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Synthesis of dehydrated magnesium borate powders and the effect on the properties of MgO-C refractories

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For the synthesis of magnesium borate powder, magnesium carbonate and boric acid powders were mixed in ethanol and then investigated by differential thermal analysis (DTA) and thermogravimetry (TG). X-ray diffraction (XRD) results of the samples showed the formation of $Mg_2B_2O_5$ phase at 500 °C and $Mg_3B_2O_6$ at 650 °C. The synthesized powder used as an antioxidant additive in magnesia-graphite bodies containing 20% graphite. After curing at 200 °C and firing at 1200 °C and 1400 °C for 2 hrs in a coke bed environment, its physical and mechanical properties and also microstructural features were investigated. The results showed that after curing at 250 °C, the addition of magnesium borate led to an increase in cold crushing strength at about 20%. Comparing the samples with additives and without any additives at 1200 and 1400 °C showed that the cold crushing strengths were improved about 45%, 35%, respectively. In addition, the results clarified that magnesium borate ($Mg_3B_2O_6$) phase led to improve oxidation resistance.

Key words: Magnesium borate, MgO-C refractories, Oxidation resistance.

Introduction

Carbon-containing refractories such as magnesiagraphite (MgO-C) are widely being used in various applications such as basic oxygen furnaces (BOF), electric arc furnaces (EAF), and steel ladles for different zones [1-3]. The excellent thermal shock and corrosion resistance are due to the presence of graphite in MgO-C refractories. The presence of graphite in these refractories leads to a decrease in oxidation resistance and also low mechanical strength. To overcome this, antioxidants are added to the MgO-C refractories [4-7].

The antioxidants commonly used in MgO-C refractories include metals (such as Al, Si,...), alloys (Such as Al-Mg, Al-Si-Mg,...), carbides (such as B_4C , $Al_8B_4C_7$, SiC) and boron-based compounds (such as CaB_6 , ZrB_2 , MgB_2) [8-13].

Magnesium borates are divided into two categories; hydrated and dehydrate magnesium borate. Hydrated magnesium borate compounds have MgO.3B₂O₃.nH₂O formula, which n can be (3.5, 5, 6, 7 and 7.5). On the other hand, dehydrated magnesium borates exist as compounds such as $Mg_3B_2O_6$, $Mg_2B_2O_5$, and MgB_2O_4 [14].

This powder has a verity of applications such as a good catalyst for the conversion of hydrocarbons, luminescent materials for using X-ray screens and electronic ceramics reinforcement, and plastics or aluminium/magnesium matrix alloy production. Magnesium borate is being used in basic oxygen steelmaking, due to many desirable properties such as excellent corrosion and erosion resistance and also thermal shock resistance [15-19].

For the synthesis of magnesium borate, different of precursors had been used. (MgCl₂· $6H_2O$, H₃BO₃, and Na₂B₄O₇), (MgCl₂· $6H_2O$ and NaBH₄), (Mg(OH)₂ and H₃BO₃) were used by Kipcak et al.[20], Li et al.[21], and Elssfah et al.[22], respectively. According to previous studies, different methods such as mechanochemical technique and sintering process, thermal evaporation, partial precipitation technique, solid-state Method, and etc. have been used to synthesize magnesium borate [13, 20, 22].

In this research, a simple and low-cost method was used to synthesize magnesium borate powders. After that, the resulted powder was used as an antioxidant in MgO-C bodies. The reason of using this antioxidant was due to its low-cost preparation and synthesize against other antioxidants. Oxidation resistance and microstructural, mechanical, and physical properties of MgO-C bodies with and without this antioxidant were investigated, too.

Experimental

Synthesis of magnesium borate (Mg₂B₂O₅)

The raw materials used in this study for the synthesis of $Mg_2B_2O_5$ were $MgCO_3$ and H_3BO_3 with commercial grade (99.5% purity, China). For the synthesis of magnesium borate, 45 wt.% of $MgCO_3$ and 55 wt.%

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Table 1. Chemical properties of china sintered magnesia.

	MgO	CaO	SiO_2	Al_2O_3	Fe ₂ O ₃
China sintered magnesia Density: 3.3 g/ cm ³	97.5	1.2	0.6	0.3	0.4

Table 2. Physical properties of china flake graphite.

	carbon	Ash (%)	moisture	voltaire's matter (%)
China flake graphite Density: 2.24 g/ cm ³	92	5.1	0.6	2.2

Table 3. Composition of the MgO-C brick samples.

		Comp	osition ((wt. %)
Raw material	Size distribution	S	S4	S6
	$<$ 74 μm	25	25	25
Sintered magnesia	74 μm-500 μm	33	33	33
	500 μm- 1000 μm	22	22	22
Total (wt .% MgO)		80	80	80
Flaky graphite	< 250 µm	20	20	20
Borate magnesium powder		_	+4	+6
Liquid novolak resin		+6	+6	+6
Hexamine (additive of the resin)		+0.2	+0.2	+0.2

H₃BO₃ were mixed in a jar mill for 24 hrs (the powder to ball ratio was 1 : 10). Then, in order to evaporate ethanol, the suspension placed on a hot plate at 70 °C. The resulted powder was characterized by using DTA/ TG analysis (STA, Bahr thermal analysis Germany) to study the reaction mechanisms at a heating rate of 10 K/min in air. X-Ray diffractometry (XRD, JDX-8030, Japan), using Cu-ka ($\lambda = 0.1540$ nm) radiation and scanning electron microscope (SEM, Mira 3-XMU, Czech Republic) were used for evaluating the phase analysis and microstructure analysis of the powders.

Preperation of magnesia-graphite specimens

The raw materials used in the present study were dead-burn magnesia(MgO), flake graphite, magnesium borate(Mg₂B₂O₅), liquid phenolic resin, and hexa (additive of the resin). Chemical properties of china sintered magnesia and physical properties of flake graphite are indicated in Tables 1,2, respectively.

Andreasen equation (formula 1) [23] was used for the preparation of the samples.

$$\mathbf{w} = (\mathbf{D}/\mathbf{D}_1)^n \times 100 \tag{1}$$

where w is the percentage of the material with the size less than D, D_1 is the maximum particle size in

distribution and n is an empirical parameter, which was taken 0.45 to obtain optimum bulk density and apparent porosity.

The raw materials were hand mixed (25 min) at room temperature. After mixing, they were aged for 12 hrs. Then, the powders were uniaxially pressed at 150 MPa. The prepared samples were cured at 250 °C for 15 hrs. Details of all the batch compositions are presented in Table 3.

In order to evaluate physical properties (bulk density and cold crushing strength (CCS), the cured samples were placed in a SiC saggar and then filled with coke. Then SiC saggar placed in an electrical furnace at 1200 and 1400 °C. Soaking time and heating rate at both temperatures were 2 hrs and 5 K/min, respectively. Furthermore, bulk density and cold crushing strength (CCS) of the specimens were measured according to ASTM (C 830-00) and ASTM (C 133-97), respectively.

In order to evaluate oxidation resistance, the cured samples were placed in a tube furnace at various temperatures (1000,1200, and 1400 °C) with a heating rate of 10 K/min in a neutral atmosphere (Ar). After that, in order to obtain an oxidizing atmosphere for the oxidation resistance test, injecting air into the furnace tube at maximum temperature was performed and the samples were kept at the desired temperatures for 2 hrs.

In order to enhance the accuracy of the weight change and omit the volatiles from phenolic resin, before heating for oxidation resistance tests, the samples placed in a coke bed environment at 550 °C for 2 hrs in an electrical furnace. Samples weight changes for oxidation resistance were measured according to formula 2[24].

Carbon loss (wt.%) = $((m_1 - m_2)/(m_3 \times \% G))*100$ (2)

where m_1 is the weight of the heat-treated sample (in coke bed environment at 550 °C for 2 hrs), m_2 the weight of the oxidized sample, m_3 is the primary sample weight and G is the wt.% graphite.

The phase and microstructure analysis of the specimens were performed by X-ray diffractometry and scanning electron microscopy.

Results and Discussion

Evaluation of thermal and phase analysis for mixture powders

Fig. 1 indicates the TGA plot of the mixture powders. As shown in this figure, there is an endothermic peak at 130 °C which was related to the removing of the moisture. The endothermic peak at 180 °C (according to the HSC chemistry software (Fig. 2) and reaction 2) and the endothermic peak at 290 °C (according to the HSC chemistry software (Fig. 3) and reaction 3)[25] were related to the decomposition of boric acid and magnesium carbonate, respectively. According to the



Fig. 1. DTA/TG analyses curve of the mixture powders by a heating rate of 10 °C/min.



Fig. 2. Standard Gibbes free energy vs. temperature for the decomposition of H_3BO_3 .



Fig. 3. Standard Gibbes free energy vs. temperature for the decomposition of MgCO₃.

XRD results of the mixture powders at 500 °C and 650 °C, which are shown in Figs. 4 and 5, the exothermic peaks were related to the formation of suanite ($Mg_2B_2O_5$) and magnesium borate ($Mg_3B_2O_6$), respectively.



Fig. 4. XRD pattern of the mixture powders at 500 °C.



Fig. 5. XRD pattern of the mixture powders at 650 °C.

The weight loss of mixture powders is due to the decomposition of boric acid and magnesium carbonate. Boron oxide (B_2O_3) can evaporate according to the partial pressure of oxygen and lead to the release of



Fig. 6. SEM image of the mixture powders heat-treated at 500 °C for 2 hrs.



Fig. 7. Bulk density of specimens cured at 250 °C and then fired at 1200, 1400 °C in a coke bed environment for 2 hrs.

gasses such as BO₂, B₂O₂ and etc. [26]. Fig. 6 shows SEM image of the mixture powders, which were heated in an electrical furnace at 500 °C for 2 hrs. As shown in this figure, magnesium borate particles are pseudo-spherical. Furthermore, the size distribution was observed between about 0.4-0.6 μ m.

The effect of magnesium borate on MgO-C refractories

Fig. 7 indicates the results of the bulk density of the specimens. According to this figure, the specimens without additives (S) had the least bulk density. In addition, comparing the specimens with/without antioxidants at 1400 °C indicated that the bulk density was improved about 5%. No significant differences between the bulk density of S4 and S6 were observed.

The results of the cold crushing strength of the



Fig. 8. CCS of specimens cured at 250 °C and then fired at 1200, 1400 °C in a coke bed environment for 2 hrs.



Fig. 9. SEM image of the specimen containing 6 wt.% $Mg_2B_2O_5$ after firing in a coke bed environment at 1400 °C for 2 hrs (SM: sintered magnesia, G: graphite).



Fig. 10. XRD pattern of the sample containing 6 wt. % $Mg_2B_2O_5$ fired at a 1400 °C and b) 1200 °C in coke bed for 2 hrs.

specimens indicated in Fig. 8. According to this figure, the results of CCS of the specimens containing magnesium borate after firing was about 20% better than the specimens without magnesium borate. This is because of the presence of resin bond (because of phenolic resin) in curing specimens which can improve CCS. In addition, by increasing the temperature from 250 to 1400 °C, due to the conversion of resin bond to amorphous carbon bond in all samples, CCS of the



Fig. 11. XRD patterns of MgO-C refractory specimens containing 6 wt. % $Mg_2B_2O_5$ used in oxidation tests at: (A) 1400 °C; (B) 1200 °C.



Fig. 12. Cross section of MgO-C samples after oxidation at 1400 °C for 2 hrs in the air: (A) without antioxidant; (B) containing of 6 wt. % $Mg_2B_2O_5$.



Fig. 13. Carbon loss % of samples with/without antioxidant at various temperatures, in the oxidized atmosphere for 2 hrs.

specimens were decreased [27].

Fig. 9 shows the SEM images of MgO-C refractories containing 6 wt. % $Mg_2B_2O_5$ fired in a coke bed environment at 1400 °C for 2 hrs. Magnesium borate (Mg₃B₂O₆) phase was not possible to observe because EDS could not identify the element boron. But, the results of XRD shown in Fig. 10 clarified the presence of magnesium borate(Mg₃B₂O₆) phase in MgO-C refractories.

Fig. 11 shows XRD result of magnesia-graphite sample containing 6 wt.% $Mg_2B_2O_5$ and oxidized for 2 hrs at 1200 and 1400 °C. According to these results, $Mg_3B_2O_6$ is formed at both temperatures, but the same amount of $Mg_3B_2O_6$ formed at 1200°C compared to 1400 °C.

Fig. 12 depicts the oxidation resistance of MgO-C specimens after 2 hrs at 1400 °C. Fig. 13 shows the carbon loss (wt. %) of refractory bricks with and without antioxidant. It can be seen that the sample containing 6 wt. % Mg₂B₂O₅ showed a better oxidation resistance at 1400 °C. Moreover, the results clarified that the sample without antioxidant showed lower oxidation resistance. According to this figure, by increasing the temperature from 1000 to 1400 °C, the oxidation resistance of specimens was improved. Furthermore, the oxidation resistance at 1400 °C of S6 was about 40% better in compare to S. According to Fig. 11, XRD results of the sample containing 6 wt.% Mg₂B₂O₅ indicates the formation of Mg₃B₂O₆ phase. This phase can easily fill the block porosities. Furthermore, Mg₃B₂O₆ may melt above 1340 °C and forms a liquid phase which leads to the formation of a dense layer in MgO-C refractory. Because of these two reasons, the diffusion of oxygen along the refractory can be prevented, which were in a good agreement with those reported by the previous studies [28, 29].

Conclusions

In the first step, magnesium borate $(Mg_2B_2O_5)$ was successfully synthesized by powder mixing technique. According to the result of STA and XRD, Mg₂B₂O₅ phase was formed by heating at 500 °C for 2 hrs in an electrical furnace. In the second step, the effect of $Mg_2B_2O_5$ (as an antioxidant) on the physical and mechanical properties and also oxidation resistance of MgO-C refractory samples were investigated. The addition of Mg₂B₂O₅ in refractory samples led to the formation of $Mg_3B_2O_6$. The presence of this phase in refractories improved the mechanical properties and oxidation resistance. The Mg₃B₂O₆ phase improved the oxidation resistance of the specimens compared to the samples without antioxidant (about 40%). This phase can fill porosities and melt at 1340 °C and consequently, the liquid phase may be formed, which led to the filling of porosities and the formation of a dense layer in MgO-C refractories. However, this phase had an excellent effect on the oxidation resistance.

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