Preparation of mullite fine powder and its characterization were prepared by sol-gel method

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Abstract. High purity mullite powder was prepared by sol-gel method. Mullite was prepared with Ethyl orthosilicate, nitric acid aluminum, hydrochloric acid, anhydrous alcohol and distilled water as raw material by sol-gel method. After drying, calcining and grinding, the precursor gel is prepared with mullite powder. This paper tries to adopt the control variable method and the properties of mullite powder are studied under different pH values and other experiment conditions. All the studies showed that when the PH value was 2-3, the prepared mullite micropowder generally had smaller particle size and higher purity.

1. Introduction
Mullite (Al_{4+2x}Si_{2-2x}O_{10-2x}) is the only stable crystalline compound in SiO_{2}-Al_{2}O_{3} system at atmospheric pressure. The crystal structure is a stable skeleton structure formed by (Al, Si)O_{4} tetrahedra disordered along the c-axis to form a double chain between the octahedral connections parallel to the c axis (AlO_{6}) [1].

Mullite has many excellent physical and chemical properties, such as excellent electrical insulation chemical stability and high temperature and strength [2,3], good thermal shock resistance, high temperature and creep resistance, low density thermal conductivity and thermal expansion coefficient [4], and low electrical conductivity and dielectric constant [5]. From the 1950s to 1970s, phase equilibrium of mullite was the main direction. From 1970s to today, application in the fields of mechanics, electronics and optics have gradually become the focus of research. Since 1990, the preparation process of high-purity ultrafine ceramic powder has been improved. After process improvement, greatly improve the efficiency of the preparation of high purity mullite ceramics [6]. As an important structural and functional material, mullite has been paid more and more attention. High purity ultrafine mullite powder is the premise of ensuring high quality mullite products, and many properties of the powder are closely related to the size of particles, that is, these basic properties of the powder will change greatly with the size of particles[8]. Mullite powder with high purity can be used to prepare high-quality mullite ceramics and mullite base composite materials. It is mainly used in ceramics, metallurgy, refractories, electronic, casting and other industries, so it has a broad application prospect [8].

Mullite is usually made artificially. The properties of mullite mainly depend on its microstructure, but the microstructure depends on the production process. At present, the processes and methods of mullite synthesis at home and abroad include that solid phase reaction sintering [9], hydrolytic precipitation[10], Hydrothermal crystallization [11] and Sol-gel method [12]. The synthesis of high-purity
mullite power by chemical method at low temperature has attracted more and more attention, especially the rapid development of sol-gel method [13].

2. Experiment

2.1. Reagents and instruments
TEOS (tetraethoxysilane, C8H20O4Si), Shanghai zhongqin chemical reagent co. LTD. Aluminium nitrate (Al(NO3)3·9H2O), Yantai shuangshuang chemical co. LTD. Absolute ethyl alcohol(CH3CH2OH), Tianjin fuyu fine refinement co. LTD. Hydrochloric(HCl), Tianjin tianli chemical reagent co. LTD. Lsser particle analyzer (RISE.2002, Jinan runke technology co. LTD), High-performance surface and micro-hole analyzer (3H.2000PM1, Bechtel analytical instrument technology (Beijing) co. LTD ), thermal analyzer(HCR.3, Beijing eternal science instrument factory).

2.2. Preparation of mullite precursor
TEOS prehydrolysate was prepared under the condition that the volume ratio of TEOS to anhydrous ethanol and distilled water was 1:4:2, the magnetic stirrer stirs for 0.5h, place at room temperature for 24 hours, and let the TEOS hydrolyze fully. An aqueous solution of 0.6mol/L aluminum nitrate was prepared. Pre hydrolysate of TEOS was mixed with aluminum nitrate aqueous solution in an 80℃ water bath and stirred for 30 min, pH value was adjusted through hydrochloric acid. The gel was obtained. The gel was placed for 24 h, and the distilled water was centrifuged and washed until pH = 7. Then the gel was decayed once with anhydrous ethanol. Dry under 80℃, and grind to get mullite precursor.

3. Results and Discussion

3.1. The influence of pH on granularity
The collosof mullite precursor was yellow or light yellow with a slightly cloudy color. When pH was 2, 3, 4, 5 and 6, the reaction system of No1, No2, No3 and No4 respectively, the product particle size changes as follows.

| Table 1. The experimental reagent changes scale. |
|-----------------------------------------------|
| Aluminium nitrate solution (The volume of water). | Ethanol solution of TEOS (Volume of ethanol). |
| No1 | 13.5g(60ml) | 70ml(20ml) |
| No2 | 40.5g(180ml) | 110ml(60ml) |
| No3 | 54.0g(240ml) | 130ml(80ml) |
| No4 | 67.5g(300ml) | 150ml(100ml) |
Figure 1. Particle size distribution map of the No1.
The particle size of the sample was stable at about 60μm. As pH increases, the content of mullite particles decreases. When pH was 2, the particle content was highest. The results indicated that at the concentration of pH was 2, more mullite powder could be prepared.

Figure 2. Particle size distribution map of the No2.
The results showed that the particle size of the sample was stable at about 65 μm. As pH increases, the content of mullite particles decreases. When pH was 2, and more mullite powder could be prepared.
The experimental results showed that the particle size of the sample was stable at about 150μm. With the increase of pH, the content of mullite particles decreased. When the pH was 3, the reaction was the most sufficient, and more mullite microns could be prepared.

3.2. TG-DTA
The Thermogravimetric-differential thermal analysis was shown in the figure 5. As can be seen from the figure, the TG curve drops sharply from 27 ℃ to 387.3℃, while the corresponding DTA curve rises sharply with an upward exothermic peak. The decomposition reaction occurred in this temperature range due to the evaporation of crystal water in mullite precursor. From 365.1℃ to 402.3℃, the DTA curve has a distinct downward endothermic peak, it is indicated that the precursors of mullite undergo heat absorption reaction during this process, which may be caused by the reaction between the precursors and the air. In the temperature range of 402.3℃ to 1122.1℃, the DTA curve has an upward exothermic peak with a wide peak, indicating a slow decomposition reaction at this stage. The corresponding TG curve is relatively gentle, which also conforms to this exothermic process.
3.3. The influence of burning temperature
In the experiment, the gel precursor produced was analyzed by TG-DTA, and it can be seen from the figure that the exothermic peak of 1122.1 on the DTA curve was the phase transition temperature of mullite. Respectively at 1000℃, 1050℃, 1150℃, 1200℃ and 1250℃ calcinations temperature experiment, the results show that mullite can be formed after 1000℃ calcining for 1h, after 1200℃ calcinations mullite crystal phase well developed, 1250℃calcination temperature of mullite no impure phase, crystallization in good condition.

3.4. The surface and micropore analysis
At constant temperature, a certain amount of adsorption pressure can only exist on the solid surface. The adsorption isotherm can be obtained by measuring the corresponding adsorption amount. We can study the properties of surfaces and pores and calculate specific surface area and pore size distributions. Compared with the surface analyzer, 11 points were randomly selected to obtain different nitrogen partial pressure and corresponding adsorption amount. Due to the large adsorption amount, it was converted into a voltage value. The partial pressure of nitrogen at 11 points was taken as the abscissa, and the voltage value of the corresponding adsorption amount was taken as the ordinate, the green dots in figure 6 are shown. BET multi-point test results are as follow, slope is 0.016540, intercept is 0.0002424, coefficient of association is 0.99989, the closer the correlation coefficient is to 1 and the better the fitting degree is and the more accurate the experimental results are. Specific surface area is 259.7983 m²/g.

4. Conclusion
It is feasible to prepare mullite by sol-gel method with aluminum nitrate and ethyl orthosilicate as the main raw materials. In the process of gel preparation, the temperature and time of water bath heating can be controlled at about 80 and 6h, which helps to form a transparent and uniform gel. Mullite powder was prepared from ethyl orthosilicate and aluminum nitrate by sol-gel method. After comparing the different groups of experiments, with the change of pH value from acid to base, the particle size of sol-gel increases gradually. With the same pH value, the grain size decreases with the increase of calcining temperature. The results show that the increase of calcining temperature is conducive to the crystallization refinement of mullite grains, and the minimum is about 50nm. It was found that when the pH value was 2-3, it was relatively easy to prepare mullite micropowder with higher purity and smaller particle size, so the pH value played a key role in the successful preparation of mullite micropowder.

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