Pore evolution and its effect on slag resistance of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables

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\( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables with different particle size distributions (PSD) corresponding to different Andreassen distribution modulus (\( q \)) values, were fabricated, and their apparent porosity, permeability, pore size distribution and mean pore size, examined, after heat-treatment at different temperatures. The apparent porosity of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castable samples dried at 110°C for 24 h or fired at 1450°C for 3 h, decreases with increasing the \( q \) value from 0.21 to 0.23, but starts to increase on further increasing the \( q \) value to >0.23, i.e., it reaches the minimal value when \( q = 0.23 \). The change of permeability with \( q \) is similar, although it reaches the minimal value when \( q = 0.22 \). The mean pore sizes of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castable samples dried at 110°C for 24 h increase with increasing \( q \) from 0.21 to 0.25, whereas for samples fired at 1450°C for 3 h, they have no obvious regularity. Pore size distributions of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castable samples after treated at different temperatures, are evidently scattered when \( q = 0.21, 0.22 \) and 0.25, but tend to become continuous when \( q = 0.23 \) and 0.24, in particular when \( q = 0.23 \). The \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castable with \( q = 0.23 \) shows the best slag resistance because of its relatively narrow pore size distribution. In addition, our results reveal that PSD has little, whereas temperature has more obvious, effect on apparent porosity, permeability, mean pores size and pore size distribution of \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castables.

Key-words: Particle size distribution, \( \text{Al}_2\text{O}_3-\text{SiC}-\text{C} \) castable, Apparent porosity, Permeability, Pore size distribution, Slag resistance

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were derived according to Table 1, thus, particle size gradings corresponding to different q values were obtained (Table 2).

Castable samples of 160 mm × 40 mm × 40 mm were prepared based on Table 2. The dry raw material powders were mixed initially in a mixer for 30 s, followed by a one-step addition of 6.5 wt% water in 10 s while the mixer was running. After 5 min wet mixing, samples were cast under vibration and then cured for 24 h at a constant temperature and humidity in a curing box, dried for 24 h at 110°C and fired at 1450°C for 3 h in a furnace. To protect carbon in the samples from oxidation on firing, the samples were embedded in coke powders contained in a refractory saggar sealed with a refractory lid. Apparent porosity, permeability, mean pore size and pore size distribution of samples prepared with different PSD were pre-inserted into the lining of the induction furnace (21WGJL0.025-100-2.5P). Then iron (6 kg) and slag (2 kg) were fed into the furnace. The samples were fired at 1500°C for 3 h in air under the simulated condition of blast main trough. The schematic diagrams of the experiment are shown in Fig. 1.

An Axioskop40 optical microscope (Zeiss, Germany) and an scanning electron microscope (SEM, FEI, Nova 400 Nano) equipped with energy dispersive X-ray spectroscopy (EDS, EDAX) were used to carry out microstructural analysis on some typical samples heat-treated at different temperatures, so as to assist clarifying the pore evolution mechanism.

3. Results and discussion

3.1 Effect of PSD on apparent porosity

The apparent porosities of Al2O3–SiC–C castables prepared with different PSD after treated at different temperatures are shown in Fig. 2. The apparent porosities of Al2O3–SiC–C castables dried at 110°C or fired at 1450°C, decrease with increasing q from 0.21 to 0.23, but start to increase upon further increasing q to >0.23, which indicates that the minimum porosity is achieved when q = 0.23. It is well known that finer particles can fill the voids between coarse grains, which reduces the friction between coarse grains, thus improving the flowability of the resultant casting.

![Fig. 1. Schematic diagrams of the slag corrosion test in induction furnace.](image)

![Fig. 2. Apparent porosity of Al2O3–SiC–C castables prepared with different q value.](image)

Table 1. PSD calculated according to Andreessen’ model, wt%  
| q value | 8–5 mm | 5–3 mm | 3–1 mm | 1–0.088 mm | 0.088–0 mm |
|---------|--------|--------|--------|------------|-----------|
| 0.21    | 9.40%  | 9.22%  | 16.77% | 25.83%     | 38.79%    |
| 0.22    | 9.82%  | 9.59%  | 17.30% | 26.21%     | 37.08%    |
| 0.23    | 10.25% | 9.95%  | 17.82% | 26.54%     | 35.44%    |
| 0.24    | 10.67% | 10.31% | 18.32% | 26.83%     | 33.88%    |
| 0.25    | 11.09% | 10.66% | 18.79% | 27.08%     | 32.59%    |

Table 2. PSD of Al2O3–SiC–C castable with different q value, wt%  
| Raw materials            | Particle size [mm] | 0.21 | 0.22 | 0.23 | 0.24 | 0.25 |
|--------------------------|-------------------|-----|-----|-----|-----|-----|
| Fused alumina            | 5–8               | 9.40| 9.82| 10.25| 10.67| 11.09|
|                          | 3–5               | 9.22| 9.59| 9.95| 10.31| 10.66|
|                          | 1–3               | 16.77| 17.30| 17.82| 18.32| 18.79|
|                          | 0.088–1           | 14.83| 14.21| 14.54| 14.83| 14.08|
|                          | ≤0.074            | 10| 10| 10| 10| 10 |
| Silicon carbide          | 0.088–1           | 8| 8| 8| 8| 8 |
|                          | ≤0.074            | 5| 5| 5| 5| 5 |
| α-Al2O3                  | 13.79| 12.08| 10.44| 8.88| 7.39 |
| Calcium Aluminates cement| 3| 3| 3| 3| 3 |
| Silicon fume             | 4| 4| 4| 4| 4 |
| Pitch ball               | 3| 3| 3| 3| 3 |
| Micro silica             | 3| 3| 3| 3| 3 |
| Additives                | 0.1| 0.1| 0.1| 0.1| 0.1 |
The permeability of samples fired at 1450°C is much higher than that of the samples dried at 110°C. The change of permeability with \( q \) is the same as that seen in the case of apparent porosity, except that permeability reaches the minimum value when \( q = 0.22 \), whereas apparent porosity reaches its minimum value when \( q = 0.23 \). Permeability is a property used to characterize the size and amount of through pores in a refractory, while the apparent porosity characterizes only the amount of open pores and through pores, so the two do not have exactly the same relationship with the PSD of the refractory. A little bit more fine particles could be beneficial to having smaller permeability, because fine particles can fill the through pores, and change them to closed pores. This is the reason why the \( q \) for the minimal permeability is smaller than that for the minimal apparent porosity.

### 3.3 Effect of PSD on pore size distribution and mean pore size

Pore size distribution quantifies the amount of each sized pore in the material. It is often illustrated with a curve of cumulative amount of pore volume versus mean radius of pores. Pore size distributions of Al\(_2\)O\(_3\)–SiC–C castable prepared with different PSD after treated at 110°C for 24 h are shown in Fig. 5.

As seen from Fig. 5, for the samples treated at 110°C for 24 h, their pore size distribution curves look similar. There are two or three peaks in the curves. The only main difference is that with increasing \( q \), the mean pore size increases as well. The mean pore size and pore size distribution were determined by the mercury filling method, and 4–8 mm chunks cut from the mother samples were used. So these two parameters indicate some characteristics of the inner pores in the material. As shown in Table 1, with increasing \( q \), the amount of fine particles decreases, so some big pores cannot be filled due to insufficient fine particles, consequently the mean pore size increases with increasing \( q \). The mean pore sizes of samples with different PSD treated at 1450°C for 3 h (Fig. 6), have no obvious regularity. However, for pore size distribution, 3 obvious peaks appear in the curves corresponding to \( q = 0.21 \) and 0.22, indicating the scattering in the pore size distribution, i.e., large differences between small and big pores in the material. On the other hand, when \( q = 0.23 \) and 0.24, in particular when \( q = 0.23 \), the corresponding curves show only two obvious peaks, and the peak at around 70 nm is lower than that in the cases when \( q = 0.21 \) and 0.22. This means that pores in samples with \( q = 0.23 \) and 0.24 vary in a very narrow range, namely they exhibit a continuous distribution. But for \( q = 0.25 \), three peaks again appear.

### 3.4 Temperature effect on the pore evolution

Figures 3 and 4 show that apparent porosity and permeability of Al\(_2\)O\(_3\)–SiC–C castables with different PSD after fired at 1450°C for 3 h are much bigger than those of the samples dried at 110°C for 24 h. The pores evolution with heating has a close relationship with dehydration of hydration products of CAC, the melting and evaporation behavior of pitch, as well as the effect from the silicon powder. Some residual sphere-liked pitch balls are seen in the Al\(_2\)O\(_3\)–SiC–C castable structure after dried at 110°C for 24 h [Fig. 7(a)], which is attributed to their high melting point (about \( \sim 120°C \)). However, with increasing the temperature to 1450°C, pitch balls transform into gaseous species, resulting in pores [Fig. 7(b)]. Consequently, the apparent porosity increases.

The actual atmosphere during the firing process was equivalent to a mixture of 35 vol% CO and 65 vol% N\(_2\). Therefore, the following reactions during firing would occur.
When the temperature is above 1420°C, silicon powder (2.34 g/cm³) used as an antioxidant for the Al₂O₃−SiC−C castable would melt into liquid phase and react with CO(g) diffused into the inner structure through pores according to Eq. (2). SiC can also react with CO(g) according to Eqs. (3) and (4). In terms of the densities of SiC(s) (3.2 g/cm³), C(s) (2.28 g/cm³) and SiO₂(s) (2.38 g/cm³), the volume changes associated with Eqs. (2) and (3) are calculated as about +41% and +228% respectively. This means that the above two reactions could lead to reduction in porosity and pore structure change. This could be explained further based on Figs. 8 and 9.

As shown in Fig. 8(a), some whisker-shaped phases formed in the pores. SEM-EDS verified that they were SiC [see Fig. 8(b)]. These newly-formed SiC whiskers fill in pores and reduce the pore size, thus changing the permeability, pore size distribution and mean pore size. However, the SiC whiskers were mainly formed through gas phase involved reactions severely affected by the partial pressures of involved gases, especially CO.19) Nevertheless, under the test condition, the partial pressure for samples prepared with different PSD was the same. In fact, only CO(g) was absorbed by pores in the material, it can react to form SiC whiskers according to Eq. (2). So its amount absorbed by pores has influence on the SiC whisker formation. It was known that the smaller the pore size, the bigger its specific surface area, and the more CO(g) absorbed,20) and thus the more SiC whisker formed. Meanwhile, the pores provide spaces for the SiC whisker to form, so the bigger the pore size, the more SiC whiskers it can accommodate. In terms of these, there must be a balanced point for pore size, which allows much more SiC whiskers to form for samples having different mean pore sizes. This is probably the reason why samples with q = 0.23 and 0.24 showed relatively narrow pore size distributions.

It should be pointed out that reaction between SiC and CO(g) [Eq. (3)] actually occur in two stages. Initially, the active oxidation Eq. (4) of original SiC particles near surface occurs, making the SiC particles much more porous [Figs. 9(c) and 9(d)]. Then the passive oxidation Eq. (5) of SiC particles occurs on the surface, resulting in a dense layer formed on the surface [Figs. 9(a) and 9(b)].21)

3Si(l) + 2CO(g) = 2SiC(s) + SiO₂(s)  \hspace{1cm} (2)
SiC(s) + 2CO(g) = SiO₂(s) + 3C(s) \hspace{1cm} (3)
SiC(s) + CO(g) = SiO(g) + 2C(s) \hspace{1cm} (4)
SiO(g) + CO(g) = SiO₂(s) + C(s) \hspace{1cm} (5)

3.5 Effect of PSD on slag resistance of Al₂O₃−SiC−C castable

Slag resistance of Al₂O₃−SiC−C castables prepared with
different PSD was tested using the induction furnace method. After test, samples were cut along vertical direction in the center, and their cross-sections are shown in Fig. 10. Al$_2$O$_3$–SiC–C castable samples with $q = 0.21$, 0.22 and 0.25 were obviously corroded by the slag, especially at the interface between gas, liquid and solid phases, while samples with $q = 0.23$ and 0.24, were almost not corroded. These results indicate that the optimal $q$ value for the corrosion resistance is the same as that for the pore size distribution, which further indicates that the slag resistance of Al$_2$O$_3$–SiC–C castables with different PSD has a close

![Fig. 6. Pore size distribution and mean pore size of Al$_2$O$_3$–SiC–C castables with different particle size distribution, after fired at 1450°C for 3 h. (a), $q = 0.21$, (b) $q = 0.22$(c) $q = 0.23$, (d) $q = 0.24$(e) $q = 0.25$.](image)

![Fig. 7. SEM morphology of Al$_2$O$_3$–SiC–C castables after treated at different temperatures, (a) after dried at 110°C for 24 h, (b) after fired at 1450°C for 3 h.](image)
relationship with the pore characters, especially with the pore size distribution. This could be explained according to the following Eq. (6), in which, \( K_p \) is the slag penetration depth in pore, \( r \) the radius of pore, \( \sigma \) the surface tension of liquid slag, \( \theta \) the contact angle of liquid slag with the refractory, \( \eta_p \) the viscosity of liquid slag in pore, and \( R_p \) a coefficient of penetration resistance of refractory. For a specific slag and refractory, \( \sigma, \theta, \) and \( \eta_p \) are constant, so \( K_p \) is mainly affected by the mean pore size \( r \) and \( R_p \), which has a close relationship with the pore size distribution. This well explains the above slag resistance results.

\[
K_p = \sqrt{\frac{r \sigma \cos \theta}{2 \eta_p R_p^2}}
\] (6)

4. Conclusions

The apparent porosity and permeability of Al\(_2\)O\(_3\)–SiC–C castables after dried and fired at different temperatures reach their minimal values when \( q = 0.23 \) and \( 0.22 \), respectively. Furthermore, the apparent porosity and permeability of fired samples are much greater than those of dried ones. The mean pore size of dried samples increases with the \( q \) value, whereas for fired ones, it appears to be irregular and much bigger. The pore size distributions for both dried and fired samples are discrete when \( q = 0.21, 0.22 \) or \( 0.25 \), but tend to be continuous when \( q = 0.23 \) and \( 0.24 \). The apparent porosity, permeability, mean pore size and pore size distribution of dried Al\(_2\)O\(_3\)–SiC–C castables, mainly
depend on the PSD, and to some extent, on the water evaporation and dehydration of the CAC hydration products. However, during heating at high temperatures, the effect of temperature on the pore evolution becomes significant, while the characters of pores derived after drying also have some influence on the pore evolution. The best slag resistance of Al₂O₃-SiC-C castable when \( q = 0.23 \) is believed to be associated with its relatively low porosity, permeability, mean pore size, and especially the narrow pore size distribution.

References

1) W. Chengxun, H. Jin, Z. Liang, L. Zhaoqiu, Z. Yi and Z. Hanli, “The Damage of Refractory and Its Suppression Technology”, Ed. by Zhang Xiuzhen, Metallurgical industry press, Beijing (2009) pp. 108–112.
2) R. Salomão and V. C. Pandolfelli, Ceram. Int., 34, 173–180 (2008).
3) B. Myhre, The effect of particle size distribution on flow of refractory castables. The American Ceramic Society 30th Annual Refractories Symposium in St. Louis, Missouri, march 25 (1994).
4) Y. Kutmen Kalpakli, Archives of Materials Science and Engineering, 34, 81–88 (2008).
5) B. Myhre and A. M. Hundere, UNITECR, 97, 43–52 (1997).
6) V. G. Domiciano, M. A. Brito, T. A. Avial, A. P. Luz and V. C. Pandolfelli, UNITECR’09, 2009.
7) Sc. Vladimir, V. primachenko, Valery V. Martynenko, Alexander. G. Knoruzhiy, UNITECR’09, 2009.
8) Adam Molin, Ondrej Kluzu, Jacek Podworny, Teresa Wala, UNITECR’09, 2009.
9) D. N. Borzov, Refract. Ind. Ceram., 43, 141–144 (2002).
10) T. Yoshimoto, T. Suzuki and K. Sugiyama, UNITECR, 97, 5–14 (1997).
11) L. Youheng, Z. Tangwen and L. Nan, Refractories, 41, 188–190 (2007).
12) G. Licun, L. Bin and W. Chunfeng, Refractories, 42, 51–53 (2008).
13) Z. Tao, Refractories, 36, 246 (2002).
14) L. Zhaoqun, T. Junbo and W. Juncong, Refractories, 43, 260–262 (2009).
15) G. Huazhi, L. Chunyan, W. Houzhi and Z. Wenjie, Refractories, 38, 160–164 (2004).
16) D. Xiaoeling, S. Jialin, C. Junhong, Z. Houxing and H. Yanruo, Refractories, 38, 82–84 (2004).
17) T. Junbo, W. Juncong and L. Chaoyun, Refractories, 43, 19–22 (2009).
18) B. Myhre and B. Sandberg, Proceeding of International Seminar on Monolithic Refractory Materials, Tehran, Iran (1997) pp. 113–140.
19) Li Yawei, Chen Xilai, Li Yuanbing, Jin shengli, Ge Shan, Zhao Lei and Li Shuijing, Refractories, 42, 401–404 (2008).
20) G. Liwen, X. Cangyan and C. Shuzhao, J. Hunan Univ. Sci. Technol., 23, 18–21 (2008) (Nature Science Edition).
21) A. Yamaguchi, Int. J. Appl. Ceram. Technol., 4, 490–495 (2007).