

TAILORING THE EXPANSION OF ALUMINA-MAGNESIA CEMENT-BONDED CASTABLES BY BaTiO_3 ADDITION

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ABSTRACT

Owing to the *in situ* spinel and calcium hexaluminate formation, alumina-magnesia cement-bonded castables present excellent properties such as slag and thermal shock resistance. However, the expansion derived from *in situ* reactions is a key issue for keeping the integrity of castables. Normally, mineralizing compounds were used to control the overall expansion as well as the phase and microstructure evolution of castables. In this work, the influence of BaTiO_3 addition on the expansion of alumina-magnesia cement-bonded castables was investigated by combining of the effects of BaO and TiO_2 . The phase composition and microstructure of castables with BaTiO_3 addition after calcining at 1250-1450 °C were characterized by X-ray diffraction and scanning electron microscope. The results indicated that BaTiO_3 accelerated the formation of CA_6 and the growth of spinel in castables. By comparison with the reference, lower expansion and higher strength for castables with addition of 2.92 wt% BaTiO_3 calcined at 1450 °C were achieved. It was demonstrated that element Ba and Ti played a role in enhancing the bonding and tailoring the expansion.

Keywords: castables; BaTiO_3 ; CA_6 ; spinel; properties

INTRODUCTION

Due to the excellent properties including suitable workability, mechanical strength, thermal shock resistance and superior slag resistance^[1-3], alumina-magnesia refractory castables bonded with calcium aluminate cement (CAC) were widely used in steel industry such as the wall and bottom impact of steel ladles^[4]. However, in order to satisfy the more tough service environment and obtain the better products, the properties of alumina-magnesia castables should be improved^[5].

Mineralizer addition in alumina-magnesia refractory castables was regarded as one of most effective methods to improve the properties of refractory^[6]. Compared with other design ways, adding additives was more economical^[7]. On the other side, the original characteristics of materials could be greatly retained by this way. TiO_2 was one of most effective mineralizers to strengthen the capacities of alumina-magnesia refractory castables. It had been proved that adding TiO_2 can accelerate the formation of CA_6 and *in-situ* spinel, improve mechanical strength of castables and control the expansion of materials^[4].

For attaining enhanced properties, other additives such as BaO were also studied in Al_2O_3 - MgO - CaO ternary system^[8]. Besides, researchers have discovered that Ba^{2+} could solute into crystal structure of CA_6 . Eventually, the thickness of CA_6 increased with the function of Ba^{2+} ^[9]. Considering the influence of TiO_2 and BaO on alumina-magnesia refractory castables, BaTiO_3 could be regarded as an alternative of them. The aim of this study was to explore the combined effect of Ba and Ti element on the phase evolution of alumina-magnesia refractory castables, and then tailor the expansion of castables by BaTiO_3 addition.

MATERIALS AND METHODS

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Alumina-magnesia refractory castables were prepared according to the compositions listed in Table 1. Coarse tabular alumina with $d \leq 6$ mm was used as aggregates. The castables' matrix comprised reactive alumina, calcined magnesia, calcium aluminate cement. 1wt% of silicon fume was added, aiming to generate a liquid phase at high temperature. Besides that, BaTiO_3 was selected as the mineralizer. The added water content for vibrocasting was about 4.5 wt%.

Tab. 1: Composition of alumina-magnesia refractory castables

Raw material	Content(wt%)		
	T0	TB0.5	TB1
Tabular alumina (≤ 6 mm) (Almatis)	61	61	61
Tabular alumina (≤ 200 mesh) (Almatis)	19	17.54	16.08
Reactive alumina (CL370) (Almatis)	7	7	7
Calcined magnesia (180mesh)	6	6	6
Calcium aluminate cement (Secar71) (Kerneos)	6	6	6
Silicon fume (951U) (Elkem)	1	1	1
BaTiO_3	0	1.46	2.92

After casting, all the castables were cured at 25 °C for 24 h with a relative humidity of 100%, and then dried at 110 °C for 24 h. All samples were calcined at 1250-1450 °C for 5 h, respectively. The permanent linear change (PLE) was measured in compliance with GB/T 5988-2007. The apparent porosity and the bulk density of samples were tested by the Archimedes technique. The cold modulus of rupture (CMOR) was measured with three-point bending tests. The phase composition of castables was analyzed by means of X-ray diffraction (XRD, Philips, X'pert Pro MPD, Netherlands). The microstructure and the chemical composition of the specimens were observed and measured with scanning electron microscopy (SEM, JEOL JSM-6610, Japan) and an energy-dispersive spectrometer (EDS, Bruker QUANTAX200 - 30, Germany).

RESULTS AND DISCUSSION

Phase composition and microstructure

The XRD patterns of alumina-magnesia refractory castables calcined at different temperature for 5 h are shown in Fig. 1. The main phases of specimens was alumina, spinel and CA_6 . There was a small amount of CA_6 generated in the samples with BaTiO_3 addition at a relative lower temperature (1250 °C), while the diffraction peak of CA_6 was only detected in sample T0 until the temperature reaching 1450 °C. Meanwhile, it could be found that the intensity of spinel in castables increased with BaTiO_3 addition, which demonstrated that the addition of BaTiO_3 decreased the forming temperature of CA_6 and speeded up

the spinel formation.

As shown in Fig. 2, the spinel peaks shifted to lower degree with BaTiO₃ content especially at the temperature 1450 °C. There were two chief causes. One was the solution of Ba or Ti into the structure of spinel, which led to the shift of diffraction peak for spinel. Another was that less alumina participated in the spinel formation because of more consumption of alumina in the CA₆ formation. Meanwhile, the CA₆ peak in samples with BaTiO₃ addition was also lower than that of reference sample at 1450 °C, which was accounted for the substitution Al (0.143 nm) by Mg (0.160 nm) and Ti (0.147 nm) with larger radius^[10] as well as Ca replaced by Ba. All substitutions resulted in the greater volume of CA₆ lattice.

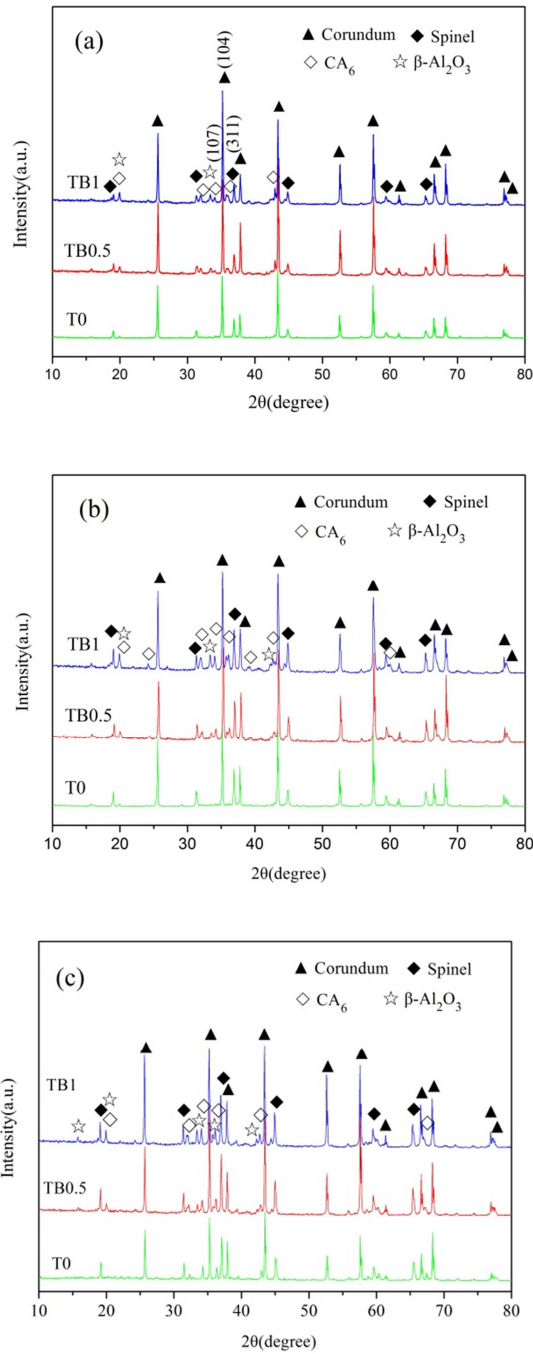


Fig. 1: XRD patterns of alumina-magnesia refractory castables sintered at different temperatures: (a) 1250 °C, (b) 1350 °C and (c) 1450 °C.

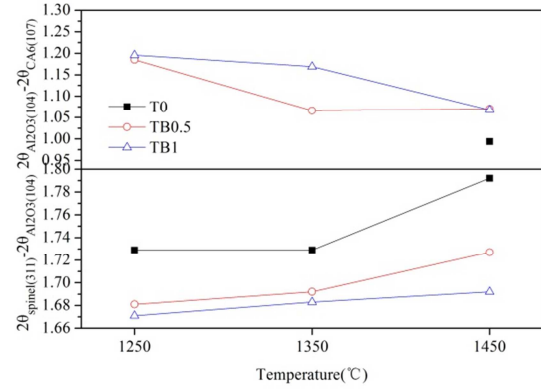
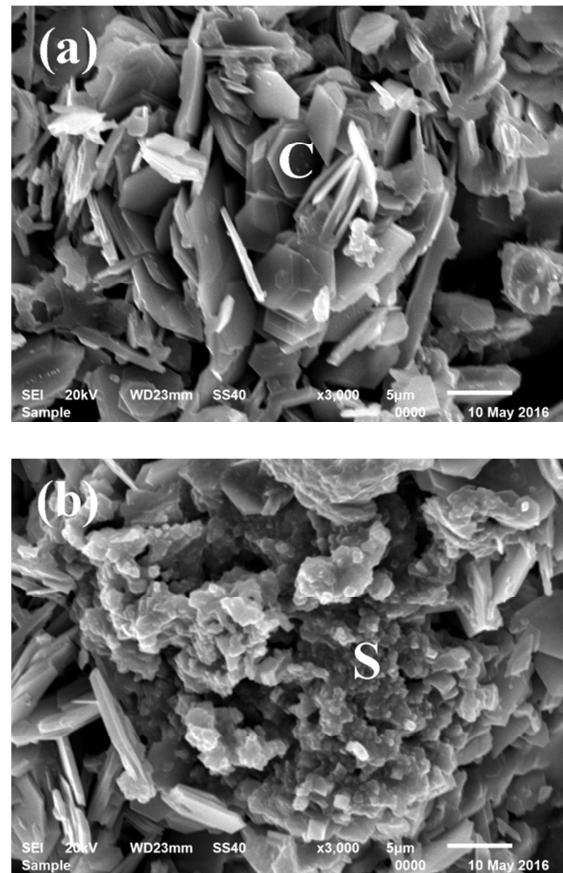
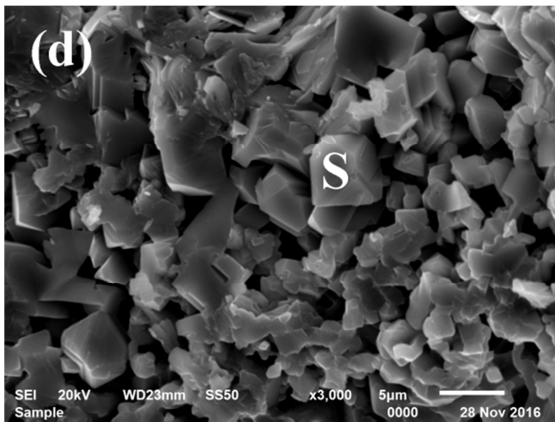
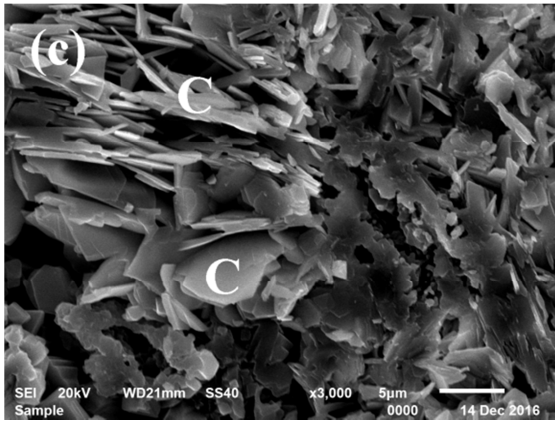


Fig. 2: The shift of the diffraction peaks about CA₆ and spinel with the firing temperature.

Figure 3 shows the microstructure of sample T0 and TB1. It can be seen that there were a plenty of hexagonal platelets with sharp edges (CA₆) stacked in the matrix of sample T0. However, the morphology of CA₆ in sample TB1 was relatively irregular than the reference sample T0. The solution of Mg and Ti atoms into the lattice of CA₆ crystal resulted in the change of its morphology. Besides, the difference for the microstructure of spinel between specimen T0 and TB1 was significant. The grain of the in-situ spinel in the sample T0 was particular small and coarse. By comparison, bigger spinel formed in the castables with BaTiO₃ addition at the same condition. Due to more vacancies induced by the substitution in the spinel crystal structure, the sintering activity as well as the grain growth of spinel was enhanced.





(C-CA₆, S-Spinel)

Fig. 3: SEM of alumina-magnesia refractory castables(T0-(a) (b) and TB1-(c) (d)) after firing at 1450 °C for 5 h.

Expansion behavior

Permanent linear expansion (PLE) of alumina-magnesia castables containing additives is shown in Fig. 4. The expansion value of sample S0 presented a continuous increase as the function of the temperature. While PLE values of other samples containing BaTiO₃ reached maximum and were greater than the reference sample calcined at 1350 °C, after that an obvious reduction of PLE was presented with further increase of the temperature. This implied BaTiO₃ promoted the in situ reaction including spinel and CA₆ formation. Compared with other specimens, sample TB1 showed a relative lower expansion value after calcined at 1450 °C because BaTiO₃ improved the activity of sintering at the higher temperature.

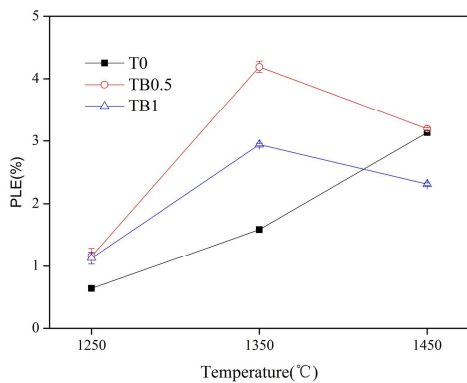


Fig. 4: Permanent linear expansion of samples at different temperatures.

Bulk density and apparent porosity

The line chart (Fig. 5) presents the bulk density of alumina-magnesia refractory castables after firing at 1250-1450 °C for 5 h. Due to the expansive reactions of spinel and CA₆^[11,12], the bulk density of sample without BaTiO₃ (S0) continuously decreased with the firing temperature rising. While there was obvious distinction for specimens containing BaTiO₃ after firing temperature above 1350 °C. When the firing temperature went up to 1450 °C, the bulk density of sample TB1 presented a relative higher value. The apparent porosity of alumina-magnesia refractory castables with different firing temperature is shown in Fig. 6. The sequence of the porosity of samples was contrary with their bulk density, while consistent with their PLE. This phenomenon could be explained by the mechanism that BaTiO₃ accelerated the reactions of components in matrix and finally promoted the sintering.

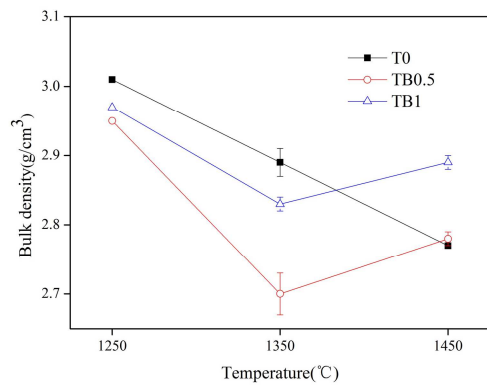


Fig. 5: Bulk density of alumina-magnesia refractories at different temperatures.

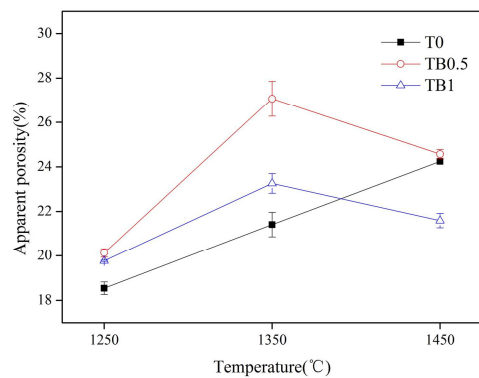


Fig. 6: Apparent porosity of alumina-magnesia refractories at different temperatures.

Cold modulus of rupture

Figure 5 pointed out the cold modulus of rupture (CMOR) of all castables. In spite of CA₆ and spinel formation, the increase for CMOR of castables with BaTiO₃ addition was significant with the firing temperature up to 1450 °C. With the function of BaTiO₃ addition, the better connections of components in the matrix were achieved. As the consequence of this, the strength of castables was raised by a certain extent.

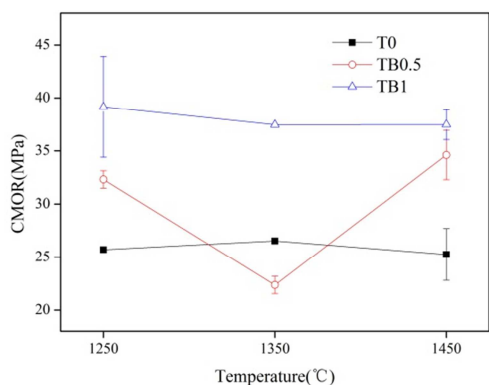


Fig. 7: Cold modulus of rapture for alumina-magnesia refractory castables containing BaTiO₃ after firing at different temperatures.

CONCLUSION

Effects of BaTiO₃ addition on the properties of alumina-magnesia refractory castables were investigated. Based on the above result, the following conclusions have been drawn. The addition of BaTiO₃ decreased the forming temperature of CA₆ and speeded up in situ reaction of spinel. Combined the effects of BaO and TiO₂, the morphology of CA₆ and spinel was significantly impacted by the solid solution containing other atoms. After firing at 1450 °C for 5 h, the cold modulus of rapture of castables increased from 25 MPa to 37 MPa, and lower expansion was achieved by the addition of 2.92 wt% BaTiO₃.

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