Effect of Self-Dispersion Nanosized AlOOH on Microstructure and Wear Resistance of Alumina Ceramic Balls

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The self-dispersed AlOOH nanopowders were prepared by the sol-hydrothermal crystallization and charging composite dispersion method. The nanosized AlOOH were dispersed evenly into the mixed slurry of alumina and fluxing agent by the new batching technology of sol homogeneous dispersion and ball-milling-free for preparation of the ceramic body containing 98.1% alumina. The ceramic ball blank formed by cold isostatic pressing was sintered into ceramic ball at ordinary pressure and the temperature lower than 1500°C for 3 h. Using this method, uniform and fine grains of ceramic ball with better wear resistance were obtained by adding 3.5 mass% nanosized AlOOH to ceramic slurry. The wear rate of the self-made ceramic ball and the compared ceramic ball (which is the most wear resistance ceramic ball at present) under the same testing conditions were 0.004 and 0.056%/h, respectively. [doi:10.2320/matertrans.MRA2008061]

Keywords: self-dispersion, alumina ceramic ball, nanosized boehmite (AlOOH), microstructure, wear resistance

1. Introduction

The alumina ceramic ball has the characteristics of high hardness, high density, wear resistance, low price, and corrosion resistance, and is widely applied to grinding and processing for cement, mineral, ceramic, electronic material, magnetic material, coating, paint, cosmetics, food, and pharmaceutical industries, and it is a high-quality milling media.1–3) The wearing mechanism of the alumina ceramic ball can be classified as brittle fracture wear and plastic deformation wear, with wear characteristics of crystal grain separation of the intercrystalline fracture and of macro-cutting of the transgranular fracture, respectively. Thus, the wear rate of brittle fracture wear is much larger than plastic deformation wear.4) It is hoped that the ceramic ball wearing mechanism is via plastic deformation wear; however, the ceramic ball inside factor has an important effect on the ceramic plastic deformation wear mechanism. When the ceramic crystal grain size is smaller, the wear mechanism is plastic deformation and partly intercrystalline fracture, and the ball shows a slight wear. When the grain size is bigger (coarsening), the wearing mechanism of the ceramic ball is mainly intercrystalline fracture, and the ball shows exfoliation with small piece chipping and suffers from a grave wear. Thus, the smaller the ceramic ball crystal grain the smaller the ball wear rate.5) and as such, the development focus of the wear-resistant ceramic ball is on microcrystallization. Despite its potential, it is difficult to popularize the use of this method in the engineering field due to the high cost of the nanometer ceramic ball. Thus, the current research direction on the alumina ceramic ball is to develop ceramic ball crystal grains of a several micron size range.

The fine and uniform distribution of the alumina ceramic crystal grains and micropore is a microcosmic manifestation of the excellent toughness and wear resistance of the alumina ceramic.5) However, only targeting for a higher ceramic density will not necessarily improve the ceramic wear resistance, as this requires an increased ceramic sintering temperature and prolonged sintering times, which are almost certain to cause the Al2O3 crystal size to increase and the liquid phase to increase, resulting in a decrease in wear resistance. The improvement of technical conditions, addition of sintering-aid, and application of low temperature and fast firing technology can control the grain growth, which is effective for improving the ceramic toughness and wear resistance.

The proper addition of inorganic nanometer crystal powders into alumina ceramic can also improve ceramic performance. However, the uniform dispersion of nanopowders in the ceramic paste is the key problem for ceramic modification with nanopowder additives. In this paper, the behavior that powder can self disperse in water into a stable suspension of glomeration single dispersing without any surface modifying agents, dispersants, additives or other special conditions (e.g. ultrasonic wave dispersion, ball-mill dispersion) is named as self-disperse. In the present study, the prepared self dispersing AlOOH nanosized crystal powders were used as the nanocrystalline additive, which were dispersed evenly into the mixed slurry of alumina and fluxing agent by utilizing the new mixture techniques of sol homogeneous dispersion and ball-milling-free. The microcrystalline alumina ceramic balls were then prepared by drying, molding, and sintering. The influence of adding self-dispersion nanosized AlOOH crystal powders on the microstructure and wear resistance of alumina balls were studied.
2. Experiments Details

2.1 Preparation of self-dispersion nanosized γ-AlOOH crystal powder

According to the mass ratio of NaOH/Al(OH)\(_3\) of 0.6, the liquid caustic, aluminum hydroxide and deionized water were added into a high pressure reaction kettle. The aluminum hydroxide was dissolved at 150°C for 1 h. After filtering, the filtrate was neutralized with an acid. The precipitate was washed and prepared as a solution with an aluminum content of 0.5 mol/dm\(^3\). A ammonium bicarbonate solution was added and the precipitate was collected and washed with deionized water. Next, the peptizer was added into the precipitate, and the peptizing process carried out at 80°C for 2 h. The resulting sol and the correct amount of additives were then added into a high-pressure reactor, and the sol-hydrothermal crystallization and charging composite powder automatically dispersed in water or some organic solvents without any surface modifying agents, dispersants, or additives. The AlOOH grains were rod-like with an average aspect ratio of 100 nm, were dispersed in water to prepare AlOOH sol. Then the sol was mixed evenly in water. The mixed slurry pH value was adjusted using nitric acid or ammonia. The same precipitate was added into the precipitate, and the peptizing process carried out at 100°C for 1 h. After filtering and washing, the filter cakes were prepared into a slurry then spray dried (inlet temperature, 190°C; exit temperature, 100°C), resulting in self-dispersion nanosized γ-AlOOH crystal powders.

2.2 Preparation of alumina ceramic balls

Two kinds of ceramic balls with same chemical compositions as shown in Table 1 were prepared; one kind added no AlOOH nanopowder and another kind contain 3.5% AlOOH nanopowder in ceramic blank.

The prepared AlOOH is a self-dispersion nanopowder. Based on the self-dispersion properties of AlOOH nanopowders, the new technology mixing process of sol homogeneuous dispersion and ball-milling-free was used for mixing ceramic raw materials. The self-prepared Al\(_2\)O\(_3\) (average grain size = 172 nm) submicron powders, calcium nitrate, magnesium nitrate, and tetraethyl orthosilicate were weighed according to the chemical constituents in Table 1, then solved and mixed evenly in water. The mixed slurry pH value was adjusted using nitric acid or ammonia. The AlOOH powder of 3.5 mass% of ceramic blank was dispersed in water to prepare AlOOH sol. Then the sol was mixed evenly with the mixed slurry. Then the ceramic slurry was dried at 100°C for 5 h. The ceramic ball blank was obtained by shaping the dry ceramic blank powders by cold isostatic pressing at 300 MPa for 3 min. The ceramic balls were sintered at 1400, 1430, 1465 and 1495°C for 2 h at ordinary pressure in MoSi\(_2\) furnace, respectively. The ball was termed as ball A.

The ceramic containing no AlOOH nanopowder in ceramic blank slurry was prepared by solving and mixing evenly the self-prepared Al\(_2\)O\(_3\) submicron powders, calcium nitrate, magnesium nitrate, and tetraethyl orthosilicate weighed according to the chemical constituents in Table 1 in water. The mixed slurry pH value was adjusted to 3–4. Then the slurry was dried, the ceramic ball blank was shaped and the ceramic ball was sintered at the same conditions as ball A. The ball was termed as ball B.

2.3 Test of samples

In order to research the influence of AlOOH nanopowder on evenly dispersing stability of ceramic slurry, the mixed slurry of self-prepared Al\(_2\)O\(_3\) submicron powders, calcium nitrate, magnesium nitrate, and tetraethyl orthosilicate was prepared and then divided into several parts with different pH values adjusted using nitric acid or ammonia. The same amount of AlOOH sol respectively dispersed evenly into each part of mixed slurry. The light transmittances of the samples were tested using a 916 type ultraviolet-visible light spectrometer (GBC Co., Australia, illumination wavelength 496 nm). The light transmittance ratio D of the samples was calculated by formula (1):

$$D = \left( \frac{T_0}{T_{24}} \right) \cdot 100\%$$

where D is the light transmittance ratio (%) of the sample, \(T_0\) and \(T_{24}\) are the light transmittance of sample in initial and after 24 h (%).

The volume density of the balls was measured according to Archimedes’ Law. The ceramic ball wear resistance was measured by milling the ball A, ball B, and the compared ceramic ball (with 98% Al\(_2\)O\(_3\), the most wear resistance ceramic ball at present) in a corundum pot using corundum ceramic ball as grinding medium at rotating speed of 1200 rpm for 24 h. The balls were dried at 300°C for 1 h, weighed. The wear rate of the balls was calculated by formula (2):

$$W = \left( \frac{m_0 - m_1}{m_0} \right) \cdot 100\% / 24m_0$$

where W is the wear rate of the balls (%/h), \(m_0\) and \(m_1\) are weights of the balls before and after milling (g).

A high-resolution transmission electron microscope (JEM-2010F type, JEOL Ltd., Tokyo, Japan) and field emission scanning electron microscope (JSM-6700 F type, JEOL Ltd.) were used to observe particle morphology, size, and ceramic ball microstructure.

3. Results and Discussion

3.1 Self-dispersal characteristics of nanosized AlOOH and its influence on evenly dispersing stability of ceramic slurry

Figure 1 is the TEM image obtained after adding the unmodified nanosized AlOOH crystal powder directly into distilled water without any surface modification, dispersant, or additives. The AlOOH grains were rod-like with an average aspect ratio of 100 nm: 10 nm, were dispersed evenly in the water, and showed a single dispersion state with no agglomeration. In this paper, the unmodified nanopowder automatically dispersed in water or some organic solvents without any surface modifying agents, dispersants,

<table>
<thead>
<tr>
<th>Component</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>CaO</th>
<th>SiO(_2)</th>
<th>Li(_2)O, K(_2)O, Na(_2)O</th>
<th>TiO(_2)</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/mass%</td>
<td>98.1</td>
<td>0.15</td>
<td>0.22</td>
<td>0.55</td>
<td>0.30</td>
<td>0.20</td>
<td>0.48</td>
</tr>
</tbody>
</table>
additives, or other special conditions (e.g. ultrasonic wave dispersion or ball-mill dispersion) into a stable single-dispersion state with no agglomeration, and the average grain diameter is smaller than 100 nm was named as nanopowders self-dispersion.

In general, the greater the value of light transmittance ratio \( D \) became, and the smaller the change in light transmittance is, the better the particle dispersion turn to be. Figure 2 is the relation diagram between light transmittance ratio \( D \) and \( \text{pH} \) of samples. Figure 2 indicated that the \( D \) values were maximum as the systems \( \text{pH} \) was 3–5, \( D \) value decreased as \( \text{pH} \) was less than 3 or greater than 5, resulting in the destruction of \( \text{AlOOH} \) particle surface electric double layer structure. The \( D \) value was minimum for the three systems as \( \text{pH} \) were respectively 7–8, 8–9 and 9. The reason for this is that \( \text{AlOOH} \) is an amphoteric substance and starts to dissolve partly when the \( \text{pH} \) was less than 3 or greater than 5, resulting in the destruction of \( \text{AlOOH} \) particle surface electric double layer structure. The \( D \) value was minimum for the three systems as \( \text{pH} \) were respectively 7–8, 8–9 and 9. The reason for this is that the isoelectric point of \( \text{AlOOH} \), \( \text{AlOOH} + \text{Al}_2\text{O}_3 + \text{additives} \), and \( \text{Al}_2\text{O}_3 + \text{additives} \) system were respectively at \( \text{pH} \) of 7.5, 8.5 and 9. When the \( \text{pH} \) was greater than 9, their \( D \) values were increased gradually. The reason for this is that the surface reacted with \( \text{OH}^- \) in alkaline medium, resulting in particles surface with negative charges \(^{(6)}\) and static repulsion between particles.

Proper addition of \( \text{AlOOH} \) can cause the \( D \) value of \( \text{Al}_2\text{O}_3 + \text{AlOOH} + \text{additives} \) (i.e. calcium nitrite, magnesium nitrite, and silicon ester) system to be greater than that of the single component of \( \text{Al}_2\text{O}_3 \). Therefore, the grains in the body slurry achieve a high steady dispersing state allowing self-dispersion of the \( \text{AlOOH} \), enabling it to disperse evenly to the surface of the \( \text{Al}_2\text{O}_3 \) grains in the body slurry, promoting the sintering of \( \text{Al}_2\text{O}_3 \).

### 3.2 Influence of \( \text{AlOOH} \) on ceramic ball sintering temperature

Three balls were sintered at each sintering temperature; the volume density of the balls at the sintering temperature was the average of the three balls. The relation diagram between sintering temperature and the ceramic balls volume density were shown in Fig. 3. The figure showed that volume density was maximum at 1465°C for ball A (3.74 g/cm\(^3\)) and at 1495°C for ball B (3.73 g/cm\(^3\)), which indicated that the optimum sintering temperature was 1465°C for ball A (containing 3.5% \( \text{AlOOH} \) in ceramic blank) and 1495°C for ball B. Generally the sintering temperature range of alumina ceramic is less than 60°C. However the figure indicated that the sintering temperature range of ball A was wide because it began to sinter at 1400°C and didn’t overburnt at 1495°C. It is obviously that small amount of \( \text{AlOOH} \) powder in ceramic blank can lower ceramic sintering temperature and widen the sintering temperature range. This is because the nanometer \( \text{AlOOH} \) powders with high surface activity and high surface energy can dehydrated and transformed into high activity newly formed superfine \( \alpha\text{-Al}_2\text{O}_3 \) during the ceramic sintering process at lower temperature (\(<1050°C\)), greatly increasing the reactivity among alumina particles. Simultaneously, the high activity superfine \( \alpha\text{-Al}_2\text{O}_3 \) can react with \( \text{SiO}_2 \), \( \text{CaO} \) and \( \text{MgO} \) etc. to form liquid phase at lower temperature, leading to the ceramic ball sinter at lower temperature and widen the sintering temperature range.

### 3.3 Effect of nanosized \( \text{AlOOH} \) on ceramic ball wear rate

Table 2 showed the wear rate of self-made ceramic balls and the compared ceramic balls after milling \( \text{Al(OH)}_3 \) powder and \( \text{Al}_2\text{O}_3 \) powder and intermilled in water. The wear rate of the ball A was lowest after milling in the three conditions. After milling in \( \text{Al}_2\text{O}_3 \), the wear rate of ball B was 1.2 times of that of ball A, and the wear rate of the Morgan’s ball was 1.1 times of that of ball A. After
intermilling in water, the wear rate of ball B was 1.4 times of that of ball A. This is because the nanosized AlOOH can disperse evenly by nanoscale particles to the surface of the Al$_2$O$_3$ grain in the body slurry and dehydrates gradually, transforming into tiny /C11-/Al$_2$O$_3$ crystal grains and distributing evenly in the ceramic primitive crystal phase in the sintering process. Diffusion transfer speed of these newly formed tiny /C11-/Al$_2$O$_3$ particles was quick and the diffusion transfer resistances were small. Their uniform distribution in alumina intergranular causes the alumina to play a bridging role, promoting the ceramic to start sintering at a lower temperature. On the other hand, these newly formed small /C11-/Al$_2$O$_3$ crystals act as nanoparticle dispersion strengthening in the sintering process, causing the grain boundary binding to be more reliable. At the same time, the uniform distribution of the small crystals in the ceramic grain boundary causes the ceramic to be denser. Therefore, this allows the ceramic to easily adopt a transgranular fracture type for improving the wear resistance of the ceramic balls.

Figure 4 was the SEM pictures of the cross section of the ceramic ball (sintered at 1465°C) after polishing corrosion. It was shown that the ceramic microstructure was dense with pore size smaller than 1 μm and the crystal grain size of the ceramic balls prepared by adding and non adding AlOOH powder were both fine and homogeneous, with average size of approximately 0.8 μm. The fine crystal grain size and dense microstructure resulting in the low wear rate of the prepared ceramic ball.

The SEM micromorphology image of the surface of ball A after abrasive wear can be seen in Fig. 5. The abraded surface was of typical furrow morphology. The crystal destruction layer was easily observed (Fig. 5(b)), and the surface layer crystal was composed of partly abraded ceramic grains which were still firmly bound. The crystal grain in the destruction layer was smaller than the original particle. These data suggest that the wearing processes of ceramic are that a part of the surface grains were abraded while the un-abraded grains still combine strongly with the ceramic, and that these un-abraded grains were further abraded as a perfect small crystal during the continuing wearing process. The grains were abraded by layer upon layer from the outside to inside, until they were milled out. These data suggest that the abrasion mechanism of ball A in the wearing process is mainly a transgranular fracture wear. As the obtained

<table>
<thead>
<tr>
<th>Milling conditions</th>
<th>Ball A (100 g)</th>
<th>Ball B (100 g)</th>
<th>Morgan’s ball (100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 g Al(OH)$_3$ + 1000 mL water</td>
<td>0.001138</td>
<td>0.001199</td>
<td>0.01527</td>
</tr>
<tr>
<td>1000 mL water</td>
<td>0.003954</td>
<td>0.006592</td>
<td>0.05585</td>
</tr>
<tr>
<td>100 g Al$_2$O$_3$ + 1000 mL water</td>
<td>0.005763</td>
<td>0.006882</td>
<td>0.06323</td>
</tr>
</tbody>
</table>

Note: Ball A sintered by adding 3.5% AlOOH; Ball B sintered by not adding AlOOH.

Fig. 4  SEM picture of the cross section the ceramic ball after polishing corrosion. (a) ball A; (b) ball B.

Fig. 5  SEM micromorphology image of the surface of ball A after abrasive wear.
ceramic crystal grains are very thin (<2 μm), the transgranular fracture wear causes the ceramic ball wear rate to be very low. Thus, the wear resistance of the ceramic ball is very strong.

4. Conclusions

The AlOOH nanopowders prepared by the sol-hydrothermal crystallization and charging composite dispersion method has good self-dispersibility. Based on the self-dispersibility of the AlOOH nanopowder, the batching of the ceramic body was carried out by the new batching technology of sol homogeneous dispersion and ball-milling-free. The blank slurry with good self-dispersion was prepared under the conditions of pH = 3–4. The ceramic ball sintering temperature was lower, sintering temperature range was wider and the wear resistance was better by adding 3.5 mass% nanometer AlOOH powder in ceramic blank. The prepared ceramic microstructure was dense with pore size smaller than 1 μm and the crystal grain size was fine with diameter about 0.8 μm. The ceramic balls grains were worn down by transgranular fracture during wearing processes.

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