Influence of Reactive Micro Alumina Contents on the Microstructures and Mechanical Properties of Gel Bonded Corundum-Spinel Refractory Castables

Nana Xu [a], Yuanbing Li [a] *, Qingheng Wang [a], Hao Wei [b], Shujing Li [a], Ruofei Xiang [a]

[a] The State Key Laboratory of Refractories and Metallurgy, Department of Materials Science and Engineering
Wuhan University of Science and Technology (WUST), Wuhan, 430081, P. R. China

[b] Alteo Shanghai Co., Ltd, Shanghai, 200000, P. R. China

*corresponding author: lybref2002@126.com

Abstract

Corundum-spinel refractory castables were prepared by using tabular alumina aggregates, fused magnesia, reactive micro alumina, calcined micro alumina and gel powder as starting raw materials. While the different contents of calcined micro alumina (CMA) were instead of reactive micro alumina (RMA), effects of RMA content on the microstructures and mechanical properties of the castables were investigated by means of X-ray diffractometer (XRD), scanning electron microscopy (SEM) and elastic modulus tester, etc. The slag resistance was tested by means of crucible test, and the results indicated that the slag penetration resistance increases and slag corrosion resistance decreases with increases in reactive micro alumina content while larger grain size of spinel could optimized the slag resistance of samples. Hence, the growth of crystalline grains and the consolidation of matrix were responsible for the better slag resistance of samples.

Key words: Corundum-spinel castables; Reactive micro alumina; Microstructure; Mechanical properties; Slag resistance

1. Introduction

Castables has been the most ubiquitous of the unshaped refractories, including plastic mixes, gunning mixes, and monolithic rammables [1]. Among these unshaped materials, alumina-spinel castables have higher resistance to structural palling and lower slag penetration than high-alumina or basic castables which are used increasingly in the steel industry [2, 3]. Alumina-spinel castables are usually produced by using one or more of the following additions: (1) coarse preformed spinel (stoichiometric or alumina-rich) grain as an aggregate, (2) fine preformed spinel as part of the bond system, and (3) MgO and Al_2O_3 fines as part of the bond-forming in situ spinel.

High pollution by-products of cement industry and relative lower strength of cement bonded castables in medium temperature have gradually put forward the purpose to instead of cement bonded system [4, 5]. ρ-Al_2O_3 is the only form of Al_2O_3 which can take reaction of spontaneous hydration in room temperature [6]. Because calcium aluminate cement is more easier to motivate the form of compounds with low melting point like gehlenite and anorthite, a reactive alumina that exhibits hydrating properties in water (ρ-Al_2O_3) has been used as a CaO-free setting agent for refractory castables [7, 8]. Nevertheless, castables prepared with this alumina are usually more susceptible to explosion during drying than cement containing materials, which constitutes the main disadvantage of this alternative setting system.

Now, one interesting question is that, whether it is possible to design and use a new type of CaO-free setting agent which can have the advantages of ρ-Al_2O_3 and reduce the disadvantages of concentrated release of hydration heat. Using two types of micro alumina, reactive micro alumina (RMA) and calcined micro alumina (CMA), a novel way is developed to change the viscosity of castable slurry and then strengthen the effect of retarder [9, 10]. Meanwhile, the Al_2O_3-rich spinel has higher lattice distortion because of the dissolution of Al_2O_3 into spinel, which may increase the slag resistance more efficiently. Therefore, on the premise of the improvement by RMA to the formed spinel, different mass ratios of RMA and CMA were used to fabricate the corundum-spinel refractory castables, and the effect of the RMA content on the slag resistance of castables was investigated.

2. Experimental

Tabular alumina aggregates and powder (Zhejiang Zili Advanced Materials Co.,Ltd), Magnesia aggregates and powder, Gel powder, RMA (Al_2O_3＞99.85 wt%, d_{50}=2.5 μm, PBR from Alteo Gardanne) and CMA (Al_2O_3＞97.0 wt%, d_{50}=4.0 μm, AC34B4 from Alteo of France) were used as raw materials. The chemical compositions of raw materials were listed in Table 1. The raw powder materials were mixed in five ratios (Table 2), using mechanical mixing for 3h. Five groups of castable were

fabricated as 40×40×160mm, 70×70×70 mm (aperture is Ø(25–30) × H 40 mm) by using the same basic aggregates and different matrices, as shown in Tables 2. Water addition of the castables was controlled at 5.2±0.05 wt%.

Table 1 chemical compositions of raw materials (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2
Magnesia	0.89	0.15	0.57	1.16	97.15			
Tabular Alumina	0.02	99.42	0.02				0.36	
Gel powder	8.00	85.55	0.17		0.08	0.04	0.03	0.05

Table 2 Formulations of castables (wt%)

Materials	A	B	C	D	E
Tabular alumina Aggregates	55	55	55	55	55
Tabular alumina powder (≤74 μm)	20	20	20	20	20
Reactive micro alumina (PBR)	9	8	7	6	5
Calcined micro alumina (AC34B4)	0	1	2	3	4
Magnesia Aggregates	8	8	8	8	8
Magnesia powder (≤74 μm)	3	3	3	3	3
Gel powder (≤44 μm)	5	5	5	5	5

The green compacts were dried at 110 °C for 24 h, and then heated at 1550 °C for 3h in an electric furnace, then furnace-cooled to room temperature. Apparent porosity (A.P) and Bulk density (B.D) of castable samples were tested by Archimedes' Principle with water as medium. The cold modulus of rupture (CMOR) and cold compressive strength (CCS) at room temperature were measured referring to Chinese standard GB/T 3001-2007 and GB/T5072-2008, respectively. After every time thermal shock, the elastic modulus of the quenched samples was measured at room temperature (RFDA-HTVP1600, IMCE, Belgium) after the samples were heated at 950 °C for 30 mins then immediately cooled by the strong wind for 5 mins. The slag resistance experiment on samples was carried out adopting the static crucible method. A certain amount of converter slag (20 g) was weighed and put in crucible and sintered at 1550 °C for 3h. Phase transformation were characterized by X-ray diffractometry (XRD, X'Pert Pro, Philips, Netherlands) with Cu/Ka radiation (λ = 1.54187 Å). The XRD patterns were recorded in the 2θ range of 10-90° with a scanning speed of 2° per minute. The microstructures were measured by a scanning electron microscope (SEM, JSM-6610, JEOL Company, Japan).

3. Results and discussions

Fig.1 and Fig.2 show the physical properties of samples dried at 110 °C and sintered at 1550 °C with the various RMA and CMA contents. As shown in Fig.1 (3), flow ability of green bodies changed according to different formulations, and the physical properties of samples dried at 110 °C decreased as the RMA content increasing. Furthermore, the physical properties of samples sintered at 1550 °C (Fig.2 (1) and (2)) also slightly decreased with the increase of RMA content. Despite the top value of LAC in group C, the higher RMA content contributed to better strength. Observed from Fig.2 (3), elastic modulus of the samples decreased with the decrease of RMA content, but the residual rate of group C showed better to indicate a strong ability in thermal shock resistance.

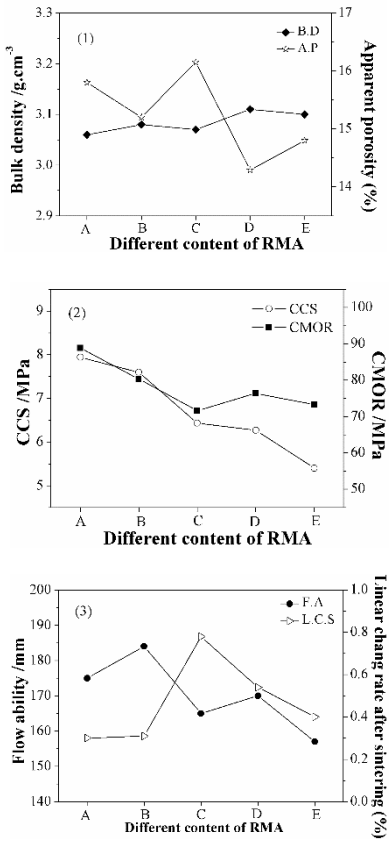

Fig.1 Physical properties of samples dried at 110 °C with various RMA and CMA contents

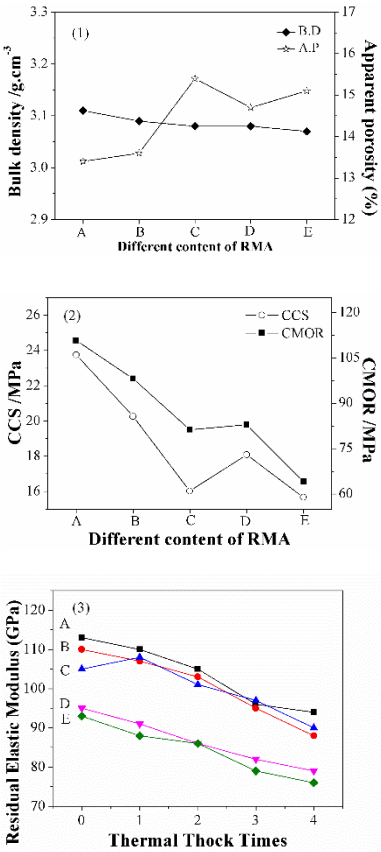

Fig.2 Physical properties of samples sintered at 1550 °C with various RMA and CMA contents

The XRD patterns of samples with the various RMA and CMA contents are shown in Fig. 3. With the introduction of CMA, the major crystalline phase detected is corundum and spinel which indicated fused MgO could take reaction with both two kinds of micro alumina to form a spinel. As increasing the content of CMA, the indensity of spinel peaks slightly decreased, which would be tested and matched with the detect of SEM.

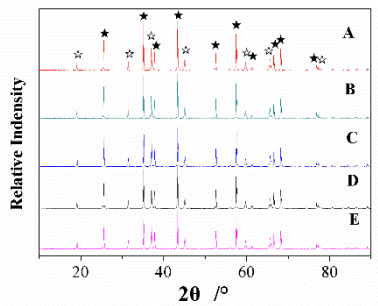

Fig.3 Effects of different RMA and CMA contents on the XRD

Fig. 4 shows the digital images of crucibles after the slag resistance tests. Five different crucibles showed good slag resistance properties, but also existed slight difference. As shown in Table 3, the corrosion index and penetration index were calculated from the corrosion area and penetration area observed from Fig. 4. From the formulation changed from A to B, the corrosion index kept stable and the penetration index decreased. When the formulation changed to C, D and E, the corrosion index and penetration index kept raising which was corresponding to the images trend of Fig. 4. Meanwhile, eroded and penetrated areas of samples were concentrated in matrices, and then would be detected by SEM. Consistent with the trend in Fig.1 (1) and Fig.2 (1), the increasing densification of the matrix could attribute to prevent the penetration of slag into the matrix.

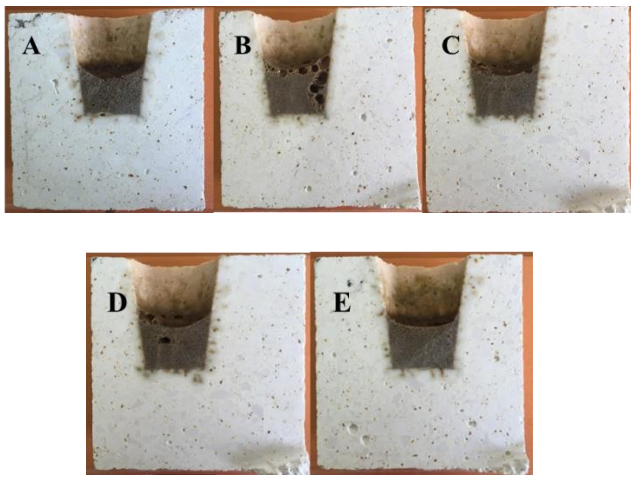

Fig.4. Images of crucibles after the test of slag resistance experiment

Table 3 Calculations of slag resistance (%)

Groups	Corrosion Index	Penetration Index
A	0.11	0.36
B	0.11	0.32
C	0.16	0.45
D	0.27	0.53
E	0.29	0.47

The SEM images of matrices from various formulations were shown in Fig. 5, revealing to the phase transformation noticed from Fig. 3. As shown, the corundum and spinel grains could be observed. While the content of RMA changed from 9.0 wt.% to 5.0 wt.%, the grain size of corundum kept stable, but the grain size of spinel kept shrunk. The slag penetration resistance of refractory materials is mostly affected by the microstructure of the materials and the viscosity of the slag. Moreover, early research showed the larger grain size of spinel could motivated stronger the slag corrosion resistance capacity [4]. This indicates that the slag penetrated into the matrices mainly through the

defects of sintering reaction. Hence, the consolidation of matrix were responsible for the better slag resistance of samples.

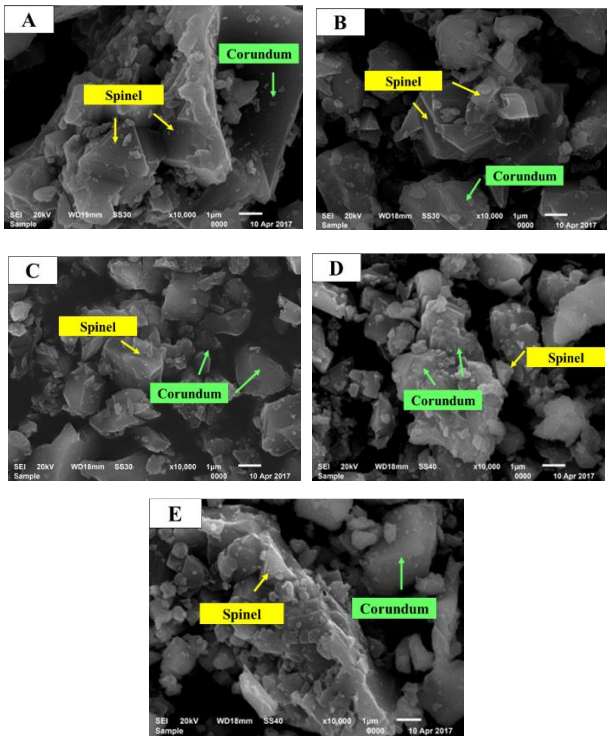

Fig.5. SEM images of samples with various RMA and CMA contents

4. Conclusions

(1) Physical properties of gel-bonded castables could be affected by the content of RMA and CMA. When the content of RMA increasing from 5.0 wt.% to 9.0 wt.%, the flow ability decreased, but mechanical properties could be optimized. While the formulation were chosen as group A, the complex properties of samples dried at 110 °C were bulk density 3.06 g•cm^{-3}, apparent porosity 15.7 %, CCS 7.7 MPa and CMOR 82.5 MPa. And the complex properties of samples sintered at 1550 °C were bulk density 3.12 g•cm^{-3}, apparent porosity 13.4 %, CCS 23.1 MPa and CMOR 113.5 MPa.

(2) The phase transformation and microstructure showed the indensity of spinel peaks slightly decreased as increasing the content of CMA, and the corrosion index and penetration index showed better when the formulation was chosen as group B. Combined with the SEM images, the larger grain size of spinel could optimized the slag resistance of samples. Hence, the growth of crystalline grains and the consolidation of matrix were responsible for the better slag resistance of samples.

Acknowledgements

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Reference

[1] H. Sarpoolaky, S.W. Zhang, B.B. Argent, W.E. Lee. Influence of Grain Phase on Slag Corrosion of Low-Cement Castable Refractories. J. Am. Ceram. Soc., 84 [2] 426–34 (2001).

[2] A.R. Studart, V.C. Pandolfelli, E. Tervoort, L.J. Gauckler. In Situ Coagulation of High-Alumina Zero-Cement Refractory Castables. J. Am. Ceram. Soc., 85 [8] 1947–53 (2002)

[3] E.Y. Sako, M.A. L. Braulio, A.P. Luz, E. Zinngrebe, V.C. Pandolfelli. Slag Resistance of Al_2O_3–MgO Refractory Castables in Different Environmental Conditions. J. Am. Ceram. Soc., 96 [10] 3252–3257 (2013)

[4] B. Pacewska. M. Nowacka, V. Antonovic M. Aleknevicius. Investigation of early hydration of high aluminate cement-based binder at different ambient temperatures. J Therm Anal Calorim (2012) 109:717–726

[5] B.K. Sahoo, T.K. Das, A. Gupta, S. De, M. Carsky, B.C. Meikap. Application of response surface analysis to iron ore slurry rheology using microwave pre-treatment. South African Journal of Chemical Engineering 23 (2017) 81-90

[6] V. Kumar, V.K. Singh, A. Srivastava, G.N. Agrawal. Low Temperature Synthesis of High Alumina Cements by Gel-Trapped Co-Precipitation Process and Their Implementation as Castables. J. Am. Ceram. Soc., 95 [12] 3769–3775 (2012)

[7] B. Long, G.Y. Xu, B. Andreas. Microstructure and physical properties of steel-ladle purging plug refractory materials. International Journal of Minerals, Metallurgy and Materials 24 (2017) 186–194

[8] A. Terzic • N. Obradovic • L. Andric, J. Stojanovic • V. Pavlovic. Investigation of thermally induced processes in corundum refractory concretes with addition of fly ash. J Therm Anal Calorim (2015) 119:1339–1352

[9] T.M. Souza, A.P. Luz, M.A.M. Brito, V.C. Pandolfelli. In situ elastic modulus evaluation of Al_2O_3–MgO refractory castables. Ceramics International 40 (2014) 1699–1707

[10] L.P. Fu, A. Huang, H.Z. Gu, D.H. Lu, P.F. Lian. Effect of nano-alumina sol on the sintering properties and microstructure of microporous corundum. Materials and Design 89 (2016) 21–26