

## Effects of $\text{Cr}_2\text{O}_3$ on physical and mechanical properties of in-situ spinel containing castable

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### Abstract

Increasing demands for cement, iron and steel industries for refractories with suitable workability in severe conditions (without any environmental risks), make the refractories' researches to be an active area. Refractories containing Spinel has been developed with addition of chromia as a substitute in refractories using Magnesite - chromite. In this research, different amounts of  $\text{Cr}_2\text{O}_3$  were applied in situ spinel containing castable and its effects on the physical and mechanical properties of the system were investigated. After mixing the raw materials, they were poured into the mold, using casting and vibrating methods. After drying samples at 110 °C, sintering process was conducted at 1400 and 1600 °C. Physical and mechanical properties were measured (including bulk density, apparent porosity and cold crushing strength (CCS)). X-ray diffraction analysis (XRD) and Scanning Electron Microscope (SEM) were used to study the formed phases and microstructure.

The results indicate that increasing the amount of  $\text{Cr}_2\text{O}_3$ , strength, bulk density and apparent porosity were decreased. Change in the apparent porosity was due to filling properties of  $\text{Cr}_2\text{O}_3$  at low temperature and it seems to be related to the liquid phase sintering at high temperature. The data indicated that the CCS was increased by increasing  $\text{Cr}_2\text{O}_3$  content and temperature.

The XRD pattern showed that  $\text{MgAl}_2\text{O}_4$ ,  $\text{Mg}(\text{Al,Cr})_2\text{O}_4$  and  $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$  were the main detected phases in the system.

**Keywords:** Chromium oxide, Spinel, Castable, XRD, SEM.

### 1. Introduction

In the advent of quality steel making processes, it became essential to optimum for good quality of refractories, especially monolithic castables is suitable in the presence of molten slag and metal<sup>1)</sup>. The growing demand and application for these castable materials encourage researchers and producers to investigate their physical, chemical thermo-mechanical and mechanical properties. Magnesium aluminate spinel is now extensively applied in high performance refractory castables materials<sup>2,3)</sup>. However, these unshaped castables materials in various forms (e.g. low, ultralow and no cement, etc.) become increasingly popular

in both ferrous and nonferrous industries due to the number of operational flexibilities, in comparison with shaped refractories<sup>4)</sup>. Magnesium aluminate spinel possesses an unusual combination of properties. They are important materials for scientists. High melting point, excellent high temperature mechanical, thermal, chemical and spalling properties have made it an essential refractory for many applications, such as, lining materials, for bottom and sidewalls of steel ladles, transition and burning zones of cement rotary kilns and checker work of glass tank furnace regenerators<sup>5)</sup>.

Development of magnesium aluminate spinel bodies and the methods of production of these refractories have been started nearly a century ago (about 1905)<sup>6)</sup>. The main system of  $\text{MgO}-\text{Al}_2\text{O}_3$  was established in 1916. However, the use of spinel products was limited due to the high cost of their production. With the advancement in science and technology, significant development made in this regards<sup>7)</sup>. In the castable Refractories with additive  $\text{Cr}_2\text{O}_3$ , spinel phase (in situ one) is formed due to reaction of  $\text{MgO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ .  $\text{Cr}_2\text{O}_3$  makes solid solution with spinel. It

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enters into the spinel lattice (chromium ion substitutes aluminum ion due to ionic similarities, chromium ion size is 0.6 Å and aluminum ion size is 0.5 Å) and increases diffusivity of cations and improves the mass transfer for densification process. The studies have shown that at higher temperatures, oxidation state of chromium shifts to higher values causing a defective spinel structure, with cation vacancy, which in turn enhances the mass transfer and densification<sup>8)</sup>. Increasing the Cr<sub>2</sub>O<sub>3</sub> content improves the spinel crystals density as well as direct spinel–spinel bonding strength and improves the bulk density of compositions<sup>9)</sup>.

The detailed studies on the effect of Cr<sub>2</sub>O<sub>3</sub> addition on the properties of the stoichiometric spinel are not available. The aim of this study is to determine how additive materials affect the mineralogical composition, the chemistry of the coexisting phases, and the behavior of MA spinel-based refractories. The study mainly deals with refractory properties. Cr<sub>2</sub>O<sub>3</sub> was added at 1, 2 and 3 wt.% to three spinel compositions. After mixing castable materials, they were poured into the mold. Then the samples were dried at 110 °C and were sintered in the temperature range 1400 to 1600 °C.

## 2. Experimental Procedure

In the present study, it was used the dead burn magnesite (MgO > 97.36 %), tabular alumina and reactive alumina (Al<sub>2</sub>O<sub>3</sub> > 99.5%), microsilica (SiO<sub>2</sub> > 95), Cement (secar 71), chromia and Castament FS20 as raw materials. It was used 0 to 3 wt% chromia as additives; these contents were labeled as CCr0, CCr1, CCr2 and CCr3, respectively (see Table 1). Particles size distribution of raw materials were as follows: finer than 0.5 mm for magnesia, 2 µm for reactive alumina, 0-0.045, 0-0.2, 0-0.5, 0.5-1, 1-2, 2-5 mm for tabular alumina, 0.15 µm for microsilica, and 80 µm for chromia. After mixing castable materials for

3 min in a laboratory mixer with a binding agent, the samples were shaped to cubic form (4×4×4 cm). After the castables were poured into the mold, they were vibrated for 1min to remove the bubbles. The castables were aged in a plastic container at room temperature for 24 hrs. The samples were dried at 110 °C and sintered at 1600 °C with 2 hrs soaking time at peak temperature. The following studies were conducted: X- ray diffraction method (using Cu-Kα radiation) in order to phase analysis, bulk density and apparent porosity and CCS. Microstructural analysis was conducted using a scanning electron microscope (LEO SEM-440i).

## 3. Results and Discussion

### 3.1. Bulk density and apparent porosity

Figs. 1 and 2 show the results of bulk density and apparent porosity with different amounts of chromium oxide at 110, 1400 and 1600 °C, respectively. As is obvious, bulk density has been increased with increasing temperature; so it indicates that the sintering progress at high temperature. Bulk density has been also increased with increasing chromia content at 110 °C.

The results are indicated a relatively slow increase in the density of samples which can be due to density difference between Cr<sub>2</sub>O<sub>3</sub> (with density 5.2 gcm<sup>-3</sup> for) and other substances. In the sintered samples at 1600°C, it was observed a similar behavior with increasing Cr<sub>2</sub>O<sub>3</sub> from 1 to 3%. The apparent porosity is also reduced with increasing temperature.

The results confirmed that apparent porosity of alumina-magnesia ultra low castable cement is decreased with increasing Cr<sub>2</sub>O<sub>3</sub> in the dry state. The Change in the apparent porosity may be due to filling properties of Cr<sub>2</sub>O<sub>3</sub>. At high temperature i.e. 1600 °C, It seems that decrease in porosity with increasing Cr<sub>2</sub>O<sub>3</sub> to be related to liquid phase sintering at high temperature.

Table 1. The Code of samples at different temperature with different amounts of additive

Sample Code	Cr <sub>2</sub> O <sub>3</sub> wt%	Heat treatment Temperature (°C)
CCr0-11	0	110
CCr1-11	1	110
CCr2-11	2	110
CCr3-11	3	110
CCr0-14	0	1400
CCr1-14	1	1400
CCr2-14	2	1400
CCr3-14	3	1400
CCr0-16	0	1600
CCr1-16	1	1600
CCr2-16	2	1600
CCr3-16	3	1600

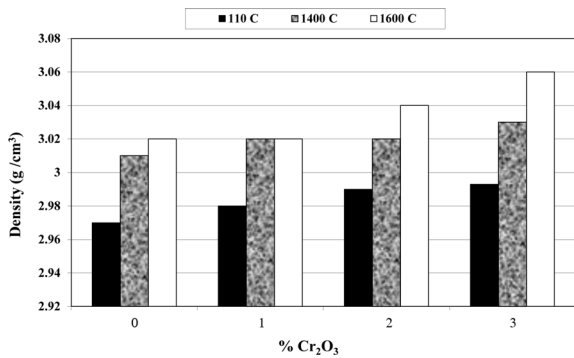


Fig. 1. Bulk Density vs. the amount Cr<sub>2</sub>O<sub>3</sub> at different temperatures.

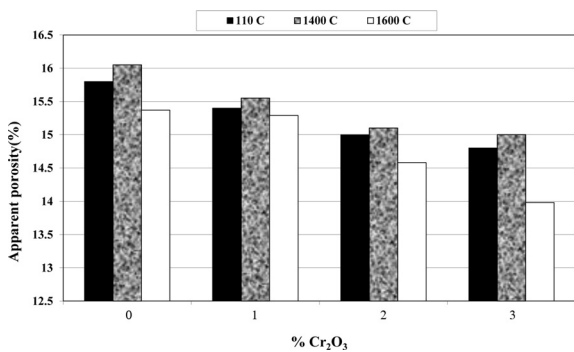


Fig. 2. Apparent porosity vs. the amount of Cr<sub>2</sub>O<sub>3</sub> at different temperatures.

### 3.2. Mechanical properties

Fig. 3 shows the results of Cold Compressive Strength (CCS) vs. different amounts of Cr<sub>2</sub>O<sub>3</sub> at different temperatures (at 110, 1400 and 1600 °C, respectively). As shown in this figure, with increasing Cr<sub>2</sub>O<sub>3</sub> and temperature, the CCS is increased. This is related to the formation of amount chromium rich spinel which was enhanced with temperature, probably, due to the direct and stronger link and joints between grains. The chemical corrosion resistance was also improved. Sound likes that Cr<sub>2</sub>O<sub>3</sub> has entered into the spinel structure to form solid solution, and this was also enhanced with temperature. Another and secondary spinel phase [Mg(Al,Cr)<sub>2</sub>O<sub>4</sub>] is

also formed within the grain boundary, counts for mechanical improvement.

### 3.3. phase and microstructural Analysis

As in Figs. 4 (a) and (b) shown in the dried samples without additive, Al<sub>2</sub>O<sub>3</sub> and MgO phases were only observed. At higher temperatures (1200 °C and higher), Al<sub>2</sub>O<sub>3</sub> and MgO react with together to form spinel. At higher temperatures (1400 °C and 1600 °C), spinel (MgAl<sub>2</sub>O<sub>4</sub>) and Al<sub>2</sub>O<sub>3</sub> (corundum) or solid solution of (Al<sub>1-x</sub>Cr<sub>x</sub>)<sub>2</sub>O<sub>3</sub> phases were the major phases in the system. By increasing the temperature, the grain growth is also was occurred (probably, due to the liquid phase process) along with the formation of more spinel phase.

Fig. 4 (b) shows the effect of Cr<sub>2</sub>O<sub>3</sub> (with 3wt% additive) at 1600 °C. Sounds like that substitution of Cr<sup>3+</sup> to Al<sup>3+</sup> in the spinel network, Cr<sub>2</sub>O<sub>3</sub> rich solid solution of spinel is formed. XRD pattern has shown the at 1600 °C with different amount of additive in Fig. 5. Besides the above mentioned phases, the solid solution of Alumina is also observed [(Al<sub>1-x</sub>Cr<sub>x</sub>)<sub>2</sub>O<sub>3</sub>]. As is obvious from XRD pattern, in the sintering process, the main peaks of MgAl<sub>2</sub>O<sub>4</sub> and Mg(Al,Cr)<sub>2</sub>O<sub>4</sub> become sharper along with diminishing the main peak of chrome oxide. Some displacements in the main peaks of spinel was observed, due to the dissolution of chromium oxide at sintering stage.

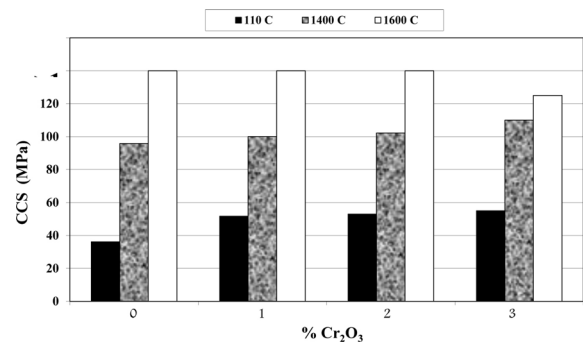
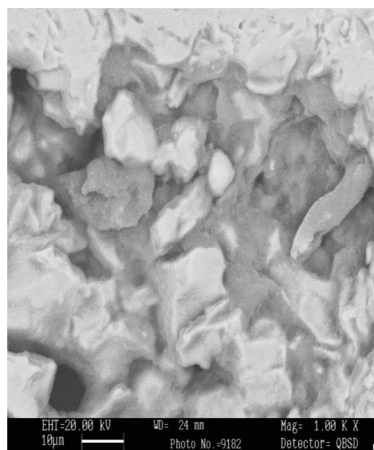
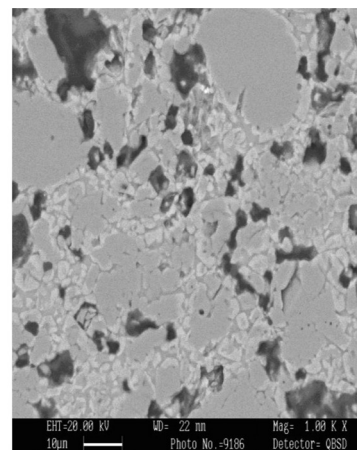


Fig. 3. CCS vs. the amount of Cr<sub>2</sub>O<sub>3</sub> at different temperatures.



(a)



(b)

Fig. 4. SEM Image of (a) CCr 0-16 sample and (b) CCr 3-16 sample.

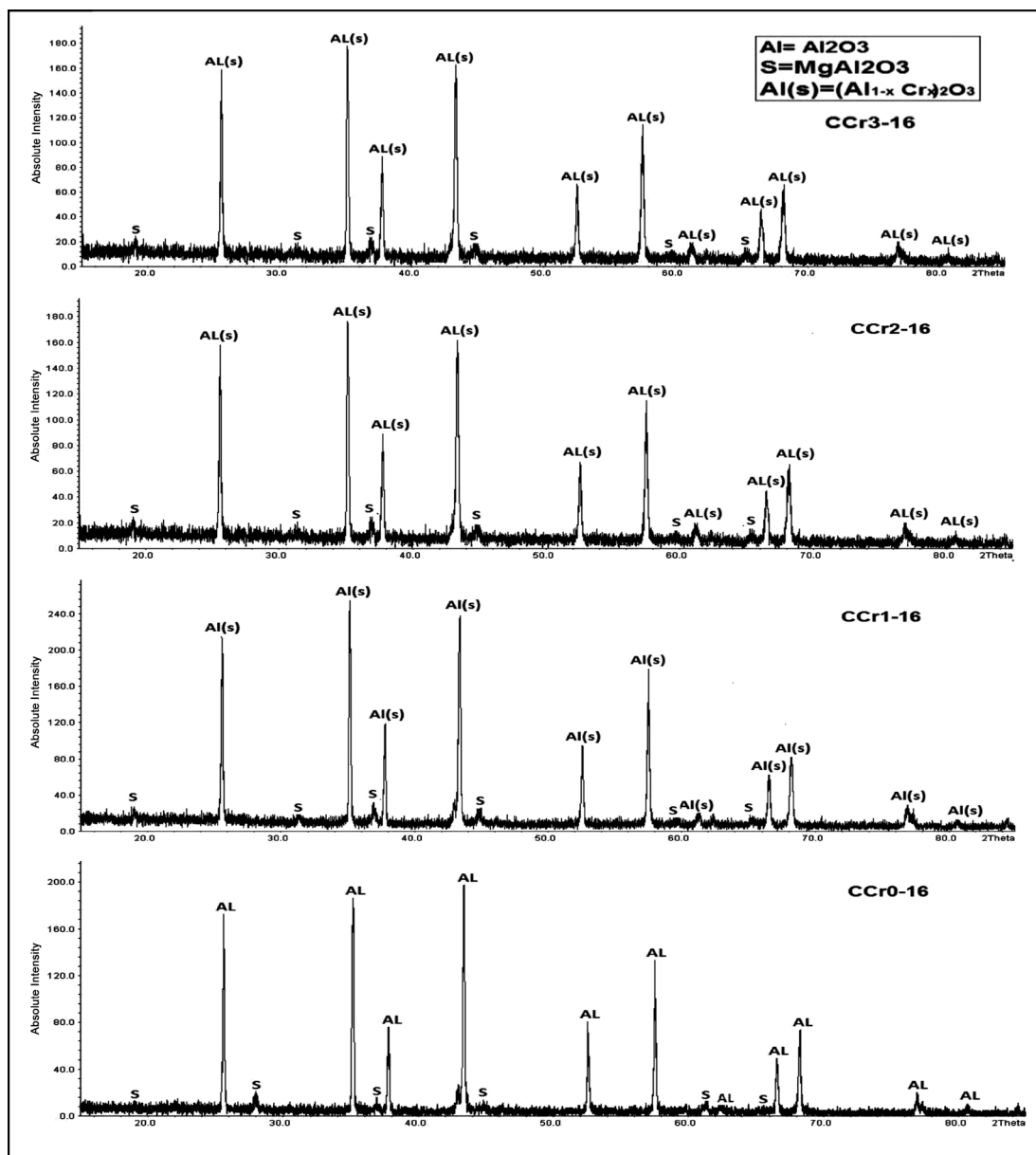


Fig. 5. X-ray diffraction patterns of samples with different values  $Cr_2O_3$  at temperature  $1600\text{ }^\circ\text{C}$ .

#### 4. Conclusion

Based on the above discussion, it can be concluded that:

- The bulk density was increased with temperature and with increasing of chromia content, indicating the sintering progress at high temperature.
- In the samples sintered at higher temperature, a similar behavior was observed.
- At high temperature, the change in the porosity (decreasing with increasing of  $Cr_2O_3$ ), seems to be related to the liquid phase sintering.
- CCS was increased with increasing  $Cr_2O_3$  content and temperature.
- $MgAl_2O_4$ ,  $Mg(Al,Cr)_2O_4$  and  $(Al_{1-x}Cr_x)_2O_3$  were the main detected phases in the system.

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