Effect of in-situ carbon containing calcium aluminate cement on properties of Al$_2$O$_3$-SiC-C based trough castables

Shoulei Yang$^{a,b}$, Guoqing Xiao$^a$, Donghai Ding$^b$ and Jianying Gao$^c$

$^a$School of Materials Science and Engineering, Zhengzhou University of Aeronautics, Zhengzhou, China; $^b$College of Materials Science and Engineering, Xi’an University of Science and Technology, Xi’an, China; $^c$Imerys Technical Center China, Tianjing, China

ABSTRACT

The properties of Al$_2$O$_3$-SiC-C castables bonded by in-situ carbon containing calcium aluminate cement (CCAC) were investigated in this study. The results showed that after the Al$_2$O$_3$-SiC-C castables were dried at 110°C, their cold crushing strength (CCS) and cold modulus of rupture (CMOR) increased with the percentage of CCAC. The sample with CCAC content exceeding 2.5% by mass (named C2.5) had higher CCS and CMOR values than those of the model Al$_2$O$_3$-SiC-C castables (named BPS) with ball pitch as the carbon source. After being fired at 1100 and 1450°C, all the castables exhibited increased CCS and CMOR values, while the high apparent porosity of the BPS sample lowered its CCS and CMOR values. Compared with the BPS sample, the carbon materials of the castables bonded by CCAC exhibited improved dispersion in the matrix and excellent oxidation resistance, which enhanced the corrosion resistance of the refractory castables.

1. Introduction

Thanks to the high thermal conductivity, low thermal expansion, and molten slag/metal non-wettability of SiC and carbon materials, Al$_2$O$_3$-SiC-C based castables exhibit excellent corrosion resistance, thermal shock stability and good mechanical properties. Thus, they are usually used in iron troughs [1–4]. Unfortunately, the ball pitch, which is one of the main carbon sources used for Al$_2$O$_3$-SiC-C castables, releases harmful gases at elevated temperatures, pollutes the environment; and there is still a great challenge for the incorporation of the graphite flakes into castables owing to their poor water wettability [5]. All these drawbacks generate serious obstacles to the development of Al$_2$O$_3$-SiC-C based castables.

Presently, several technologies, including micro-pellets [6,7], coatings [8–14], and graphitic carbon spheres [15,16], have been employed to overcome the above issues. However, in practical applications, these technologies suffer from such drawbacks as discontinuous coating, agglomeration and uneven distribution of carbon materials in the castables. More importantly, owing to the particle sizes of graphite flakes (including modified graphite), and the non-hydrophilic property of graphitic carbon spheres, it is difficult for these carbon materials to be uniformly dispersed in castable matrices, which are crucial for the corrosion resistance of castables [17,18]. Recently, the modification of refractory matrices by in-situ carbon composites has gained popularity [19–22]. The present authors synthesized in-situ carbon-containing calcium aluminate cement (CCAC) with the phase composition close to that of Secar71 via the carbon bed sintering method, and found that the water dispersion and oxidation resistance of CCAC were enhanced, and that the corrosion resistance of the MgO-Al$_2$O$_3$ castables bonded by CCAC were remarkably improved [23–25].

To avoid the release of harmful gases from the pyrolysis of ball pitch, the Al$_2$O$_3$-SiC-C castables in the present work were prepared using CCAC as binder and carbon source replacing the ball pitch. The effects of CCAC content on the flowability, physical properties, mechanical properties, oxidation resistance, and corrosion resistance of the Al$_2$O$_3$-SiC-C castables were investigated. Also, for comparison, the model iron trough castables with ball pitch as carbon source and Secar71 as binder were prepared and their properties were tested.

2. Experimental

2.1. Preparation of Al$_2$O$_3$-SiC-C castables

The in-situ carbon containing calcium aluminate cement (CCAC) with the phase composition close to that of Secar71 was synthesized, and the details of the process were presented in our previous works [23,25]. The in-situ carbon content of CCAC was 1.45% by mass. The specific surface areas of Secar71 (Imerys, China), and CCAC, determined according to the BET method, were approximately 4084 and 5458 cm$^2$/g, respectively. The particle size distributions were determined.
by means of a laser particle size analyzer, and the obtained results are listed in Table 1.

Four groups of Al$_2$O$_3$-SiC-C castable samples were prepared using ball pitch and different CCAC contents (1.5, 2.5 and 4.0% by mass); these were named BPS, C1.5, C2.5, and C4, respectively. The water contents of all the samples were fixed at 4.8% by mass. Based on the formulations of the Al$_2$O$_3$-SiC-C castables (as listed in Table 2), the raw materials were weighed, dry mixed for 2 min, and then wet mixed for another 5 min following the addition of water. The castable mixtures were placed into cuboid samples (40 × 40 × 160 mm), and crucible samples (70 × 70 × 70 mm with a hole size of 40 mm×Ø 40 mm), and vibrated on a vibration table. The cast samples were cured at room temperature for 24 h and then were de-mold. They were subsequently cured at room temperature for another 24 h, and then dried at 110 °C for 24 h. Finally, the dried samples were fired at 1100 and 1450 °C, respectively, for 3 h in air atmosphere.

2.2. Tests and characterization methods

The flowability values of the four Al$_2$O$_3$-SiC-C castable mixtures were measured using the vibrating flowing table method. The bulk density (BD) and apparent porosity (AP) values of the castable samples, after they were dried and fired, were tested based on the Archimedes method. The cold modulus of rupture (CMOR) and cold crushing strength (CCS) were measured in accordance with the relevant national standards of China (GB/T3001-2007, GB/T5072-2008). The hot modulus of rupture (HMOR) was tested at 1450°C after a holding time of 0.5 h, in accordance with the GB/T3002-2004 standard. To evaluate the oxidation resistance of the Al$_2$O$_3$-SiC-C castables, the cross-sections of the prism-shaped samples (40 × 40 × 160 mm), which had been fired at 1450 °C for 3 h, were photographed, and the decarbonation layers in the cross-sections were measured using a vernier caliper.

For the corrosion resistance test, the hole of each prepared crucible sample was filled with 30 g slag powder (its chemical composition was listed in Table 3). The crucible samples were then fired at 1450 °C for 3 h. The corroded samples were cooled and then cut axially, and the corroded depth value (mm) was measured using a vernier caliper. The cross-section was further observed via a field-emission scanning electron microscopy (SEM, SU6600, Japan).

3. Results and discussion

3.1. Flowability

Figure 1 shows the flowing values of the four Al$_2$O$_3$-SiC-C castable mixtures. The initial flowing values of the four castable mixtures were similar. After being set for 30 min, all the samples exhibited reductions in their flowing values. The flowing values of BPS, C1.5 and C2.5 exhibited no distinct differences, but were higher than that of C4. After being set for 60 min, BPS had no pronounced change in its flowing value, while the other three Al$_2$O$_3$-SiC-C castables bonded by CCAC presented lower flowability owing to the higher hydration rate of CCAC resulted from its higher surface area.

3.2. Bulk density and apparent porosity

The AP and BD values of the dried and fired Al$_2$O$_3$-SiC-C castables are listed in Table 4. It can be seen that the BD values of the C1.5, C2.5, and C4 samples after being dried at 110°C were similar, and slightly higher than that of BPS. The BD values of all the samples changed little after they were fired at 1100 and 1450 °C. Compared with the castables after being dried at 110 °C, the four Al$_2$O$_3$-SiC-C castables after being fired at 1100 °C exhibited evidently higher AP values owing to the decomposition of the hydration products of calcium aluminate. Moreover, the AP value of BPS was higher than that of the other three samples because of the pyrolysis of ball pitch. Interestingly, the porosities of the four castable samples decreased after they were fired at 1450 °C due to formation of the liquid phases, which caused the pores to close. The carbon materials from the pyrolysis of ball pitch were oxidized easily, resulting in BPS having highest AP value among all the samples.

3.3. Strengths

The CCS and CMOR values of the dried and fired Al$_2$O$_3$-SiC-C castables are depicted in Figure 2. After being dried at 110 °C, the sample BPS had

---

**Table 1. Particle size distributions of CCAC and Secar71.**

| Cement   | Particle size distribution (um) |
|----------|---------------------------------|
|          | D10 | D50 | D90 |
| CCAC     | 1.7 | 11.52 | 36.86 |
| Secar71  | 1.66 | 29.76 | 77.98 |

**Table 2. Formulations of the Al$_2$O$_3$-SiC-C castables (% by mass).**

| Constituents               | Sample BPS | Sample C1.5 | Sample C2.5 | Sample C4 |
|---------------------------|------------|-------------|-------------|-----------|
| α-alumina                 | 77         | 77          | 77          | 77        |
| Silica Fume               | 2.5        | 2.5         | 2.5         | 2.5       |
| Silicon Carbide           | 16         | 16          | 16          | 16        |
| Ball pitch                | 2          | -           | -           | -         |
| Anti-oxidant (Al)         | 0.2        | 0.2         | 0.2         | 0.2       |
| Anti-oxidant (Si)         | 1.5        | 1.5         | 1.5         | 1.5       |
| Binder (Secar71)          | 2.5        | -           | -           | -         |
| Binder (CACCC)            | -          | 1.5         | 2.5         | 4         |
| Deflocculant (HMP)        | 0.06       | 0.06        | 0.06        | 0.06      |
| Deflocculant (Sodium lignosulphonate) | 0.1       | 0.1         | 0.1         | 0.1       |
| Water                     | 4.8        | 4.8         | 4.8         | 4.8       |
CCS and CMOR values of 60 and 11MPa, respectively. These were higher than those of C1.5 owing to the higher content of aluminate cement in BPS resulting in higher bonding strength than that in C1.5 [26]. The strength values of the sample BPS were lower than those of the C2.5 and C4 samples. It was believed that the ball pitch added to the BPS sample played negative roles in the formation of interlocked networks of the hydration products of calcium aluminates, thereby, reducing strength development. After being fired at 1100°C, the BPS, C1.5, C2.5 and C4 samples exhibited increases in their CCS and CMOR values of 13.33 and 36.36%, 35.29 and 70.00%, 11.76 and 50.00%, 7.89 and 5.00%, respectively, owing to the growth of ceramic phases forming the interlocking structures [27]. The C2.5 and C4 samples possessed higher strength values than that of the sample BPS. These can be associated with the higher AP value of the sample BPS, as an increase in cement content is beneficial to the development of bonding and aggregates. Interestingly, the CCS value of the C2.5 sample after it was fired at 1450°C, increased from 70 to 85MPa, but the strength values of the other three castables declined slightly. Although the CMOR value of the C2.5 sample declined by 36.8%, it remained higher than those of the others.

Figure 3(a,b) show the microstructures of the BPS and C2.5 samples after they were fired at 1450 °C for 3 h. The ceramic bonds between the matrix and aggregate in C2.5 were better than those in the BPS sample. These observations can explain why the strength values of the C2.5 sample are higher than those of the BPS sample. The lower values of CCS and CMOR observed in C4 can be associated with the formation of low melting phases owning to the increased content of CaO originating from CCAC [26]. The HMOR values of the Al2O3-SiC-C castables were tested at 1450°C after a holding time of 0.5 h. The results (as shown in Figure 4) indicated that C1.5 possessed the highest HMOR value (2.15 MPa), and C4 presented the lowest value, which was attributed to the more liquid phase at high temperatures owing to the increased content of CaO originating from CCAC [28]. In addition, the HMOR value of C2.5 was 1.72 MPa, which exhibited no difference compared with that of BPS.

Table 3. Chemical composition of slag powder.

| Compositions | MgO | Al2O3 | SiO2 | P2O5 | SO3 | K2O | CaO | TiO2 | V2O5 | Cr2O3 | Na2O |
|--------------|-----|-------|------|------|-----|-----|-----|------|------|-------|------|
| Content (wt.%) | 9.15 | 15.39 | 32.62 | 0.049 | 2.44 | 0.44 | 36.17 | 0.84 | 0.02 | 0.10 | 0.56 |

Table 4. Bulk density (BD) and apparent porosity (AP).

| Sample | Bulk Density (BD, g/cm³) | Apparent Porosity (AP, %) |
|--------|--------------------------|---------------------------|
|        | 110°C | 1100°C | 1450°C | 110°C | 1100°C | 1450°C |
| BPS    | 3.04  | 2.95  | 2.98  | 11.17 | 19.84 | 17.63 |
| C1.5   | 3.11  | 3.07  | 3.10  | 14.25 | 16.8  | 15.21 |
| C2.5   | 3.13  | 3.07  | 3.10  | 12.94 | 16.53 | 15.15 |
| C4     | 3.11  | 3.07  | 3.10  | 11.29 | 15.15 | 14.75 |
Figure 3. BSE images of the Al$_2$O$_3$-SiC-C castables after being fired at 1450 °C for 3 h. (a): BPS; (b): C2.5.

Figure 4. The HMOR of the Al$_2$O$_3$-SiC-C castables.
3.4. Oxidation resistance

The cross-sections of the Al$_2$O$_3$-SiC-C castables after they were fired at 1450 °C for 3 h are shown in Figure 5. The oxidized regions (light gray area) were visibly observed from the image of the BPS sample, and the average thickness of the decarbonation layers was approximately 9.72 mm. However, there were no pronounced oxidation regions in the cross-sections of the castables bonded by CCAC, and the existing dark gray color of the cross-sections was deepened with the percentage of CCAC. These observations implied that the carbon materials incorporated into the Al$_2$O$_3$-SiC-C castables through CCAC had better oxidation resistance than that of the carbon materials from the pyrolysis of ball pitch, and that the residual carbon materials in the castables increased with the addition of CCAC.

3.5. Corrosion resistance

In Figure 6, the cross-section images of the Al$_2$O$_3$-SiC-C castables after corrosion were depicted, indicating that the shapes of the four crucibles remained intact. Compared with those in BPS, the boundaries between the slag and crucibles in C1.5, C2.5 and C4 remained regular. The three-phase slag-air-sample junctions at the top of BPS were seriously corroded, which was not found in the cross-sections of the Al$_2$O$_3$-SiC-C castables bonded by CCAC. In addition to C2.5, the bottoms of the C1.5 and C4 samples exhibited distinct cracks. It can be concluded that the iron trough castables with the addition of 2.5% by mass of CCAC possessed better corrosion resistance.

The corrosion depth of the C2.5 sample, as measured using a vernier caliper, was 1.2 mm, which was...
lower than that of the BPS sample (3.5 mm). These results can be attributed to the pores left by the decomposition of ball pitch and oxidation of carbon materials, resulting in increased slag corrosion channel within the BPS sample. The carbon materials introduced into the castables by CCAC had improved dispersion and oxidation resistance, which resulted in lower porosity, and prevented the penetration of molten slag into the castables owing to the molten slag non-wettability of carbon materials.

The microstructures of the Al$_2$O$_3$-SiC-C castables after the corrosion resistance test were observed via SEM, and their backscattered electron (BSE) images are shown in Figure 7. It can be seen that in the BPS sample (Figure 7(a)), the outermost layers of the castable matrices, which were in contact with the slag, had already been corroded, leaving the corundum aggregates directly exposed to the slag. Furthermore, the slag had penetrated into the corundum aggregates, forming CA$_6$ and calcium aluminosilicates (CAS) in the slag-corundum aggregate interface zones. Meanwhile, the boundaries of the corundum aggregates in the C2.5 sample (Figure 7(b)) remained intact. The reasons for these observations were that the matrix containing CCAC, which possessed excellent corrosion resistance, coated the corundum aggregates, isolating the molten slag from the oxide grains.

**Figure 7.** The BSE images of the Al$_2$O$_3$-SiC-C castables after corrosion resistance test. (a): BPS; (b): C2.5.
4. Conclusions

The content of CCAC had significant effects on the physical properties, strengths, and oxidation resistance, especially corrosion resistance of the \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables. Compared with the castables prepared with ball pitch as the carbon source, the \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables bonded by CCAC had lower AP values after being dried and fired. Increasing the content of CCAC improved the CCS and CMOR values of the castables, but degraded their HMOR. In addition, CCAC enhanced the dispersion and oxidation resistance of the carbon materials in the \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castable matrices. This lowered the porosity of the castables, hindered molten slag penetration, and avoided the chemical attack of the corundum grains by molten slag. Hence, the \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables with 2.5% by mass of CCAC had better corrosion resistance than those of the trough castables bonded by Secar71 and using ball pitch as the carbon source. The increased content of CaO with the percentage of CCAC deteriorated the corrosion resistance of the refractory castables.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 51772236, 51372212, 51502236), and China Postdoctoral Science Foundation (2016M602940X). The authors thank the engineer Xinyue Ma, Imerys Technical Center China for helping with the preparation and testing of the \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables, and Prof. Wei, State Key Laboratory of Advanced Refractories, for helping with the SEM observation.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the China Postdoctoral Science Foundation [2016M602940X]; National Natural Science Foundation of China [51772236, 51372212, 51502236].

References

[1] Lian JW, Zhu BQ, Li XC, et al. Effect of in situ synthesized SiC whiskers and mullite phases on the thermo-mechanical properties of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) refractories. Ceram Int. 2016;42:16266–16273.

[2] Pillin V, Sarkar R. Effect of spinel content on the properties of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castable mullite. Ceram Int. 2016;42:2969–2982.

[3] Shan J, Liao N, Li Y, et al. Influences of novel \( \text{Si}_2\text{B}_3\text{C}_1 \) N antioxidant on the structure and properties of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables: in air and coke bedded atmosphere. Ceram Int. 2019;45:3531–3540.

[4] Chan CF, Argent BB, Lee WE. Influence of additives on slag resistance of \( \text{Al}_2\text{O}_3-\text{SiO}_2-\text{SiC}-\text{C} \) refractory bond phases under reducing atmosphere. J Am Ceram Soc. 1998;81:3177–3188.

[5] Mukhopadhyay S. The influence of surface-modified graphites on the rheological pattern of alumina-carbon cementitious refractory castable matrix. Ceram Int. 2019;45:19991–20001.

[6] Palčo S, He H, Paransky E, et al. The challenges of adding natural graphite into castables. Interclerm Int Ceram Rev. 2005;2:16–19.

[7] Rigaud M, Palčo S, Zhou N Alumina and magnesia-based castables containing graphite: comparison. Iron Steelmaker. 2002;29:45–51.

[8] Sunwoo S, Kim J, Lee K, et al. Preparation of \( \text{ZrO}_2 \) coated graphite powders. J Mater Sci. 2000;35:3677–3680.

[9] Mukhopadhyay S, Mondal C, Chakraborty A, et al. In depth studies on cementitious nano coatings on graphite for its contribution in corrosion resistance of alumina based refractory composite. Ceram Int. 2015;41:11999–12010.

[10] Yoshimatsu H, Fujiwara S, Konishi R, et al. Wettability by water and oxidation resistance of alumina-coated graphite Powder. J Ceram Soc JPN. 1995;103:929–934.

[11] Ansar S, Bhattacharya S, Dutta S, et al. Development of mullite and spinel coatings on graphite for improved water-wettability and oxidation resistance. Ceram Int. 2010;36:1837–1844.

[12] Liu X, Wang Z, Zhang S. Molten salt synthesis and characterization of titanium carbide-coated graphite flakes for refractory castables applications. Int J Appl Ceram Technol. 2011;8:911–919.

[13] Ye J, Zhang S, Lee W. Molten salt synthesis and characterization of \( \text{SiC} \) coated carbon black particles for refractory castable applications. J Eur Ceram Soc. 2013;33:2023–2029.

[14] Liu Z, Deng C, Yu C, et al. Molten salt synthesis and characterization of \( \text{SiC} \) whiskers containing coating on graphite for application in \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables. J Alloys Compd. 2019;777:26–33.

[15] Li S, Liu J, Wang J, et al. Fabrication of graphic carbon spheres and their application in \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) refractory castables. Int J Appl Ceram Technol. 2018;15:1166–1181.

[16] Li S, Liu J, Wang J, et al. Catalytic preparation of graphic carbon spheres for \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables. Ceram Int. 2018;44:12940–12947.

[17] Zou Y, Gu H, Huang A, et al. Effects of \( \text{MgO} \) micro-powder on microstructure and resistance coefficient of \( \text{Al}_2\text{O}_3-\text{MgO} \) castable matrix. Ceram Int. 2014;40:7023–7028.

[18] Sarpoolaky H, Zhang SW, Argent BB, et al. Influence of grain phase on slag corrosion of low-cement castable refractories. J Am Ceram Soc. 2001;84:424–434.

[19] Gong W, Li X, Chen P, et al. Effects of in situ synthesis of \( \text{CNTs/SiC}_x \) on microstructure and properties of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) composites. Int J Appl Ceram Technol. 2019;16:1337–1346.

[20] Ding DH, Lv LH, Xiao GQ, et al. One-step synthesis of in situ multilayer graphene containing \( \text{MgAl}_2\text{O}_4 \) spinel composite powders. Ceram Int. 2019;45:6209–6215.

[21] Lv LH, Xiao GQ, Ding DH, et al. Combustion synthesis of \( \text{C/MgAl}_2\text{O}_4 \) composite powders using magnesium oxalate as carbon source. Int J Appl Ceram Technol. 2019;16:671–677.

[22] Ding DH, Lv LH, Xiao GQ, et al. Improved properties of low-carbon \( \text{MgO}-\text{C} \) refractories with the addition of multilayer graphene/MgAl_2O_4 composite powders. Int J Appl Ceram Technol. 2019;10.1111/jrac.13347.

[23] Xiao GQ, Yang SL, Ding DH, et al. One-step synthesis of in-situ carbon-containing calcium aluminate cement
as binders for refractory castables. Ceram Int. 2018;44:15378–15384.

[24] Ding DH, Yang SL, Xiao GQ, et al. Investigations on the properties of Al$_2$O$_3$-MgO refractory castables bonded by in-situ carbon containing calcium aluminate cement. Mater Res Express. 2018;5:095205.

[25] Ding DH, Yang SL, Xiao GQ, et al. One-step synthesis of in-situ nanocarbon containing calcium aluminate cement in reducing atmosphere. Int J Appl Ceram Technol. 2019; 16:1416–1424.

[26] Cogtas C, Lopez HF, Sobolev K. Role of cement content on the properties of self-flowing Al$_2$O$_3$ refractory castables. J Eur Ceram Soc. 2014;34:1365–1373.

[27] Wang Y, Li X, Zhu B, et al. Microstructure evolution during the heating process and its effect on the elastic properties of CAC-bonded alumina castables. Ceram Int 2016;42:11355–11362.

[28] Lee WE, Vieira W, Zhang SW, et al. Castable refractory concretes. Int Mater Rev. 2001;46:145–167.