Fabrication of composite particles with core-shell structures by a novel processing

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In order to solve the difficult problem of heterogeneity of different components in the procedure of ceramic preparation, novel processing (heterogeneous nucleation-and-growth processing) was used to prepare a homogeneous distribution of powders. Composite coated particles with core-shell structures were prepared by the heterogeneous nucleation-and-growth processing. The effects of silica content in composite coating particles versus concentration of tetraethylorthosilicate, pH value, reaction time and reaction temperature were studied. The amorphous silica shell on the cores was confirmed by X-ray diffraction, transmission electron microscopy and zeta potential measurement. © *2002 Kluwer Academic Publishers*

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is important for electronic, optical, and high-temperature structural applications [1–6]. This is due to its superior electrical, thermal and physicochemical properties (i.e., low dielectric constant, low thermal expansion, high creep resistance, high mechanical strength at elevated temperature, good thermal shock resistance, good infrared transparency and good chemical stability). In order to prepare high performance mullite ceramics, it is important to prepare highly homogeneous precursors. A number of studies have been reported on coating of different kinds of fine particles with a silica layer [7–16]. The ideal ceramic should be based on extremely well characterized ceramic powders of tailored particle size, shape with no agglomerates and a narrow particle-size distribution, as well as high purity and high homogeneity. [High homogeneity is very important especially in the different component system. Meaning = ?]

In this paper, we try to find a novel process route to solve the difficult problem of heterogeneity of the second constituent in the preparation of ceramics. Coating of the second constituent on the cores is a good choice. The heterogeneous nucleation-and-growth processing is the preferable coating processing because it can provide greater control in the distribution of the second constituent.

2. Experimental
2.1. Processing

Fig. 1 shows the flow diagram of the procedure used for the preparation of composite coated particles. γ-Al_2O_3 (average particle size 0.40 μm) was used as raw materials and was dispersed in ethanol solution by ball milling and ultrasonication. The appropriate pH value of the suspension was adjusted by adding aqueous ammonia solutions. Tetraethylorthosilicate (TEOS) was added to the core particles/ammonia solution/ethanol suspension step by step while the suspension was stirred at 55°C for 6 h. Alumina/silica ratio was adjusted to the mullite stoichiometric ratio by controlling TEOS concentration. Composite coating particles were collected by centrifuge, washed with deionized water and dried in an oven at 110°C.

2.2. Characterization

The alumina/silica ratios of composite coating particles were obtained using chemical analysis. Phase analysis

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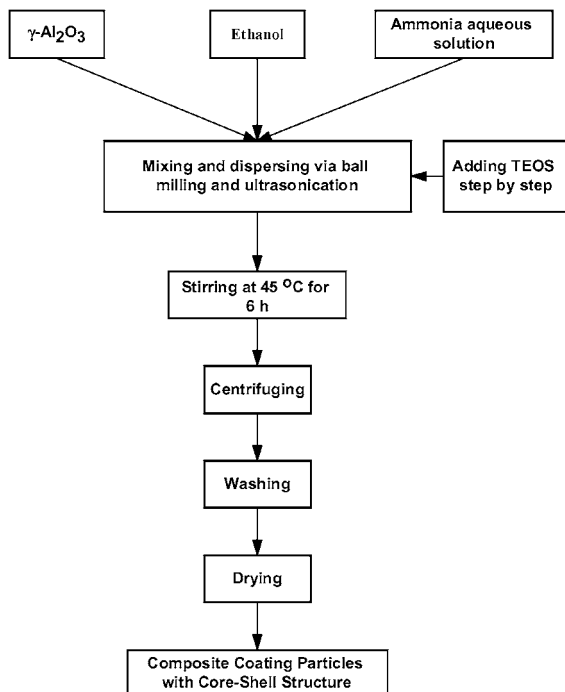
*Author to whom all correspondence should be addressed.

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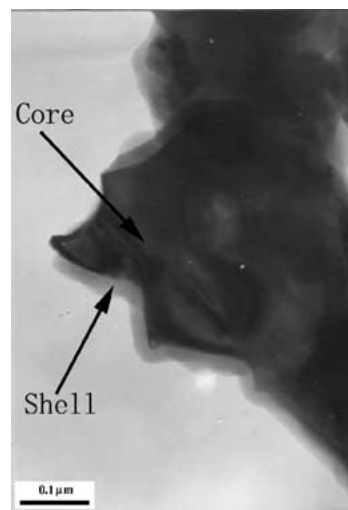Figure 1 The procedure of coating composite particles.

Figure 2 TEM micrograph of composite coating particles.

Figure 3 XRD patterns of raw materials and composite coating particles (a is amorphous silica, A is α-Al$_2$O$_3$, G is γ-Al$_2$O$_3$).
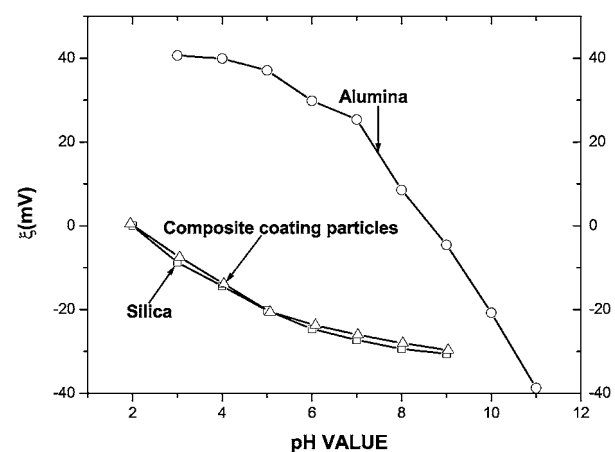

Figure 4 Plots of the zeta potentials of silica, alumina and composite coating particles versus pH values (square is zeta potential of silica, triangle is zeta potential of composite coating particles, and circle is zeta potential of alumina).

was performed on raw materials and composite coating particles by X-ray diffraction (XRD, Model Dmax/rb, Rigaku, Japan) using nickel-filtered Cu K$_\alpha$ radiation. Transmission electron microscopy (TEM, Model STEM H-800, Hitachi, Japan) was used for microstructure observations on composite coating particles. The zeta potentials of silica, alumina and composite coating particles were measured by Laser electrophoresis instrument (Lasser Zee, Model 500, USA).

3. Results and discussion

In order to obtain the optimized conditions for formation of a uniform layer, a broad range of reaction conditions was tested, which included 0.2884–0.5768 mol/L TEOS, 1–24 h reaction time, 1–12.3 pH value and 45–65°C reaction temperature. A typical successful procedure was as follows: 65.0 g/L γ-Al$_2$O$_3$ powders was added into an ethanol solution including 0.358 mol/L TEOS and 0.004 mol/L ammonia at 55°C under agitation with a magnetic bar in a 100 mL conical flask.

Fine particles can provide nucleation centers, and can decrease the kinetic barrier to nucleation of a supersaturated solution. In this experiment, γ-Al$_2$O$_3$ was used as nucleation centers in a supersaturated silica sol suspension, so silica sol can form a layer on γ-Al$_2$O$_3$ cores by the heterogeneous nucleation-and-growth processing. Fig. 2 shows the TEM micrograph of composite coated particles. It has been found that there is a shell on the γ-Al$_2$O$_3$ cores, and the thickness of shell is about 20 nm. The alumina/silica ratio of composite coating particles is controlled by the concentration of TEOS. By chemical analysis, alumina/silica ratio of composite coating particles is 72.3 wt%/27.7 wt%.

Comparing with XRD pattern of γ-Al$_2$O$_3$ raw materials (Fig. 3a), with the XRD pattern of composite coating particles (Fig. 3b), there is an expanding peak in the range of $2\theta \approx 22°$ which is characteristic of amorphous silica which implies that there is amorphous silica in composite coating particles. On the basis of this observation and examination of Fig. 2, the shell on γ-Al$_2$O$_3$ cores is amorphous silica.
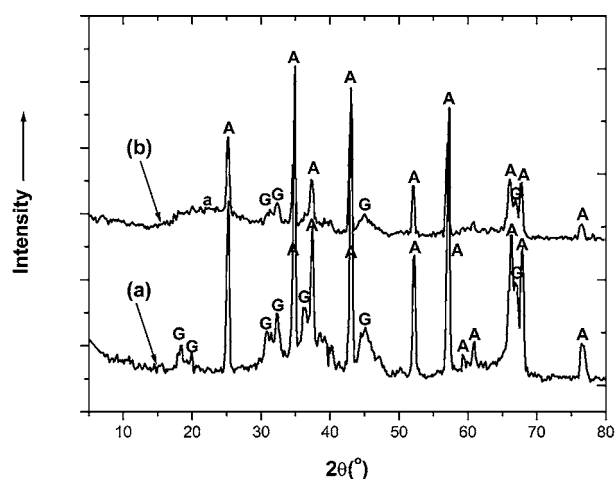
Fig. 4 shows the results of the zeta-potential measurement at different pH values. Comparing with zeta

potential of silica and zeta potential of gamma alumina, zeta potential of composite coating particles is similar to the zeta potential of silica, and it is different from the zeta potential of gamma alumina. On basis of this fact, silica sol has not self-nucleated to form silica powders. On the contrary, silica forms as a shell on the γ-Al$_2$O$_3$ cores. Based on Fig. 2, it is confirmed again that γ-Al$_2$O$_3$ cores are coated with a silica layer.

4. Conclusions

Composite coating particles (γ-Al$_2$O$_3$ cores with a silica shell) of 72.3 wt%/27.7 wt% have been prepared using γ-Al$_2$O$_3$ particles and TEOS as starting materials by the heterogeneous nucleation-and-growth processing. A silica shell on γ-Al$_2$O$_3$ was confirmed by TEM and zeta potential of composite coating particles. The coating was amorphous silica, as confirmed by XRD.

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