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Effect of microsilica addition on the properties of colloidal silica bonded bauxite-andalusite based castables

Jia Quanli[a], Zhang Ju[b], Zhou Ying[b,*], Jia Gaoyang[a], Liu Xinhong[a,*]

[a] Henan Key Laboratory of High Temperature Functional Ceramics, Zhengzhou University, Zhengzhou 450052, China
[b] School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450000, China

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ABSTRACT

Colloidal silica bonded bauxite-andalusite based castables were prepared using homogenized bauxite and andalusite as aggregates, andalusite fines, corundum fines, ultrafine Al_2O_3 as matrixes and colloidal silica as binders. Effects of microsilica addition on the green strength, physical properties, hot strength and thermal shock resistance of castables were investigated. Moreover, phase composition and morphological evolution of specimens were characterized by XRD and SEM analysis. Green strength after demoulding, cold strength and hot strength as well as thermal shock resistance of the castables are enhanced with microsilica addition, which attribute to generating more chemical bond (–Si–O–Si–) after demoulding and heating at intermediate temperature (up to 1100 °C), and creating a stronger mullite bonding at higher temperature (1400 °C) compare to the specimens without microsilica.

1. Introduction

Bauxite-andalusite based castables have been widely used in crucial positions, like tundish, hot blast pipe system of blast furnaces because of their excellent high temperature properties, which attribute to the in-situ formation of mullite creating a ceramic bond at elevated temperatures [1]. Calcium aluminate cement has commonly used as a hydraulic binder for bauxite based castables for many years, because it can supply a good workability and stable green strength after demoulding. However, strength development of castables always exhibit a noticeably drop at intermediate temperatures caused by decomposition of hydration products, and CaO favors the formation of low melting phase (e.g. anorthite and gehlenite) to degrade high temperature performances of the castables [2,3].

Numerous studies have previously been attempted to improve the properties of conventional castables through replacing cement by hydratable alumina [4–7]. However, further improvement of castables was still restricted by its low demoulding strength, high water requirement and dehydration decomposition of hydraulic bond at elevated temperatures [6,7].

To date, nanotechnology has received many interests owing to their merits of that it could improve bonding and densification of refractory at lower sintering temperatures [8–10]. Unfortunately, dispersing drawback, agglomeration problem as well as high price of nanosized powders have been challenges in terms of using these additives [11]. Compared to oxide nanopowders, colloidal silica (CS) sol, a stable dispersion of amorphous silica, exhibits highly competitiveness because of its cheaper price, higher solid contents (~ 50 wt%) and good volumetric stability at high temperatures. It is of great interest for castable application in recent years because silica nanoparticles from CS can be absorbed on the surface of active α-Al_2O_3 forming the in-situ mullite bonding phase in alumina-rich systems [12,13], as well as its consolidation mechanism does not result in generation of hydrated phase, thereby safely and quickly drying and reducing the risk of explosive spalling of castables [8,9,14,15]. However, inadequate green strength after demoulding leading to handling problems, higher CS sol requirement leading to an increase of porosity during drying, those still needed to be perfected. [14,16] In order to improve green mechanical strength of CS bonded castables, some efforts have been conducted by using a small amount of calcium aluminate cement and hydratable alumina, silane coupling agent (KH-570), however, their green strength still needs to be improved. [17,18]

Microsilica is a by-product of silicon or ferrosilicon alloys, which consists of very fine amorphous spherical silica particles with an average diameter of 0.15 µm. [16,19] In refractory castables, microsilica fills the voids initially occupied by water, thereby decreasing the water addition and improving the flowability. [19] It also reacts with Al_2O_3 to generate in-situ mullite, herein, contribute to enhancing mechanical properties of castables [16]. The main objective of this work aims to improve the green strength of castables after demoulding and

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* Corresponding authors.
E-mail addresses: zhouying@zzu.edu.cn (Z. Ying), liuxinhong@zzu.edu.cn (L. Xinhong).

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Table 1
Formula of matrix in specimens (wt%).

Items		S1	S2	S3
Bauxite	5–3 mm	30	30	30
Bauxite aggregates	3–1 mm	25	25	25
Andalusite	1–0 mm	15	15	15
Andalusite fines	≤ 0.074 mm	8	8	8
Corundum fines	≤ 0.044 mm	18	17	16
Ultrafine Al_2O_3	d_{50} = 1.2 μm	4	4	4
Microsilica	Elkem 95	0	1	2
Colloidal silica	–	8.2	7.2	7.0

high temperature properties by adding microsilica. Effects of microsilica on the physical properties, hot modulus of rupture (MOR), Thermal shock resistance (TSR), phase composition and microstructure of castables after firing at different temperature were investigated in details.

2. Experimental

Homogenized bauxite (5–3 mm, 3–1 mm; Al_2O_3 ≥ 80 mass%, Tongda Refractory), andalusite (1–0 mm, ≤ 0.074 mm; Al_2O_3 ≥ 57%, Damrec), fused corundum fines (≤ 0.044 mm, Al_2O_3 ≥ 99%), ultrafine Al_2O_3 (d_{50} = 1.2 μm, Al_2O_3 ≥ 99.2%, Kaifeng Tenai Co.), microsilica (d_{50} = 0.15 μm, SiO_2 ≥ 95%, Elkem) and CS (SiO_2 ≥ 30.6%, pH = 10.1, Yuda chemical Co.) were used in this work. MgO, citric acid and sodium hexametaphosphate were used as setting agent and additives [20].

Starting materials were mixed according to the formulation listed in Table 1. After mixing, castables were shaped into 40 mm × 40 mm × 160 mm bar-shaped specimens, then demoulded after curing at room temperature for 24 h and then dried at 110 °C for 24 h, finally the specimens were fired at 1100 °C, 1300 °C and 1400 °C for 3 h, respectively. The matrix specimens were the same as the castables except coarse aggregates (> 0.5 mm), which were prepared for analysis of phase evolution.

Green strength of castables after demoulding was tested. Bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), cold MOR and permanent line change (PLC) of castables after drying and firing were performed. Hot MOR of 1100 °C, 1300 °C and 1400 °C were measured by three point bending test using specimens after drying at 110 °C for 24 h. TSR of castables after firing at 1400 °C for 3 h were detected by water quenching method (ΔT = 1100 °C, one cycle), and then residual MOR was tested. The phase compositions in matrixes castables were identified by X-ray diffraction (XRD, Panalytical X′pert). Microstructures and morphological evolution of specimens were evaluated by scanning electron microscopy (SEM, JEOL, JSM 5610LV), equipped with an energy-dispersive X-ray spectroscopy (EDS, INCA).

3. Results and discussion

Fig. 1 shows green strength of castables after demoulding at room temperature. Both cold MOR and CCS of specimens after demoulding are noticeably increased with microsilica addition rising from 0% to 2%. During setting, the hydroxyl groups (Si–OH) on the surface of the colloidal particles and microsilica generate siloxane bonds (Si–O–Si), accelerating the coagulation of CS sol, the chemical bond of –Si–O–Si– and –Si–O–Mg–O–Si– form through the condensation reaction between the particles when MgO was used as setting agent [8,14]. The enhancement to green strength of castables attributes to the total content of high activated SiO_2 between several nanometers and micron from colloidal silica and microsilica, which can form a three dimension network (-Si-O-Si-) gel network of branched chains of silica particles [9], thereby creating a green strength improvement after demolding.

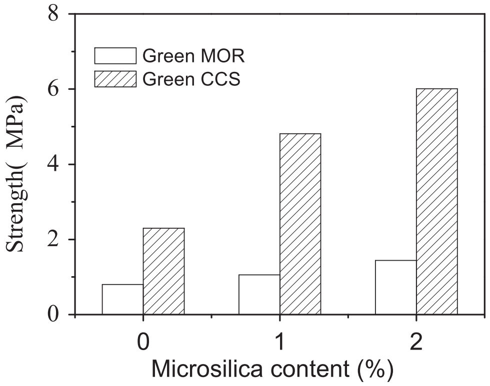

Fig. 1. Green strength of castables after demoulding at room temperature.

Presented in Fig. 2 are physical properties of castables after heating at different temperatures. As seen in Fig. 2a, BD of castables of after drying and firing exhibits higher values compared to the specimens without microsilica, and AP of castables decreases significantly (Fig. 2b). On increasing of temperature from 110 °C to 1100 °C, AP values only present a slight decrease, further increasing to 1400 °C, AP values decrease from 17.2% to 15.2%.

As shown in Fig. 2c & d, the CCS and MOR of castables are improved with the heat temperature rising from 110 °C to 1100 °C, which can be contributed to the Si–O–Si bonding network and microsilica can promote the sintering among the particles, thereby reinforcing the interlocking structure of the castable after firing.[21] On increasing the temperature to 1300 °C, which, on the contrary, appears a strength drop compared to that fired at 1100 °C. Further increasing the temperature to 1400 °C, the castables exhibit the maximum cold CCS and MOR values. The PLC of samples after firing at 1100 °C and 1300 °C are slightly increased, and are noticeably increased from 0.35% to 0.5% (Fig. 2e) after firing at 1400 °C with the microsilica content from 0% to 2%. The increase in PLC is caused by the amount and crystal size of in-situ mullite in castables after firing at 1400 °C (*it is verified by XRD and SEM)*, therefore generating volumetric expansion. In this study, microsilica comprises some impurities such as R_2O, Fe_2O_3, MgO, CaO, etc, and colloidal silica also contains Na_2O impurity. Those impurities leads to forming low-melt glass phase after firing at higher temperature, which contributes to decreasing the AP, moreover, it is also beneficial to the formation of in-situ mullite. Herein, AP of samples decreases and PLC increases with increasing of microsilica content.

Fig. 3, as an example, gives hot MOR tested at 1100 °C, 1300 °C and 1400 °C for 30 min. Hot MOR of castables at 1100 °C, 1300 °C and 1400 °C all exhibits an increasing trend with increasing of microsilica content, which increases from 9.0 to 19.4 MPa at 1100 °C, from 1.9 to 3.4 MPa at 1300 °C and from 5.4 to 7.9 MPa at 1400 °C, respectively. As Shown in Fig. 3, the hot MOR at 1100 °C is the highest and is enhanced with increasing microsilica addition, the more Si–O–Si chemical bond is formed at low temperature and reinforced with the increasing heat temperature and microsilica content, thus the hot MOR is increased with the microsilica addition, which is due to the Si–O-Si bonding network reinforcing the strength [22]. Some cracks were generated by thermal expansion mismatch of the major crystal phases (coefficient of thermal expansion for corundum and andalusite is 8.5 and 7.6 × 10^{-6} $°C^{-1}$) during the firing process. The hot MOR values at 1100 °C are slightly higher than cold MOR after firing at 1100 °C, which may be attributed to the cracks healing during the heating process, thereby creating an improvement of hot strength. However, it presents a sharp decrease in Hot MOR on heating to 1300 °C, which attributes to the lower melting phase formed by impurities and the meta-stable liquid silica phase [23]. On the other hand, in-situ formation of mullite during the hot MOR testing process is minor because the soaring time is only 30 min at 1300 °C, thus its strengthening effect is little. Thus the hot MOR at 1300 °C is the lowest because of the liquid formation and