Effects of particle size of Al(OH)₃ on the properties of porous purging materials

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Porous purging plug is promising in the course of steel-making especially for producing the pure steel. Five designed castables containing the same aggregates and different matrixes were fabricated successfully. Air permeability tests, microstructural characterization and grey incidence analysis were carried out to analyze the particle size of aluminum hydroxide [Al(OH)₃] effects on the properties of porous purging materials. According to the attained results, the smaller particle size of Al(OH)₃ seemed to be suitable to improve the properties of such materials, as it induced the formation of connected pores and hot modulus of rupture changed slightly. When the particle size was 36.1 μm, the air permeability could reach 13.4 m². Moreover, the grey incidence analysis matched to the experimental observations, attesting the smaller particle sizes (10–20 μm) were helpful for enhancing the air permeability while the bigger particle sizes (≥100 μm) had the opposite effects.

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Key-words: Porous purging materials, Al(OH)₃, Air permeability, Grey incidence analysis, Microstructure

1. Introduction

Secondary refining technology is becoming more and more important in the process of steelmaking, and purging plug is a vital component for the secondary refining technology. Gas bubbling through the purging plug installed at the bottom of the ladle is being used extensively to homogenize the temperatures and content of chemical elements and to promote the removal of non-metal inclusion and decreasing of gas content. It includes directional, silt and porous three kinds of purging plugs. Compared with the directional and silt, the porous purging plug is promising in the course of steel-making especially for producing the pure steel due to easiness of gas flow control, high reliability on gas purging and cost effectiveness.

The Al₂O₃–Al(OH)₃ system can produce high refractoriness porous ceramics for thermal insulation and hot gas filtration, amongst other applications. After thermal treatment, Al(OH)₃ suffers an intense mass loss, which increases density and generates pores around and inside the particles. Adriane et al. evaluated the porogenic behavior of three grades of α-Al(OH)₃ (gibbsite) of different average particle sizes (0.9, 10 and 107 μm). Deng et al. made porous alumina ceramics by decomposition of Al(OH)₃. Li et al. described the preparation of porous corundum-mullite ceramics, using Al(OH)₃ powder and kaolinite gangue. Li et al. prepared porous corundum-spinel ceramics by an in situ decomposition pore-forming technique Al(OH)₃ and basic magnesium carbonate. It will not bring any impurities for the Al₂O₃ system using aluminum hydroxide [Al(OH)₃] as the pore-forming agent. Nonetheless, up to now, no systematic studies have been reported about porous purging materials using Al(OH)₃ as the pore-forming agent.

The present work is to address the effects of particle size of Al(OH)₃ on the properties of porous purging materials and grey incidence analysis is also used to analyze the correlation between particle sizes and the air permeability.

2. Experimental procedure

2.1 Preparation of the different particle sizes of Al(OH)₃

Al(OH)₃ (Chalco Shandong Advanced Material Co., Ltd. China) was ground using corundum balls as the abrasive media. The weight ratio of balls to Al(OH)₃ was 1:1, and the rotation rate of rotor drum was 30 r/min. And the milling time was 0, 3, 6, 9 and 12 h respectively. The chemical compositions of Al(OH)₃ is listed in Table 1.

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Table 1. The chemical compositions of Al(OH)₃ (wt %)

|    | Al₂O₃ | Fe₂O₃ | Na₂O | SiO₂ | water | IL |
|----|-------|-------|------|------|-------|----|
| Al(OH)₃ | 65.081 | 0.005 | 0.284 | 0.01 | 4.15  | 34.62 |

Table 2. Formulations of specimens

| Raw materials | wt% |
|---------------|-----|
| Tabular alumina | 0–3 mm | 70 | 70 | 70 | 70 |
| Al₂O₃ | ≤0.088 mm | 18 | 18 | 18 | 18 |
| 3 h(milling time) | 12 |
| Al(OH)₃ | 6 h(milling time) | 12 |
| 9 h(milling time) | 12 |
| 12 h(milling time) | 12 |

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persant, followed by wet mixing for 3 min. The mixed preparation was placed by vibration into a 160 mm × 40 mm × 40 mm cubic mold and a 50 mm × 50 mm circular cylinder mold, then cured at ambient temperature for 24 h and dried at 110°C for 24 h. Finally, all the specimens were fired in an electric furnace at 1550°C with a heating rate of 3 °C/min and a holding time of 3 h before cooling to room temperature.

2.3 Testing and characterization methods

The linear change was measured by the percentage difference between the initial and the final length (before and after heat treatment) divided by the initial sample dimension. Apparent porosity and bulk density of all the fired specimens were detected by Archimedes’ Principle with water as medium. The cold modulus of rupture (CMOR) was determined using the three-point bending test at ambient temperature, and the cold crushing strength (CCS) was evaluated using a Hydraulic Testing Machine. The hot modulus of rupture (HMOR) was measured by three-point bending test at 1400°C for a soaking time of 0.5 h by means of electronic digital control system (EDC120; DOLIC company, Germany). The air permeability was examined according to the Chinese standard GB/T 3000-1999. Particle size distribution was measured by Laser Particle Size Analyzer (Mastersizer 2000; Malvern Instruments Ltd., Worcestershire, UK). The specific surface area was evaluated by a BET method from N2 adsorption isotherms (AUTOSORB-1-MP; Quantachrome Instruments Ltd., USA). Microstructure of the specimens were analyzed by using the scanning electron microscope (SEM, JSM-6610, JEOL, Japan). The grey incidence analysis was calculated through a mathematical software (MATLAB; The MathWorks company, USA).

3. Results and discussion

3.1 Particle size distribution of Al(OH)3

Figure 1 showed the particle size distribution of Al(OH)3 with different milling time (0, 3, 6, 9 and 12 h), and the d50 value (the middle level diameter of the particles) was 105.5, 55.7, 42.5, 41.6, 36.1 μm respectively. The specific surface area was 0.22, 0.44, 0.63, 0.65, 0.73 m2/g respectively. It was obvious that the d50 value decreased and the specific surface area increased with the milling time from 0 to 12 h. And the particle distribution became wider.

3.2 Microstructure

The microstructure of the specimen adding Al(OH)3 with 36.1 μm medium diameter was shown in Fig. 2. It included two kinds of gas phase (crack and pore). Crack A located between the aggregates and the matrixes. Crack B and pore C located among the matrixes. The sample was prepared with both matrixes and aggregates. The matrixes were easier to sinter than aggregates.

3.3 Physical properties

The linear shrinkage of specimens sintered at 1550°C was given in Fig. 3. With decreasing the particle size of Al(OH)3 from 105.5 to 36.1 μm, the linear shrinkage increased from 0.85 to 1.23%. The reason was that the sintering driving force improved as the particle size decreased which shorten the ion diffusion distance and facilitated the sintering process at high temperature. When the medium diameter was more than 50 μm, the specimens had good volume stability since their linear change was lower than 1%.

Figure 4 showed that with the decrease of the medium...
diameter, the apparent porosity increased and the bulk density decreased. On the one hand, the result was attributed to the green densities of the samples. Because the green density (Fig. 5) of the sample with smaller particle size of Al(OH)₃ was lower than that of the sample with bigger particle size. On the other hand, the result was attributed to the volume of Al(OH)₃. The smaller the particle size is, the larger the volume will be. The sample with smaller particle size of Al(OH)₃ could generate more small pores after thermal treatment. Moreover, the smaller size of Al(OH)₃ shrunk larger after thermal treatment which increased the size of the cracks (Fig. 2) between the aggregates and matrixes.

The relationship between the Al(OH)₃ medium diameter in the specimens and the air permeability was shown in Fig. 6. It could be seen that the air permeability gradually increased which was in accordance with the variation trend of apparent porosity (Fig. 4). The air permeability could reach 13.4 m². Ohji et al. reviewed recent progresses of porous materials including (a) partial sintering, (b) sacrificial fugitives, (c) replica templates, (d) direct foaming and (e) gelation-freezing. Compared with the other processes in pore size range of 10⁻¹⁻¹ m, the porous ceramics fabricated by the freeze-dry processes showed higher Darician permeability (>10⁻¹¹ m). A portion of the volume originally occupied by the Al(OH)₃ particles becomes partially empty because the density of the Al(OH)₃ is lower than α-Al₂O₃ (ρₐ-Al(OH)₃ = 2.4 g/cm³; ρₐ-Al₂O₃ = 3.8–4 g/cm³). The smaller the particle size of Al(OH)₃ was, the larger the volume of Al(OH)₃ had which improved the air permeability.

Figure 7 showed the cold compressive strength (CCS) and the cold modulus of rupture (CMOR) of specimens sintered at 1550°C. The CCS and the CMOR both decreased with the decrease of the Al(OH)₃ medium diameter. One the one hand, the result was attribute to the apparent porosity increment. Because of it, the contact area between the grains decreases leading to the diminution of CMOR and CCS. On the other hand, the result was attribute to the amount and size of the cracks between the matrixes and aggregates which facilitated the interconnected pores formation. The other hand, the volumetric shrinkage of Al(OH)₃ generated cracks in the process of thermal treatment which improved the air permeability. Moreover, the result was mainly attribute to the transformation from Al(OH)₃ into α-Al₂O₃ after thermal treatment. The thermal decomposition of Al(OH)₃ occurs according to the general expression: 2Al(OH)₃ → Al₂O₃ + 3H₂O. A portion of the volume originally occupied by the Al(OH)₃ particles becomes partially empty because the density of the Al(OH)₃ is lower than α-Al₂O₃ (ρₐ-Al(OH)₃ = 2.4 g/cm³; ρₐ-Al₂O₃ = 3.8–4 g/cm³). The smaller the particle size of Al(OH)₃ was, the larger the volume of Al(OH)₃ had which improved the air permeability.
the properties of such materials, and induced the formation of Al(OH)₃ medium diameter in the specimens and the hot modulus increased, the strength decreased. The relationship between the size of the cracks (Fig. 2) between the aggregates and matrixes much smaller than that of the lamellar. Because the amount and the lamellar, because the pore size of the cellular structures was much smaller than that of the lamellar. Because the amount and size of the cracks (Fig. 2) between the aggregates and matrixes increased, the strength decreased. The relationship between the Al(OH)₃ medium diameter in the specimens and the hot modulus of rupture (HMOR) was shown in Fig. 8. As shown in Fig. 8, the HMOR was from 1.4 to 1.8 MPa with the decrease of the medium diameter of Al(OH)₃, which changed slightly.

3.4 Grey incidence analysis

The Table 3 showed the volume of different particle size intervals of Al(OH)₃ with different milling time (0, 3, 6, 9, 12 h) which will be used by grey incidence analysis and Fig. 9 showed the results of grey incidence analysis. It pointed out the proportion of 10–20 and ≥100 μm particle sizes had the highest relevance coefficient with the air permeability. From Table 3, it could be seen that the proportion of 10–20 μm particle sizes gradually increased which was similar to the tendency of the air permeability and the proportion of ≥100 μm gradually decreased which was opposite to the tendency of the air permeability. It may conclude that the more the proportion of 10–20 μm particle sizes is and the less the proportion of ≥100 μm particle sizes is, the higher the air permeability will be. This may offer some guidance when use Al(OH)₃ as the pore-forming agent for the porous purging materials.

4. Conclusions

The smaller particle size of Al(OH)₃ was suitable to improve the properties of such materials, and induced the formation of connected pores. When the particle size was 36.1 μm, the air permeability could reach 13.4 μm². Moreover, the grey incidence analysis matched to the experimental observations, the smaller particle sizes (10–20μm) were helpful for enhancing the air permeability while the bigger particle sizes (≥100 μm) had the opposite effects.

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Table 3. Volume of different particle size intervals of Al(OH)₃

| Range of particle size/% | X₁ (0–10μm)% | X₂ (10–20μm)% | X₃ (20–40μm)% | X₄ (40–60μm)% | X₅ (60–80μm)% | X₆ (80–100μm)% | X₇ (≥100μm)% |
|-------------------------|-------------|---------------|---------------|--------------|--------------|--------------|--------------|
| 0h                      | 5.98        | 3.50          | 1.72          | 6.46         | 15.39        | 13.81        | 53.14        |
| 3h                      | 12.55       | 8.80          | 15.99         | 18.24        | 12.76        | 12.56        | 19.10        |
| 6h                      | 19.55       | 11.95         | 15.98         | 16.42        | 10.78        | 10.28        | 15.04        |
| 9h                      | 19.68       | 10.93         | 17.50         | 18.01        | 11.38        | 10.19        | 12.31        |
| 12h                     | 22.42       | 12.85         | 17.42         | 15.52        | 10.00        | 9.36         | 12.43        |

Fig. 8. HMOR of specimens with different medium diameter of Al(OH)₃.

Fig. 9. Grey incidence analysis on the Air permeability of specimens.
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