak at 300 °C indicating serpentine like gangue material. The physical properties of both MgO and chrome ore has been depicted in Table 2. Mineralogical properties of chrome ore and MgO have been given in Table 3.

Table 1
Chemical analysis of raw materials

Constituents	Sintered MgO	Chrome ore
SiO_2	2.0	0.4
Al_2O_3	0.6	9.8
Fe_2O_3	0.3	12.3
CaO	0.6	0.4
MgO	95.9	14.5
K_2O	0.1	0.01
Na_2O	0.2	0.02
LOI	1.1	–
Cr_2O_3	–	61.9

Table 2
Physical properties of raw materials

Properties	Sintered MgO	Chrome ore
Specific gravity	3.57	4.34
Sieve (BS mesh) analysis of as received materials (wt.%)	–	(−18 + 36) 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
Surface area of vibro-milled materials (m^2/g)	1.0	–

3.2. Densification

The bulk density (BD) and apparent porosity of different mag–chrome aggregates (5% Cr_2O_3, 18% Cr_2O_3 and 30% Cr_2O_3) are shown in Fig. 1a–c. In 5% Cr_2O_3 aggregates with TiO_2 addition, initially the BD increases followed by decrease for higher additive concentration. For 18% Cr_2O_3 and 30% Cr_2O_3 aggregates the BD starts falling from 3 wt.% TiO_2 onwards for both firing temperatures at 1700 and 1750 °C. Increase in the chromite content in the batch lowers the densification, because the sintering tendency of chromium oxide is poor [14]. In general, the average relative density for the samples sintered at 1750 °C varies between 91 and 96%. TiO_2 alter the grain boundary phase assemblage and morphology and ultimately changes the dihedral angle [4]. TiO_2 also helps in liquid phase sintering of MgO which is the main phase in 5% Cr_2O_3 mag–chrome composite. The magnitude of density increases in higher percentage of Cr_2O_3 (18 and 30%) is related to adding more amount of denser chromite ores. However, the sintering tendency of higher chrome containing batches fall as revealed from the high porosity level of the sintered products.

3.3. Microstructure

The photomicrographs of different mag–chrome aggregates sintered at 1750 °C are shown in Figs. 2–4. In 5% Cr_2O_3 aggregates with 1 wt.% TiO_2 the magnesia grains are mainly visible with few chrome spinel precipitated over MgO. In 18 and 30% Cr_2O_3 aggregates with 3 wt.% TiO_2 (Figs. 3 and 4) rounded magnesia grains and chrome spinels is present as exsolved phase over magnesia (white dots). Remnant chrome grains are also visible in the microstruc-

Table 3
Mineralogical properties of raw materials

Properties	Sintered MgO	Chrome ore
DTA endothermic peak (°C)	–	300
XRD (major phase)	MgO	Spinel

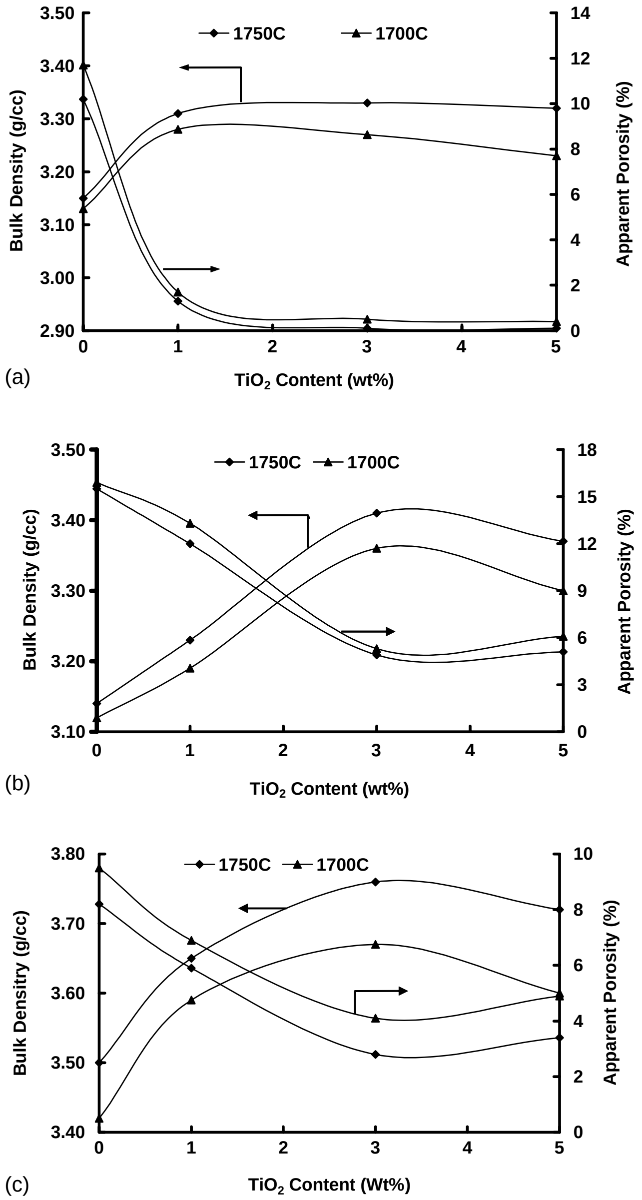

Fig. 1. Densification of mag–chrome aggregates: (a) 5% Cr_2O_3, (b) 18% Cr_2O_3 and (c) 30% Cr_2O_3.

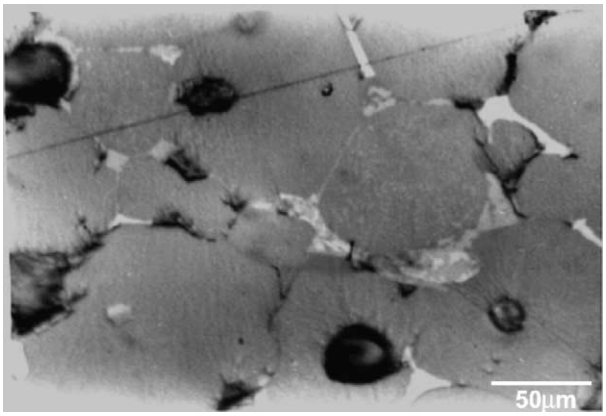

Fig. 2. Optical photomicrograph of 5% Cr_2O_3 mag–chrome aggregates sintered at 1750 °C with 1 wt.% TiO_2.

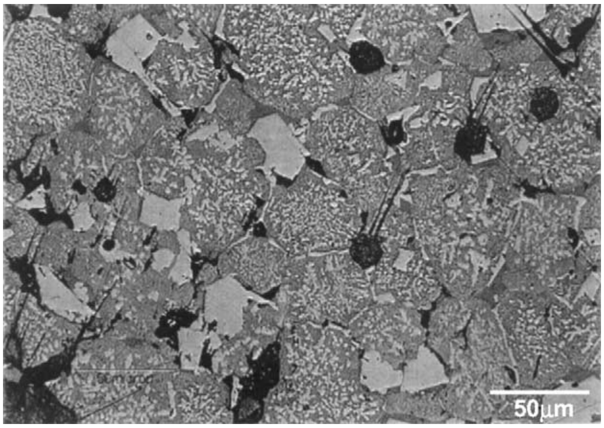

Fig. 3. Optical photomicrograph of 18% Cr_2O_3 mag–chrome aggregates sintered at 1750 °C with 3 wt.% TiO_2.

ture. $MgO–Cr_2O_3$ phase diagram suggests that 16% Cr_2O_3 can enter into MgO and exist as spinel solid solution at 1700 °C. The extra chrome is present as unreacted grain. Pores are visible in the intergranular position between MgO grains (18% Cr_2O_3 aggregates).

The microstructure of 30% Cr_2O_3 aggregates depicts a composite phase of magnesia and chrome grains (Fig. 4). The magnesia grains are not rounded and the size is less compared to the previous micrographs. In this case the diffusion of Mg^{2+} is obstructed in the presence of large amount of remnant chrome grains. Therefore, the densification is hindered with increase in pore phase. However, this composite microstructure is otherwise helpful to increase the mechanical properties of the aggregates.

3.4. Hot modulus of rupture (HMOR)

The hot modulus of rupture at 1300 °C of the sintered mag–chrome aggregates is shown in Fig. 5a–c. It reveals that TiO_2 incorporation up to 3 wt.% increases the HMOR of all the samples. TiO_2 addition in this level improves densification, which is responsible for higher strength of the product. Hot strength of the samples with 5 wt.% TiO_2 deteriorates due to presence of excessive liquid phase. Therefore, the liquid phase above a certain level lowers the hot strength of the composites. Aggregates containing higher amount of chromite (30% Cr_2O_3) possess better hot strength. In spite of lower density of 30% Cr_2O_3 aggregates, presence of homogeneously distributed composite phase of chrome spinel and magnesia in this sample is responsible for improving the strength. The initial crack formation in the first phase is arrested in the second dissimilar phase resulting in delayed fracture of the aggregates.

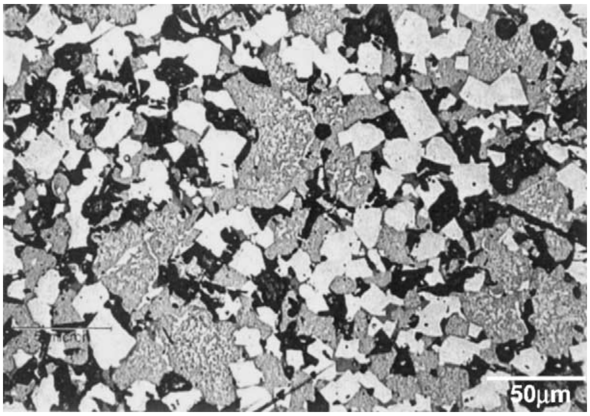

Fig. 4. Optical photomicrograph of 30% Cr_2O_3 mag–chrome aggregates sintered at 1750 °C with 3 wt.% TiO_2.

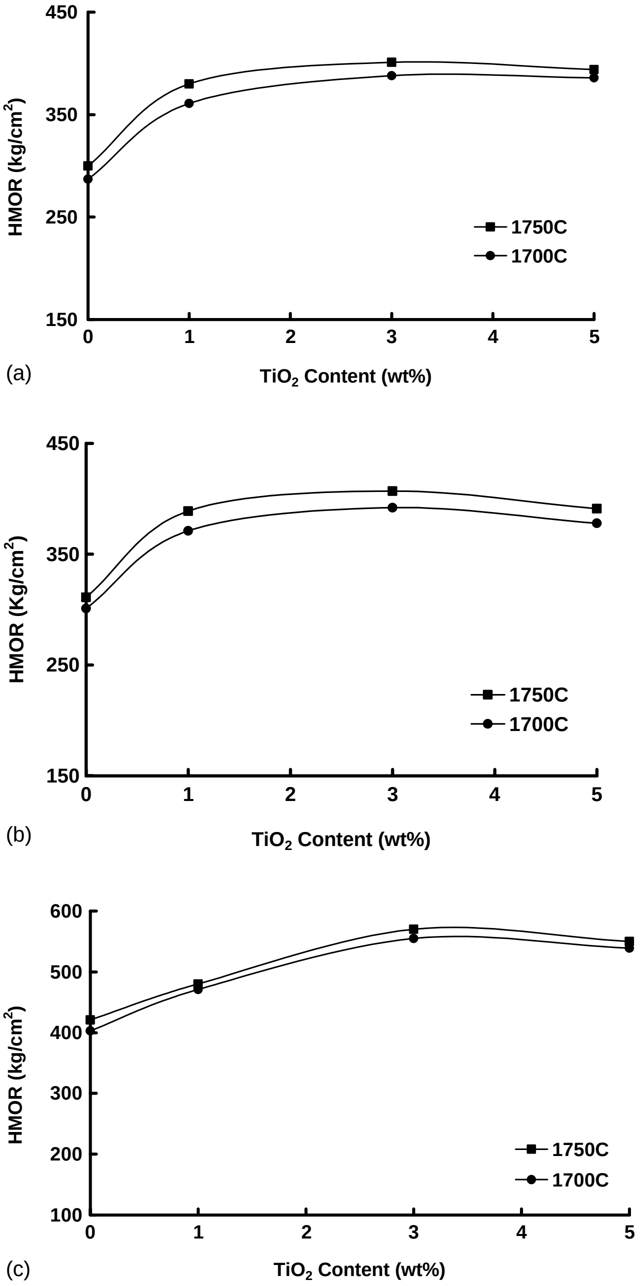

Fig. 5. Hot MOR of mag–chrome aggregates: (a) 5% Cr_2O_3, (b) 18% Cr_2O_3 and (c) 30% Cr_2O_3.

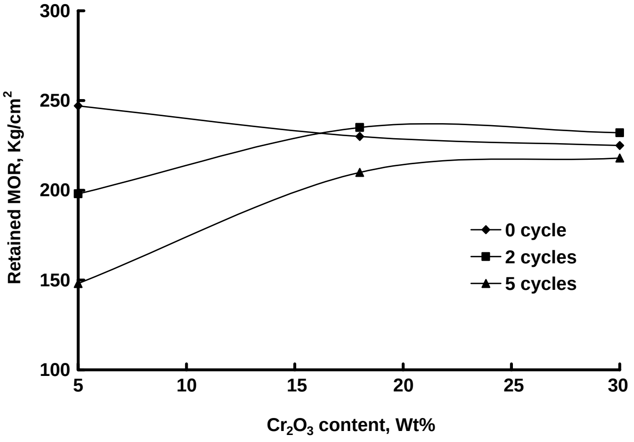

Fig. 6. Retained strength after thermal shock of mag–chrome aggregates.

3.5. *Retained strength after thermal shock*

Cold strength of the batches shows (Fig. 6) 5% Cr_2O_3 aggregates having a slightly higher strength compared to high chrome batches. The relatively lower strength of high chrome aggregates is attributed to higher porosity which breaks at lower load. Introduction of thermal shock results a drastic fall in strength for 5% Cr_2O_3 mag–chrome aggregates. In spite of having higher densification in this sample the presence of majority rounded MgO grains, which possess higher thermal expansion fails at lower strength. On the contrary for higher chrome containing samples though have higher porosity does not deteriorate the strength even after five cycles of thermal shock. The thermal expansion mismatch between remnant chrome grain and MgO develops microcracking in the grain boundary and arrest the crack propagation [16,17]. Moreover, the reduction in pore size and lower thermal expansion coefficient of chrome spinel controls the strength degradation of these samples. Finally, exsolution of secondary spinel over MgO acts as grain to grain bonding and maintain the retained strength.

4. Conclusions

(a) Densification of magnesite chrome aggregates (5 to 30% Cr_2O_3) is enhanced in the presence of additive TiO_2. The additive alters the grain boundary phase assemblage and promotes liquid phase sintering.
(b) Densification tendency deteriorates with the increasing chrome content as the sintering tendency of chromium oxide is poor.
(c) The microstructure of mag-chrome aggregates consist MgO with exsolved chrome spinel precipitates over MgO and the rest present as remnant phase.
(d) TiO_2 incorporation up to certain level improves the hot strength due to increase of densification. Thereafter, the strength falls due to excessive liquid phase.
(e) Thermal shock resistance of aggregates containing high chrome is superior, due to presence of multiphase microstructure consisting different thermal expansion. This creates microcracking and the strength degradation is delayed.

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