Synthesis of in-situ high-content carbon-containing calcium aluminate cement and its effect on the properties of Al2O3-SiC-C castables

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ABSTRACT
The in-situ high-content carbon-containing calcium aluminate cement (HCCAC) with the carbon content of 20.1 wt.% was prepared by the soft chemistry method with citric acid, calcium carbonate, and alumina as raw materials. The cement product was characterized by X-ray diffractionmetry, scanning electron microscopy, and Raman spectroscopy. In HCCAC, plate-like and fibrous carbon formed by the pyrolysis of organic acids were uniformly embedded between the calcium aluminate grains. Moreover, the carbon floating ratio of HCCAC in water was lower than that of the mechanical mixing powder of calcium aluminate cement (CAC) and carbon black, which indicated that the water dispersion of carbon was improved. Besides, the slag corrosion resistance properties of Al2O3-SiC-C castables bonded with HCCAC and CAC respectively were compared, and the results showed that the corrosion resistance depth of the HCCAC bonded castables was 45% lower than that of the CAC bonded castables. Therefore, HCCCA can be used as a novel binder of carbon-containing refractory castables.

KEYWORDS
Carbon-containing calcium aluminate cement; Al2O3-SiC-C; refractory castables; corrosion resistance; calcium citrate

1. Introduction
With the development of metallurgical technology, the carbon-containing castables have gradually become an important refractory. Carbon-containing castables have the characteristics of both convenient industrialization and rapid construction, and the advantages of thermal shock resistance and slag corrosion resistance properties of shaped carbon-containing refractory products. Therefore, it has a broad application prospect in the metallurgical industry [1–4]. General carbon materials such as graphite and spherical asphalt are now extensively applied in the preparation of carbon-containing castables because of their low cost and extensive source. However, graphite is difficult to be dispersed in the castables, due to its poor water wettability, which leads to the increase of water demand and apparent porosity of castables [5–7]. Although its dispersion of asphalt is improved in castables, various kinds of toxic gases are released in the process of pyrolysis, such as naphthalene and anthracene, which not only causes environmental pollution but also is not conducive to the densification of castables [8,9].

To overcome the disadvantages of graphite, the surfactant method [10,11], the coating method [12–14] and other methods [15–17] have been applied to the surface modification of graphite. The surface modification technology is dedicated to the use of surfactants or preparation of hydrophilic coatings on the surface of graphite, as the solution to the poor dispersibility of graphite in the castables, in order to improve the water demand, oxidation resistance, and corrosion resistance of carbon-containing castables. However, the current preparation method of modified graphite is a complex work, with its long-term preparation, easy foaming of surfactants, and easy abscission of the coating layer, and therefore it has difficulty in industrialization. In recent years, some researchers have fabricated and used carbon composite powders [18–20] or graphitic carbon spheres [2,21] as the carbon-containing castables. Carbon composite powders with high hydrophilicity and graphitic carbon spheres can be evenly dispersed in the castable matrix, and effectively improve the fluidity and mechanical properties of the castables.

In the previous work, we prepared a novel cement called in-situ carbon-containing calcium aluminate cement (CCAC) [19]. The carbon in this cement with favorable water dispersibility has been used in Al2O3-C [20], Al2O3-SiC-C [22], and Al2O3-MgO-C [23] castables and the oxidation resistance, slag corrosion resistance, and thermal shock resistance of castables have been improved. However, calcium citrate is used as a carbon source in CCAC with a carbon content of only 1.45 wt.%, which results in extremely low carbon residue...
content in the matrix and limits the improvement of castable properties.

In this paper, aiming to prepare the in-situ high-content carbon-containing calcium aluminate cement (HCCAC), one of the water-soluble calcium salt of citric acid was selected as the carbon source precursor to replace calcium citrate, which was beneficial to increase the carbon content in the process of pyrolysis. Moreover, the soft chemistry method was used to ensure that the carbon can be uniformly in-situ formed and embedded in calcium aluminate grains. In addition, the HCCAC was also applied to Al2O3-SiC-C castables and its physical properties, mechanical properties, and corrosion resistance were studied.

2. Materials and methods

2.1. Synthesis of HCCAC

Citric acid monohydrate (C6H5O7·H2O), calcium carbonate (CaCO3), and alumina (Al2O3) were supplied by Sinopharm Chemical Reagent (Shanghai) Co. Ltd. The CaO/Al2O3 molar ratio was maintained at 0.8, which was similar to commercial calcium aluminate cement (CAC).

The cement precursor was prepared by the soft chemistry method, which was conducive to a more uniform formation of in-situ carbon. Citric acid and calcium carbonate were reacted in water in the molar ratio of 4:1 to prepare water-soluble precursor solution, and the main component of the solution is calcium dihydrogen citrate. Further, the solution was dried at 80°C until the water has completely evaporated. In order to avoid excessive gas generated to expand the sample during sintering, the precursor was pre-treated at 210°C for 1.5 h to decompose and release excess water and CO2. The alumina powder with the CaO/Al2O3 molar ratio of 0.8 was added into the precursor powder, and the CaO content in the precursor was determined by the weight-loss test. Finally, the mixed powder was pressed into a block and placed in a graphite crucible, and sintered at 1500°C for 4 h in an argon atmosphere.

2.2. Preparation of Al2O3-SiC-C refractory castables

Raw materials for preparing Al2O3-SiC-C castables samples included white fused alumina (>99%, 8–5 mm, 5–3 mm), dense fused alumina (>98%, 3–1 mm, 1–0 mm), tabular alumina (>99%, 200 mesh, 325 mesh; Almatis, China), silica fume (971 U; Elkem, Norway), and silicon carbide (>99%, 1–0 mm, 325 mesh).

HCCAC cement was ground and passed 170 mesh sieve to ensure its fineness similar to that of commercial calcium aluminate cement (Secar71, Kerneos, China). Two castables samples were prepared, bonded with HCCAC (Sample A) and CAC (Sample B) as binders. In order to evaluate the influence of in-situ carbon on the water demand of castables, Sample C was prepared and compared with Sample A. Sample C maintains the same calcium aluminate cement content and carbon content as Sample A. The raw materials were wet-mixed in the mixer at the ratio of Table 1 for 4 min, and all the samples were kept the same rheology. Immediately, the mixture was placed in a cuboid mold (40 mm × 40 mm × 160 mm) to test the physical properties of castables and vibrated on the vibration table. The crucible of castables (ø75 mm × 75 mm) with a cylindrical inner hole (ø40 mm × 40 mm) was prepared to test corrosion resistance. The cast samples were demolded after curing at room temperature for 24 h and dried at 110°C for another 24 h. Finally, the dried samples were fired at 1450°C for 3 h.

2.3. Characterization

The crystalline phase of the samples was identified by X-ray diffractometer (XRD, D/MAX 2400, Japan) using Cu Kα radiation (λ = 1.5406 Å), and the scan rate was 5° (2θ)/min. After the Pt sputtering treated, the microstructures and phase morphologies of the samples were observed using a field emission scanning electron microscope-energy-dispersive spectrometer (FESEM-EDS, SU6600, Japan). Raman spectroscopy was applied to evaluate the graphitization degree of carbon in HCCAC, using a 532 nm laser with a spectral resolution of 2 cm⁻¹. The carbon content of the HCCAC was tested by the weight-loss method. The HCCAC was placed in a corundum boat crucible and heated to 800°C for 5 °C/min in the air, and the carbon content was measured according to Equation (1).

\[
\text{Carbon content} = \frac{\text{Weight loss}}{\text{Original HCCAC weight}} \times 100\%
\]

The water dispersion was evaluated using the carbon floating ratio of the setting slurry, as shown in Equation

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**Table 1. Compositions of Al2O3-SiC-C castables.**

|                  | Sample A (wt. %) | Sample B (wt. %) | Sample C (wt. %) |
|------------------|------------------|------------------|------------------|
| White fused      | 27               | 27               | 27               |
| alumina          |                  |                  |                  |
| Dense fused      | 28               | 28               | 28               |
| alumina          |                  |                  |                  |
| Tabular alumina  | 15               | 15               | 15               |
| SiC fume         | 2.5              | 2.5              | 2.5              |
| Silicon carbide  | 16               | 16               | 16               |
| Reactive alumina | 5                | 5                | 5                |
| Anti-oxidant     | 1.7              | 1.7              | 1.7              |
| Secar71          | -                | 2                | 2                |
| HCCAC            | 2.5              | -                | -                |
| Carbon black     | -                | -                | 0.5              |
| Spherical asphalt| 2                | 2.5              | 2                |
| Deflocculant     | 0.13             | 0.13             | 0.13             |
| Water            | 5.4              | 4.8              | 7.0              |
Table 2. Chemical composition of blast furnace slag (mass%).

|        | CaO  | SiO2 | Al2O3 | MgO  | Fe2O3 | K2O | TiO2 | Others |
|--------|------|------|-------|------|-------|-----|------|--------|
|        | 36.17| 32.61| 15.40 | 9.15 | 0.70  | 0.44| 0.84 | 4.69   |

(2), which is similar to that of Zhang et al. [13]. 3 g HCCAC or CCB (80% CAC and 20% carbon black mechanical mixing powder) and 20 mL water were placed in glass bottles respectively. After ultrasonic vibration for 5 min, the slurry was set aside for 0.5 h, 1.0 h, 2.0 h, and 3.0 h. Finally, the floating carbon in the bottle was separated, dried, and weighed.

Carbon floating ratio = \[ \frac{\text{Floating carbon weight}}{\text{Original weight}} \times 100\% \] (2)

The bulk density (BD) and apparent porosity (AP) of the castables samples were measured according to the Archimedes method with water as the medium. The cold modulus of rupture (CMOR), cold crushing strength (CCS), and permanent linear change (PLC) of the castables samples were measured according to Chinese national standards (GB/T 4513.6–2017). The measurement method of PLC is shown in Equation (3).

\[ \text{PLC} = \frac{\text{Length variation of sintered sample}}{\text{Original length of sample}} \times 100\% \] (3)

Corrosion resistance was determined by the static crucible method at 1450°C for 3 h adopting blast furnace slag, which chemical compositions were listed in Table 2. The crucible castables after the experiment were cut in the axial direction, and the corrosion depth of the castables was measured.

3. Results and discussion

3.1. Phase formation and morphology of HCCAC

HCCAC is black powder due to its relatively high carbon content. The carbon content of cement was measured according to the weight-loss test, and the result showed that the carbon content of HCCAC was 20.1 wt.%. Its carbon content was nearly 15 times higher than that of calcium aluminate cement prepared by Xiao, et al. [20]. Therefore, it has more engineering value for castables. The main reason for the increased carbon content of HCCAC is to choose the appropriate calcium salt of citric acid as the carbon source precursor. In the previous work, calcium citrate (Citric acid:Ca^{2+} = 3:2) is selected as the carbon source, which limits the amount of carbon produced during pyrolysis. Furthermore, in this work, when the ratio of citric acid to Ca^{2+} is 4:1, the main product is water-soluble calcium dihydrogen citrate (I–III steps) [24]. As a kind of calcium salt of citric acid, the pyrolysis behaviors of calcium dihydrogen citrate are similar to that of calcium citrate, which have been studied by Ding [19] and Mansour [25]. During the pyrolysis of the precursor, CaO and carbon were formed (IV and V steps). CaO reacts with Al_{2}O_{3} in raw material to form calcium aluminate phase, including CaAl_{2}O_{4} (CA) and CaAl_{4}O_{7} (CA_{2}), which is the main component of cement, and the reaction process is as shown in VI and VII steps [26].

\[ 3\text{CaCO}_3 + 2\text{CaH}_{6}\text{O}_7 \rightarrow \text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 + 3\text{CO}_2 + 3\text{H}_2\text{O} \] (I)

\[ \text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 + \text{CaH}_6\text{O}_7 \rightarrow 3\text{CaC}_6\text{H}_6\text{O}_7 \] (II)

\[ \text{CaC}_6\text{H}_6\text{O}_7 + \text{CaH}_6\text{O}_7 \rightarrow \text{Ca}(\text{C}_6\text{H}_5\text{O}_7)_2 \] (III)

\[ \text{Ca}(\text{C}_6\text{H}_5\text{O}_7)_2 \rightarrow \text{CaCO}_3 + \text{C} + \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{H}_2\text{O} \] (IV)

\[ \text{CaCO}_3 + \text{CH}_4 \rightarrow \text{CaO} + \text{C} + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \] (V)

\[ \text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{O}_4 \] (VI)

\[ \text{CaAl}_2\text{O}_4 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_4\text{O}_7 \] (VII)

Figure 1 shows XRD patterns of the CAC, HCCAC, and the product of HCCAC after pickling with dilute hydrochloric acid for 24 h. The result demonstrated that the main phases of CAC and HCCAC were CA and CA2. It can be seen that the intensities of characteristic peaks of CA and CA2 of HCCAC are close to that of CAC, implying that the main phase composition of HCCAC and CAC is similar. Calcium aluminate in HCCAC was removed after pickling and cleaning, and the sharp characteristic peak of graphite (002) at 2θ = 26.33° appeared in the XRD pattern of the product, which indicated that the carbon with high graphitization degree is formed in HCCAC.

![Figure 1. XRD patterns of the CAC, HCCAC and HCCAC after pickling.](image-url)
In order to further analyze the graphitization degree of carbon in HCCAC, the sample after pickling was also confirmed by Raman spectroscopy. As shown in Figure 2, two peaks at 1340 cm\(^{-1}\) (D band) and 1567 cm\(^{-1}\) (G band), respectively, were derived from the defects of the sp\(^2\) carbon structure and the vibration of sp\(^2\) bonded carbon atoms in a two dimensional hexagonal lattice. The intensity ratio between the D band and G band (ID/IG) was generally used to evaluate the graphitization degree of carbon materials. For the sample, ID/IG was 1.23, which indicated that a certain amount of graphitized carbon was produced in HCCAC [27].

The morphologies and existing forms of carbon and calcium aluminate in HCCAC were investigated by SEM, and the results are shown in Figure 3. The image of HCCAC is shown in Figure 3(a), and it can be seen that HCCAC was composed of irregular particle clusters with a particle size of about 50–70 µm. Figure 3(b, c) show the plate-like and fibrous substances between the grains of the particles (at the arrowhead). Based on the EDS analysis, the ratio of CaO/Al2O3 at spot A was close to 1, and the carbon content at spot B was significantly higher than that at spot A. It can be inferred that the phase composition of the particle clusters was mainly CA, and the small plate-like and fibrous substances were carbon. As the main component of HCCAC, the calcium aluminate phase remains the original micromorphology of alumina [28], thus it can be assumed that the alumina template was reacted with CaO decomposed by calcium organic acid precursor to produce CA [19]. At the same time, the carbon in-situ formed by the carbonization of organic carbon source in this process and was embedded in the grain boundaries with the growth of calcium aluminate grains.

3.2. Water dispersion of HCCAC

The water dispersion of carbon materials have an important influence on the workability and service performance of carbon-containing refractory castables. Figure 4 shows the carbon floating ratios of HCCAC and CCB in water. It can be seen that the carbon floating ratios of HCCAC was about 34% and that of CCB was about 45% after the slurry was set for 0.5 h. With the extension of the setting time, the carbon floating ratios of HCCAC and CCB increased slightly. It was worth noting that carbon floating ratio of HCCAC was always lower than that of CCB. This behavior was associated with the carbon in HCCAC, which was closely embedded in hydrophilic aluminate cement particles. The results showed that the water dispersion of HCCAC was better than that of CCB.

3.3. Physical and mechanical properties of Al2O3-SiC-C castables samples

HCCAC and CAC were used as binders for the preparation of Al2O3-SiC-C castables. In order to ensure the consistent total carbon content for both castables, 2 wt.% spherical asphalt as carbon source was added to the castables bonded with HCCAC binder (Sample A). For a given target rheology value of about 130%, the water demands for Sample A, Sample B, and Sample C were, respectively, 5.4 wt. %, 4.8 wt.%, and 7.0 wt.%. Due to the high water demand, Sample C lost the demolding strength in the same curing time as Sample A and Sample B. The water demand for Sample A was slightly higher, which may be attributed to more pores of calcium aluminate grains and high carbon content in HCCAC. From the SEM photographs, HCCAC grains contain more pores, which cause the shortened setting time and increased water demand for cement. In the preparation process, the setting time of the HCCAC bonded castables was slightly shorter than that of the CAC bonded castables, but it did not influence the workability. It should be noted that the setting time and water demand could be optimized by selecting a more appropriate proportion of
Moreover, compared with Sample A and Sample C, although the addition of carbon black can reduce the release of toxic gases produced by pyrolysis of spherical asphalt, the water demand of castables increases sharply due to the poor water dispersion of carbon. Therefore, for HCCAC, in-situ carbon is added to the castables in the form of carbon-containing cement, which reduces the deterioration of water demand caused by added carbon.

The BD and AP of the castables after firing at 110°C, 1100°C, and 1450°C are shown in Figure 5. It can be seen that the BD and AP of castables were obviously affected by the amount of water demand. As the temperature increases, the carbon inside the castables was oxidized, resulting in more pores, and the porosity of the castables was increased. At 1450°C, the dense mullite phase (see Figure 6(b)) was formed in the

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**Figure 3.** Microstructure of HCCAC particles (a) and the plate-like and fibrous carbon (b,c).

**Figure 4.** Carbon floating ratios of HCCAC and CCB in water.
inner part of the castables to block the pores, which reduced the oxidation of carbon, thus increasing the BD and reducing the AP.

Figure 6(a) shows the PLC of Sample A and Sample B after firing at 1100°C and 1450°C, respectively. It can be seen that two samples had the same trend of shrinkage and expansion, but the smaller variation range of the castables bonded with HCCAC meant that its volume stability was excellent. For the Al2O3-SiC-C castables, at the firing temperature of 1100°C, micropowders such as activated alumina and silica fume cause sintering shrinkage due to the large specific surface area, so the PLC of the castables is negative. At the firing temperature of 1450°C, in-situ mullite was formed by the reaction of free Al2O3 and free SiO2 with the volume expansion and the mullitization increased, resulting in a positive PLC [29,30]. The formation of mullite was confirmed by XRD patterns of the matrix of sample A and sample B, as shown in Figure 6(b). However, the relatively high porosity of the castables bonded with HCCAC can inhibit the volume expansion of mullite formation, thus showing better volume stability.

Figure 7 shows the mechanical properties of the castables firing at various temperatures. It was commonly believed that the porosity of castables is negatively correlated with mechanical properties. For sample A, its mechanical properties should deteriorate sharply. However, compared with Sample A and Sample B, CCS and CMOR after firing at 1100°C and 1450°C for 3 h of Sample A did not decrease too much, especially CMOR. And its mechanical properties also satisfy the engineering use of castables.

### 3.4. Corrosion resistance of Al2O3-SiC-C castables samples

Photographs of the crucible section morphology and corrosion area of Sample A and Sample B are shown in Figure 8. It can be seen that the corrosion interface of Sample A was more regular and flat than that of Sample B, indicating that the carbon in the matrix of Sample A had better dispersion than that of sample B. The corrosion depth of Sample A was 0.73 mm, which was 45% lower than that of Sample B.

Figure 9 shows the microstructures and EDS analysis results of the corrosion area. The corrosion area can be divided into three parts: slag layer, reaction layer, and original layer. Figure 9(a) shows SEM photographs and EDS analysis results of the slag layer of Sample B. The slag layer was mainly composed of Si, Ca, Mg, and Al elements, indicating that the slag is mainly composed
of SiO2-CaO-MgO-Al2O3 system, which is consistent with the main components in Table 2. Moreover, the element distribution shapes of Mg and Al show the aggregation of elements. The SEM image of the aggregates shows the fishbone shape, which may be due to the crystallization of slag. With the development of corrosion, the spinel with dense structure was formed by the reaction of MgO in slag and Al2O3 in castables, which can partially resist the corrosion of slag, so this layer was called reaction layer. In the reaction layer, the matrix was corroded by slag and low-melting phases exist between aggregates. Because the slag was not wetted with the carbon in the matrix, the further corrosion of the slag to the castables was stopped. In the original layer, the aggregate was close contact with the matrix and there was no corrosion of slag.

**Figure 8.** Photographs of the crucible section morphology and corrosion area of Sample A (a) and Sample B (b).

**Figure 9(b, d)** show the microscopic analysis photographs of the reaction layer of Sample A. The maximum thickness of the reaction layer was about 125 μm, and there was no evidence of the slag corrosion to the voids in coarse aggregates at the original layer. In the reaction layer, the element distribution shapes of Mg and Al are similar, and the EDS analysis of spot A shows that it is the spinel phase. The spinel is connected into layers, and the Mg element comes from slag. In **Figure 9(d)**, the element distribution shapes of Ca and Mg are not similar to that of Si and Al in the matrix part under the spinel layer (marked by the arrow). Therefore, it can be concluded that the matrix is not further corroded by CaO and MgO in the slag. **Figure 9(c,e)** show the microscopic analysis photographs of the reaction layer of Sample B. The maximum thickness of the reaction
layer of sample B was about 400 μm, while the spinel layer was not continuous, and the matrix was obviously corroded by slag. In addition to the spinel phase (Spot B), the similar element distribution shapes of Ca, Mg, Al, and Si were also found in the reaction layer. This indicates that the low-melting phase of Si-Ca-Mg-Al-O compounds is formed by the reaction of slag and matrix (Spot C).

Compared with Sample A and Sample B, the erosion of slag on matrix is different. For Sample A bonded with HCCAC, it is difficult to further form a low-melting phase after the reaction of slag and matrix to form the spinel layer, which indicates that the matrix has good slag corrosion resistance. Because the matrix of Sample B was rapidly corroded by the slag, it was difficult to form a spinel layer rapidly and continuously. Therefore, the reaction layer was thick and the matrix between the aggregates was significantly corroded. It can be seen that HCCAC improved the slag corrosion resistance of the castables matrix, which may be related to the more uniform distribution of carbon materials in the matrix.

4. Conclusions

The in-situ high-content carbon-containing calcium aluminate cement (HCCAC) was prepared by the soft
chemistry method with carbonization using water-soluble calcium citrate as carbon source. HCCAC was used as the binder in Al2O3-SiC-C castables, and its physical properties and performances were studied.

(1) The carbon content of HCCAC was 20.1 wt.%, and the carbon was evenly embedded in the calcium aluminate grains. Therefore, the carbon in HCCAC had better water dispersion.
(2) Although HCCAC as a binder slightly increased the porosity of castables at room temperature, it had little effect on its mechanical properties.
(3) HCCAC improved the corrosion resistance of the matrix, thereby reducing the thickness of the reaction layer.

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