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Preparation and characterization of porous zircon aggregates by granulation method: Roles of the polymorphism of Al_2O_3

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Introduction:

Zircon ($ZrSiO_4$), which is the only stable silicate in the binary system of ZrO_2-SiO_2 at atmospheric pressure, processes a high melting point (2200 ℃), low thermal expansion, low thermal conductivity, excellent thermal shock resistance and high resistance to corrosion by molten glass and slag at high temperatures. As is known to all, zircon could decompose into ZrO_2 and SiO_2 at a wide temperature range (in the range of 1270 ℃ to 1683 ℃). SiO_2, which was produced by the decomposition reaction, could influence the service life of the zircon-based refractories due to SiO_2 could convert into the liquid phases at high temperature. These factors could destroy the structure and worsen the performances of the refractories. In order to solve the problem, alumina was introduced into the zircon system. Al_2O_3 could react with SiO_2 to form mullite ($3Al_2O_3 \cdot 2SiO_2$) which has a high strength, a high refractoriness (1830 ℃) and good corrosion resistance. However, Al_2O_3 has a lot of crystal types, and the activities of various crystal types of Al_2O_3 are also different. α-Al_2O_3 is the most common raw material of the various industries, which could be prepared from $Al(OH)_3$ fired at 950-1400 ℃. The preparation temperature of γ-Al_2O_3 was about 500 ℃, which was lower than that of α-Al_2O_3. The higher sintering temperature could decrease the activity of Al_2O_3 and increase the energy consumption. Therefore, the aim of this study is to investigate the influence of α-Al_2O_3 and γ-Al_2O_3 on the reaction between zircon and Al_2O_3 by the lattice and properties.

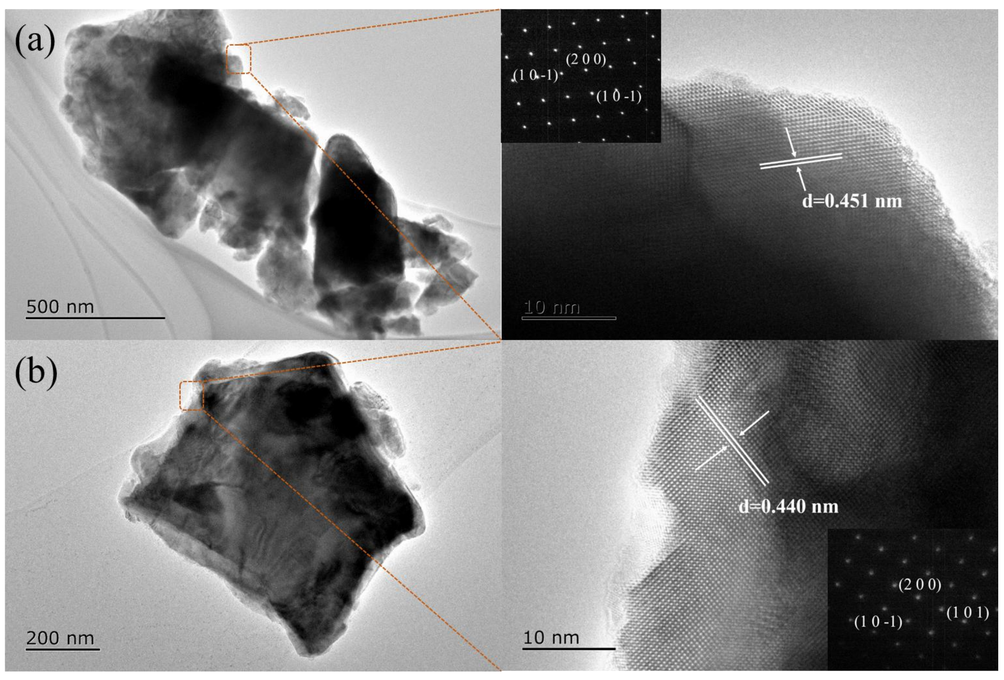

Fig. 1 The TEM images of the samples with different crystal type of Al_2O_3: (a) α-Al_2O_3; (b) γ-Al_2O_3.

The lattice fringe spacing of the sample with α-Al_2O_3 was 0.451 nm, while the lattice fringe spacing of the sample with γ-Al_2O_3 was 0.440 nm. It meant that α-Al_2O_3 doping caused a greater degree in zircon crystal compared with γ-Al_2O_3, which led to the expansion of the crystal volume. The main influence factor of α-Al_2O_3 on zircon was to change the lattice structure by the formation of interstitial solid solution, and minor α-Al_2O_3 reacted with SiO_2 to form mullite. Due to the higher Gibbs free energy of the reaction between SiO_2 and γ-Al_2O_3, the lattice fringe spacing and the changing of crystal parameters did not change significantly. These results were consistent with the crystal lattice model of zircon.

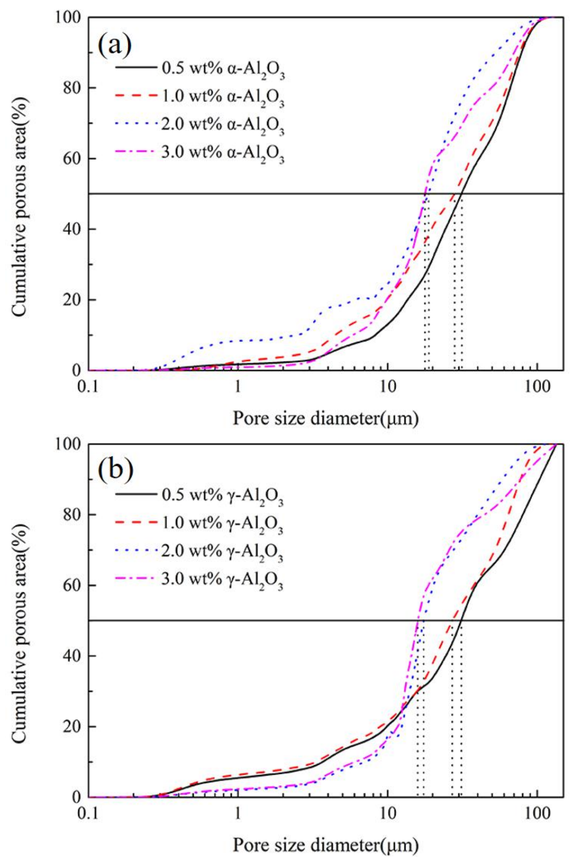

Fig. 2 The cumulative porous area of zircon aggregates with α-Al_2O_3 and γ-Al_2O_3: (a) α-Al_2O_3; (b) γ-Al_2O_3.

For the solid phase sintering process, γ-Al_2O_3 had the following advantages compared to α-Al_2O_3: (1) the higher reaction activity could accelerate the migration rate of ions; (2) the more production of mullite could fill up the pores and decrease the size of the effective pores; (3) the contact area between γ-Al_2O_3 and zircon was larger than that between α-Al_2O_3 and zircon due to the smaller median particle size and the larger surface area of γ-Al_2O_3. The larger contact area could shorten the diffusion distance of the ion. Moreover, the increased addition of Al_2O_3 could obviously exacerbate the reaction and increase the liquid phase content at 1550 ℃. The distribution of the liquid phase in the samples with α-Al_2O_3 and γ-Al_2O_3. The major difference was the content of Al_2O_3 and $NaAlO_2$. It was worth noting that the content of Na_2O in γ-Al_2O_3 was higher than that in α-Al_2O_3 which caused the higher liquid content and the lower liquid viscosity. The higher liquid content could promote Al_2O_3 and SiO_2 dissolve into the liquid phase, and then accelerated the penetration and segregation behaviors of the liquid phase, which led to the formation of mullite and $NaAlO_2$. Due to the stability of α-Al_2O_3, a small amount of α-Al_2O_3 is left in the liquid phase. On the one hand, liquid phases could promote liquid sintering; on the other hand, excessive liquid phases could cause the increment of pores due to the deposition.

Table 1 Density and porosity with various α-Al_2O_3 or γ-Al_2O_3 addition (BD-bulk density; TD-true density; AP-apparent porosity; CP-closed porosity).

	Zircon aggregates with α-Al_2O_3				Zircon aggregates with γ-Al_2O_3			
Addition (wt%)	BD (g/cm^3)	TD (g/cm^3)	AP (%)	CP (%)	BD (g/cm^3)	TD (g/cm^3)	AP (%)	CP (%)
0.5	3.08	4.63	26.8	6.7	3.21	4.59	26.5	3.7
1.0	3.12	4.61	25.3	7.0	3.24	4.57	25.0	4.1
2.0	3.14	4.59	24.2	7.4	3.27	4.57	24.1	4.3
3.0	3.12	4.57	24.8	7.5	3.26	4.57	25.2	4.6

The samples with γ-Al_2O_3 had the higher bulk density, the lower apparent porosity and the lower closed porosity in comparison with the samples with α-Al_2O_3. The bulk density increased and porosity decreased with the increase of Al_2O_3. Mullitization was accompanied by the appreciable expansion of the reaction between Al_2O_3 and SiO_2 which could decrease the porosity. And the transformation of different crystal types of Al_2O_3 led to a shrinkage that improved the densification of the samples. Compared with the samples with 2.0 wt%, 3.0 wt% α-Al_2O_3 and γ-Al_2O_3, too much liquid phases decreased the bulk density and increased the porosity.

Conclusion:

(1) The main influence factor of α-Al_2O_3 on zircon was to change the lattice structure by the formation of vacancies, minor α-Al_2O_3 reacted with SiO_2 to form mullite, while γ-Al_2O_3 had the opposite effect in Al_2O_3-$ZrSiO_4$ system compared with α-Al_2O_3. The expansion of the crystal lattice could weaken the mechanical properties.
(2) The formation of mullite and the liquid phases could influence the sintering process obviously. The higher content of Na_2O could influence the formation of mullite by the higher liquid phases content, the lower viscosity and higher rate of the penetration and segregation behaviors. The higher reaction activity of γ-Al_2O_3 could prevent icons from dissolving into crystal lattice. And the formation of mullite could improve the properties of zircon aggregates.

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