



ELSEVIER

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

One-step synthesis of in-situ carbon-containing calcium aluminate cement as binders for refractory castables

Guoqing Xiao^a, Shoulei Yang^a, Donghai Ding^{a,*}, Yun Ren^a, Lihua Lv^a, Pan Yang^a, Xing Hou^a, Jianying Gao^{a,b}

^a College of Materials and Mineral Resources, Xi'an University of Architecture and Technology, Xi'an 710055, China

^b Imerys Technical Center China, Tianjing 300457, China

ARTICLE INFO

Keywords:

Calcium aluminate
In-situ carbon
Refractory castables
Calcium citrate

ABSTRACT

In-situ carbon-containing calcium aluminate cement (CCAC) was synthesized through carbon-bed sintering with calcium citrate tetrahydrate and Al_2O_3 as raw materials. The synthesized product was characterized by X-ray diffraction, field-emission scanning electron microscopy, high-resolution transmission electron microscopy, Raman spectroscopy, and infrared carbon–sulfur analysis. The results show that after sintering at 1500 °C for 4 h, the phase compositions of the product approached that of the commercial cement Secar71. The in-situ carbons in the product had partially graphitized domains and porous structures, were uniformly embedded in calcium aluminate, and the carbon content of the product was 1.45%. The floating ratios and oxidation ratios of the CCAC were lower than those of carbon back/Secar71 (S71CB) composite powders, implying that the water dispersion and oxidation resistance of CCAC were improved. Furthermore, the cold crushing strength (CCS), and cold modulus of rupture (CMOR) of the corundum-based castables bonded with CCAC, and S71CB, respectively, were compared. The CCS and CMOR values of the castables bonded with CCAC after being fired at 1100 °C for 3 h are higher by 20% and 21%, respectively, than those of the castables bonded with S71CB, suggesting that CCAC can be applied as a promising binder for the refractory castables.

1. Introduction

In recent decades, castables, which account for the greatest percentage of unshaped refractories, have been extensively applied in the metallurgical, cement, and chemical industries, among others, owing to their quicker and cheaper installation, and properties approaching those of shaped refractories [1–5]. However, castables suffer the same drawbacks, such as, low corrosion resistance and spalling resistance, as the corresponding oxides shaped refractories, because their compositions are mainly oxides [6]. These result in decreasing their service life and hindering the application of castables in many high-temperature areas, particularly in the slag-lines of a steel ladle.

Introducing carbon to oxide-based castables would yield improved properties owing to the unique properties of carbon, such as nonwettability by molten slag, low thermal expansion, and high thermal conductivity [7,8]. For example, Hamazaki [9] and Teranishi [10] prepared carbon-containing castables by adding small amounts of carbon into the castable formulations, and found that the corrosion resistance, slag penetration resistance, and spalling resistance of the castables were significantly improved. Unfortunately, incorporating carbon into the

castables introduces many new problems arising from its poor water wettability/dispersion and poor oxidation resistance, which have hindered the development and application of carbon-containing castables [7].

Many investigations for overcoming the problems as mentioned above have been carried out. For example, graphite was treated with surfactants to improve its aqueous wettability and dispersion [11]. Although this method is easy to use at relatively low cost, its improvement in wettability and dispersion of graphite is limited; in particular, it can increase the porosity, and reduce mechanical strength of the castables because of foaming of the surfactants. According to Palčo [12] and Rigaud [13], the graphite was pre-fixed in the micropellets or briquettes with millimeter particle size, and they found that it could improve the aqueous wettability of graphite and decrease water demand of castables, but, the inhomogeneous distribution of graphite in castables degraded their corrosion resistance and mechanical strength. Recently, many researchers have coated graphite with oxides (Al_2O_3 [14,15], ZrO_2 [16], spinel [17], mullite [17], and calcium aluminates [18–21]) and carbides (SiC [22,23], TiC [24]), which have better wettability and dispersion properties in water, through the sol-gel

* Corresponding author.

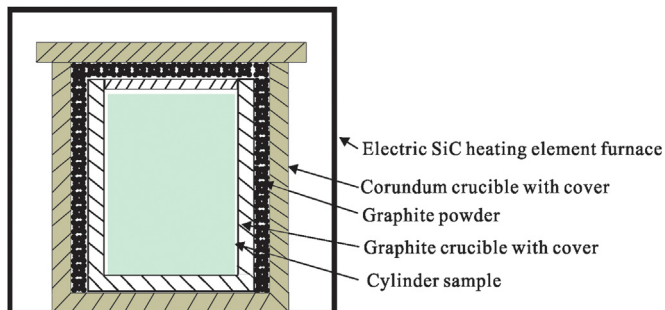
E-mail address: dingdongxauat@163.com (D. Ding).

<https://doi.org/10.1016/j.ceramint.2018.05.189>

Received 28 April 2018; Received in revised form 19 May 2018; Accepted 21 May 2018
0272-8842/ © 2018 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Table 1
Raw material ratios.

Raw materials	Purity (%)	Fineness (um)	Content (wt%)
$C_{12}H_{10}Ca_3O_{14} \cdot 4H_2O$	≥ 96.0	< 48	59.85
Al_2O_3	≥ 99.9	< 74	40.15

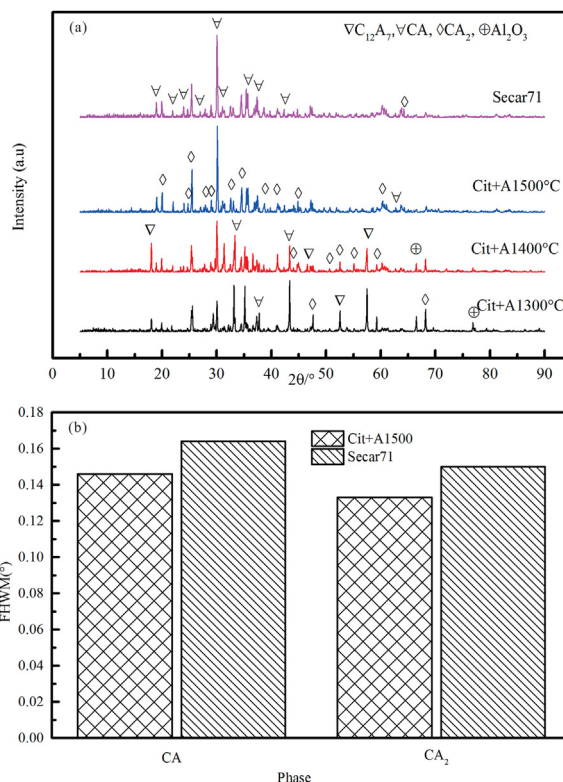
**Fig. 1.** Schematic diagram of experimental setup.**Table 2**
Formulation of the corundum based low cement castables.

	C-CA5 (wt%)	C-S5 (wt%)
Tabular alumina	–	–
3–5 mm	32	32
1–3	23	23
0–1	10	10
– 325mesh	20	20
Active alumina ($< 45 \mu m$)	5	5
microsilica	5	5
CCAC	5	–
S7CB	–	5
Polypropylene fiber	0.05	0.05
dispersant agent	0.2	0.2
water	5.0	5.0

method and molten salt synthesis method; they found that the graphite coated with these oxides and carbides had better water wettability/dispersion and oxidation resistance, and could be applied to the improvement of corrosion resistance and thermal shock resistance of castables. However, the coatings were discontinuous, and easily peeled from the graphite during the process of prolonged mixing, which would degrade the properties of castables. Additionally, the preparation processes of the coating technologies are complicated, and the raw materials are expensive.

Herein, we present a method for one-step synthesis of in-situ carbon-containing calcium aluminate cement (CCAC) for improving the oxidation resistance and water dispersion of carbon in castables via carbon-bed sintering with the raw materials of alumina and organic acid calcium, which has been applied in the preparation of porous carbon [25,26]. More specifically, organic acid calcium will be carbonized into carbon during the sintering process, and at same time, provides CaO for the generation of calcium aluminate. The in-situ carbon generated through the carbonization of organic acid calcium will be uniformly diffused in calcium aluminate. In addition, calcium aluminate cement is the most important hydraulic binder used for castables, owing to its superior refractory properties [6]; therefore, it is reasonable to expect that the CCAC should be compatible for both high alumina and basic castables.

In the present study, CCAC was synthesized through the carbon-bed sintering method with calcium citrate tetrahydrate and alumina as raw materials. Then, the oxidation resistance and water dispersion of CCAC were evaluated. Finally, as-prepared CCAC was used as binders for corundum-based castables, and their physico-mechanical properties

**Fig. 2.** (a) XRD patterns of the samples sintered at different temperatures; (b) FWHM of CA and CA₂ in the Cit + A1500 and Secar71.

including apparent porosity (AP), bulk density (BD), cold crushing strength (CCS), and cold modulus of rupture (CMOR) were also tested.

2. Experimental

2.1. Synthesis procedure for in-situ carbon-containing calcium aluminate cement

Calcium citrate tetrahydrate ($C_{12}H_{10}Ca_3O_{14} \cdot 4H_2O$) and alumina (Al_2O_3) were purchased from Sinopharm Chemical Reagent (Shanghai) Co. Ltd. The CaO/ Al_2O_3 (C/A) molar ratio in the raw material was kept constant (C/A = 0.8), and the raw material ratio is listed in Table 1.

These raw powders were mixed for 45 min in a ball mill. Then, the well-mixed powder was compressed to form a cylinder (35 mm in diameter and 30 mm in length) with a bulk density of approximately 1.04 g/cm^3 . After that, the cylinder sample was placed in a graphite crucible with a cover, which was buried in a corundum crucible with the graphite powder. Finally, the corundum crucible was covered, and heated to 600°C with a soaking time of 2 h in an electric SiC heating element furnace, after which the temperature was increased for sintering at 1300, 1400, and 1500°C , respectively, and these temperatures were maintained for 4 h. These samples were marked as Cit + A1300, Cit + A1400, and Cit + A1500, respectively. The schematic diagram of experimental setup is shown in Fig. 1.

The phase compositions of the samples were identified by X-ray diffraction (XRD, D/MAX 2400, Japan) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning speed of $5^\circ/\text{min}$. The morphologies of the product were examined by field-emission scanning electron microscopy with energy-dispersive spectrometry (FESEM-EDS, SU6600, Japan) and high-resolution transmission electron microscopy (HRTEM, JEOL 2100-F, Japan). Raman spectroscopy (Renishaw-invia) was applied to evaluate the order degree of the carbon phase in the composite powders using a 532 nm excitation laser with a spectral resolution of 2 cm^{-1} . The carbon content of CCAC determined by an infrared carbon–sulfur

Download English Version:

<https://daneshyari.com/en/article/7886244>

Download Persian Version:

<https://daneshyari.com/article/7886244>

[Daneshyari.com](https://daneshyari.com)