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Effect of B_2O_3 on Volume Stability and Strength of Corundum-based Castables

DOI 10.1515/htmp-2015-0291

Received December 22, 2016; accepted June 15, 2016

Abstract: Calcium aluminate cements (CAC) with 0.21 wt% B_2O_3 and without B_2O_3 were used as binders of corundum-based castables. The properties of the castables with and without B_2O_3 after heat treatment at 110 °C, 1,100 °C and 1,450 °C were investigated, with emphasis on studying the effect of B_2O_3 in CAC on the volume stability and high temperature strength of the castables. It is found that a very small amount (about 0.01 wt%) of B_2O_3 introduced by the cement alleviates the expansion of the castables after firing at 1,450 °C and decreases the high-temperature strength of castables as the presence of B_2O_3 should generate liquid phase.

Keywords: permanent linear change, hot modulus of rupture, boron oxide, corundum castables

PACS® (2010). 81.05.Je, Ceramics and refractories

Introduction

Calcium aluminate cement (CAC) is a widely utilized binder for refractory castables and CAC can provide suitable flowability, working time and sufficient demolding strength at ambient temperatures [1]. Furthermore, CAC-bonded corundum-based castables for steel ladles exhibit improved volumetric stability and mechanical strength due to the interlocked platelet of $CaO \cdot 6Al_2O_3$ (CA_6) formed at elevated temperatures [2, 3]. However, the presence of boron-containing additives may adversely affect

the strength at high temperature and volume stability of the castables as liquid phase forms at relatively low temperature (about 977 °C) in $CaO-Al_2O_3-B_2O_3$ [4, 5]. In fact, B_2O_3 is present in some commercial CAC as the alumina fine powder as a raw material for CAC production is the dust from the fabrication of alumina via Bayer process [6]. The alumina fine powder in CAC contains B_2O_3 because borates are used as mineralizers to promote the phase transformation and the growth of α -alumina crystals [7]. To the best of our knowledge, there have not been any reports about the effect of B_2O_3 in CAC on the properties of CAC-bonded castables. In this context, the aim of this work is to investigate the influence of B_2O_3 in CAC on the volumetric stability and high temperature strength of CAC-bonded castable as B_2O_3 may lead to the formation of liquid phase in CAC-bonded castables at high temperatures.

Experimental procedure

Two commercial calcium aluminate cements (Zhengzhou Aluminates, China) with B_2O_3 (CAC2) and without B_2O_3 (CAC1) were used as binders in this work and their chemical compositions are shown in Table 1. Table 2 presents the particle size of cements with and without B_2O_3 . As seen in Table 2, the particle size of these two cements is almost the same. Table 3 presents the formulation of CAC-bonded corundum-based castables. The castables were composed of tabular alumina aggregate (T60; Almatiss, Ludwigshafen, Germany), 0.045 mm tabular alumina powder (T60; Almatiss), reactive alumina (CL370; Almatiss), and calcium aluminate cement. FS10 (Castment; BASF) was used as the dispersant and the water content of castables was 4.6 wt%.

The mixtures were dry-mixed for 1 min, followed by 4 min wet mixing in the laboratory mixer (JJ-5; Wuxi Jianyi, China). Subsequently, the mixtures were cast into the molds of 4 cm × 4 cm × 16 cm with vibration. After curing at room temperature for 24 h, the samples were de-molded, dried for 24 h at 110 °C, and fired for 3 h at 1,100 °C and 1,450 °C.

Bulk density and apparent porosity of the castable samples were determined through the Archimedes method. Cold-crushing strength (CCS), cold modulus

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Table 1: Chemical composition of cements with and without B₂O₃.

Cement	Chemical composition, wt%							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	B ₂ O ₃
CAC1	0.47	69.93	0.19	28.92	0.12	0.03	0.20	0.00
CAC2	0.48	68.55	0.30	29.17	0.10	0.05	0.22	0.21

Table 2: Particle size of the cements with and without B₂O₃.

Cement	Particle size, μm		
	D10	D50	D90
CAC1	2.47	10.00	22.60
CAC2	2.45	10.15	23.40

Table 3: Compositions of CAC-bonded corundum-based castables (wt%).

Composition		Castable	
		Without B ₂ O ₃	With B ₂ O ₃
Cement	CAC1	5	–
	CAC2	–	5
Tabular alumina	6–3 mm	20	20
	3–1 mm	30	30
	1–0 mm	20	20
	0.045 mm	20	20
Reactive alumina		5	5
Castment-FS10		0.2	0.2

of rupture (CMOR) and permanent linear change (PLC) were tested for the castable samples after the above heat treatment. And hot modulus of rupture (HMOR) of pre-fired castable samples at 1,450 °C was performed at 1,400 °C. For these physical properties measurements,

three samples were evaluated for each temperature and the errors were calculated according to the standard deviation.

Moreover, cement pastes were prepared using a water/cement (W/C) ratio of 0.37. And the setting times of cement pastes were determined by Vicat apparatus based on the Chinese national standard GB/T 1346-2011.

Results and discussion

Figure 1 shows the effect of B₂O₃ on the bulk density (BD) and apparent porosity (AP). After drying at 110 °C, and firing at 1,100 °C and 1,450 °C, the castables bonded by CAC without B₂O₃ (CAC1) have close BD and AP with the castables of CAC-containing B₂O₃ (CAC2). However, the apparent porosity (17.39 %) of the castable containing B₂O₃ is noticeably lower than 18.16 % of the castable without B₂O₃ after firing at 1450 °C, which could be attributed to the higher level of densification. The cause of the higher degree of densification of the castable with B₂O₃ will be discussed later.

Figure 2 presents the permanent linear change (PLC) of castables after firing at 1,450 °C for 3 h. It is noticed that the castable bonded by CAC with and without B₂O₃ both exhibit the expansion after firing at 1,450 °C, resulting from the accompanied volume expansion (3 %) during formation of CA₆ [2, 8]. However, the linear expansion

Figure 1: Bulk density (a) and apparent porosity (b) of castables after heat treatment at 110, 1100 and 1450 °C.

Figure 2: Permanent linear changes of castables after firing at 1450 °C.

value (0.12%) of the castable bonded by CAC-containing B_2O_3 is lower than 0.42% of the castable bonded by CAC without B_2O_3 . This means that the castable with B_2O_3 has a higher degree of densification than the castable without B_2O_3 because the presence of B_2O_3 in the castable would generate more liquid phase, which mitigates the volumetric expansion during the formation of CA_6 at the temperature of 1,450 °C.

Figure 3 shows CCS and CMOR of the castables with and without B_2O_3 after heat treatment at 110 °C, 1,100 °C and 1,450 °C. After drying at 110 °C, CCS (86.10 MPa) and CMOR (12.03 MPa) of the castables bonded by CAC-containing B_2O_3 are higher than CCS (72.50 MPa), and CMOR (10.50 MPa) of the castables bonded by CAC without B_2O_3 . This difference in dried strength of the castables is due to the faster hydration and setting rates of the cement-containing B_2O_3 . As shown in Figure 4, the

cement paste without B_2O_3 has an initial setting time of about 133 min and a final setting time of about 158 min. In comparison, the initial setting time and the final setting time of the cement paste with B_2O_3 are about 55 min and about 90 min respectively. The faster setting rate of CAC with B_2O_3 could contribute to the higher strength of the castable with B_2O_3 after drying at 110 °C.

It is shown in Figure 3 that, after firing at 1,100 °C, CCS (75.30 MPa) and CMOR (10.47 MPa) of the castable with B_2O_3 are higher than CCS (62.07 MPa) and CMOR (9.07 MPa) of the sample without B_2O_3 . Similarly, the castable containing B_2O_3 has higher CCS than the castable without B_2O_3 after firing at 1,450 °C. The higher strength of the castables with B_2O_3 after firing at 1,100 °C and 1,450 °C is ascribed to the enhanced sintering due to the liquid phase formation generated by the presence of B_2O_3 , which is in agreement with the decreased PLC of castables with B_2O_3 (as shown in Figure 2).

Figure 4: The initial and final setting time of cement pastes with different contents of B_2O_3 .

Figure 3: Cold crushing strength (a) and cold modulus of rupture (b) of castables after heat treatment at 110, 1100 and 1450 °C.

Figure 5: Hot modulus of rupture of castables pre-fired at 1450 °C and evaluated at 1400 °C.

However, as shown in Figure 5, a significant difference is observed in HMOR between the castables with and without B_2O_3 . It is seen from Figure 5 that the castable without B_2O_3 has HMOR of 13.35 MPa. In contrast, the castable containing B_2O_3 has HMOR of 9.57 MPa. This considerable difference in HMOR should be attributed to the liquid formation generated by the presence of B_2O_3 at high temperature.

As seen in Table 1, the boric oxide content in CAC is 0.21 wt% and, as seen in Table 3, the cement content in the castables is 5 wt%. So the boric oxide content in the castable with B_2O_3 is only about 0.01 wt%. It is reported that a ternary compound $CaO \cdot Al_2O_3 \cdot B_2O_3$ and two binary compounds $2Al_2O_3 \cdot B_2O_3$ and $9Al_2O_3 \cdot 2B_2O_3$ are detected in the castables when corundum-based castables containing B_2O_3 are subjected to temperatures of 800 °C and above [9]. However, $CaO \cdot Al_2O_3 \cdot B_2O_3$ melts incongruently at 1,015 °C ($CaO \cdot Al_2O_3 \cdot B_2O_3 \rightarrow 9Al_2O_3 \cdot 2B_2O_3 + L$) [9] and liquid phase would be produced between $2Al_2O_3 \cdot B_2O_3$ and $9Al_2O_3 \cdot 2B_2O_3$ at the temperature of above 470 °C [9]. It could be deduced that the liquid phase should be present in the B_2O_3 -containing castables of this work at temperatures between 1,100 °C and 1,450 °C. Therefore, this very small amount of boric oxide (about 0.01%) could have noticeable effect on the densification of the castables at 1,450 °C, resulting in the lower expansion of the castables with B_2O_3 than that of the castables without B_2O_3 after firing at 1,450 °C (Figure 2) and the higher CCS and CMOR of the former castables than those of the latter castables after firing at 1,100 °C and 1,450 °C (Figure 3). Moreover, the lower HMOR of the former castable at 1,400 °C than that of the latter ones (Figure 5) could also be ascribed to the presence of more liquid in the former castables.

Conclusions

The presence of B_2O_3 in the castable would generate liquid phase at the firing temperature of 1,450 °C. The liquid phase not only results in a higher degree of densification of the castable with B_2O_3 than the castable without B_2O_3 , but also mitigates the volumetric expansion during the formation of CA_6 at the firing temperature. Therefore, the corundum-based castables with a very small amount (about 0.01 wt%) of B_2O_3 have lower expansion than the castables without B_2O_3 after firing at 1,450 °C. Moreover, the liquid generated by B_2O_3 leads to the lower HMOR of the castables with B_2O_3 than that of the castables without B_2O_3 at 1,400 °C.

Acknowledgments: The authors acknowledge the National Natural Science Foundation of China (51372230, 51572244), Foundation of the State Key Laboratory of Advanced Refractories of China (201301) and Foundation of the State Key Laboratory of Refractories and Metallurgy (G201409, Wuhan University of Science and Technology) for the financial support.

Funding: Foundation of the State Key Laboratory of Refractories and Metallurgy (Grant/Award Number: 'G201409') Foundation of the State Key Laboratory of Advanced Refractories of China (Grant/Award Number: '201301') National Natural Science Foundation of China (Grant/Award Number: '51372230', '51572244').

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