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Influence of particle size and aggregation state of alumina on the rheology of a ceramic paste with an organic binder of ethylene–vinyl acetate copolymer and stearic acid

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Abstract

The flow behavior of ceramic pastes with various alumina powder contents and different particle sizes, L-particles ($D_{ave.}$ = 6.7 μm) and S-particles ($D_{ave.}$ = 0.13 μm), in an organic binder of ethylene–vinyl acetate copolymer and stearic acid was investigated by dynamic viscoelasticity measurements. The rheological properties of ceramic pastes with high powder content over 19 vol% could not be investigated by the rotational method due to the high viscosity, and were analyzed by the oscillation method. Relative dynamic complex viscosities increased with the powder content, and were consistent with the Dougherty–Krieger model for evaluation of the apparent hydrodynamic shape factor (K_H) and the maximum powder content (f_{cr}^v). The f_{cr}^v and K_H of the L-paste were 0.62 and 1.6, and those of the S-paste were 0.59 and 8.2, respectively. It is considered that the L-particles were comparatively well dispersed and S-particles were aggregated in the paste. These analyses agreed with the aggregates of S-particles determined by SEM observations.

Keywords: A. Suspensions; C. Plasticity; D. Al_2O_3; Ceramic forming process

1. Introduction

Ceramic forming processes can produce complex, accurate and three-dimensional shaped ceramics. The forming process has essentially three steps of mixing, molding and sintering; a ceramic paste is prepared by mixing with an organic binder, and the ceramic paste is melted and injected into a die cavity or extruded through the die to form a green body, and the green body is then heat-treated at high temperature to extract the binder and sinter the ceramic body. The ceramic paste should exhibit good flow behavior during the ceramic forming process and a high ceramic content is also required to reduce shrinkage and crack formation during sintering [1,2]. To obtain sintered specimens without cracks and distortions, important process parameters must be considered, such as the particle size of the ceramic, the dispersion of particles in the paste, and viscoelastic properties such as the yield stress and viscosity of the ceramic paste [3].

Prior to the fabrication of a green body, it is essential that these parameters be predicted. The interparticle distance in the organic binder, the maximum powder content, and the apparent hydrodynamic shape during flow can be predicted using the Woodcock and Dougherty–Krieger models.

The interparticle distance of particles h, in the ceramic paste can be calculated using the Woodcock model [4]:

$$h = d_p\left[\left(\frac{1}{3\pi F}+\frac{5}{6}\right)^{0.5}-1\right], \quad (1)$$

where d_p is the particle size and F is the powder particle content. The interparticle distance of small-sized particles is shorter than that of large-sized particles. Therefore, it is considered that it is difficult to fill the space among small-sized particles with binder. Consequently, the viscosity of a paste

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with small-sized particles is higher and the maximum powder content is lower than that for a paste with large-sized particles.

The particle behavior in the paste during flow and the maximum powder content (f_{cr}^{v}) of the ceramic paste can be determined using the Dougherty–Krieger model [5–7]:

$$\eta_r = \frac{\eta_S}{\eta_L} = \left(1 - \frac{f^v}{f_{cr}^v}\right)^{-K_H f_{cr}^v}, \quad (2)$$

where η_r is the relative viscosity, η_S and η_L are the viscosities of the ceramic paste and the organic binder, respectively, f^v is the powder content, and K_H is the apparent hydrodynamic shape factor of the particles. The particle behavior in the paste during flow can be predicted from the obtained K_H [7].

The ceramic forming processes of alumina pastes have been widely investigated [8–11]. The flow behavior of pastes has been investigated using a capillary rheometer, where the paste is forced by a piston through a capillary in the capillary rheometer. Shear stress and the shear rate can be determined under conditions of steady flow by measurement of the pressure drop and volumetric flow rate through the capillary, from which the viscosity can then be calculated [2]. The capillary rheometer is a pragmatic approach and enables understanding of the paste behavior during flow through a die. However, in capillary rheometer measurements, the interface between the die and the paste affects the flow behavior, such as the pressure drop and the volumetric flow rate of the paste. Therefore, it is considered that the structure of the paste cannot be analyzed quantitatively.

In contrast, dynamic viscoelasticity measurements obtained using an oscillation rheometer can provide solid and liquid ratios in the linear and nonlinear regions of the paste. The influence of slip can be minimized by this method, due to the application of a small oscillatory deformation to the paste [10,11]. Therefore, the dispersibility of the particles in the paste and the viscoelastic properties of the paste, such as yield stress and viscosity, can be analyzed quantitatively using an oscillation rheometer. There are few reports where viscosities obtained by an oscillation rheometer are fitted with the Dougherty–Krieger model and where the particle behavior in the paste is discussed quantitatively.

In this study, the dispersibility of alumina particles in an organic binder was analyzed quantitatively using dynamic viscoelasticity measurements. Alumina paste consisting of an organic binder of ethylene–vinyl acetate copolymer (EA) and stearic acid was prepared, and the flow behavior of pastes with various alumina powder contents of different particle sizes (0.13 and 6.7 μm) was analyzed using an oscillation rheometer. The maximum powder content in the paste, the influence of particle size on the flow characteristics and the apparent hydrodynamic shape of the particles are discussed.

2. Experimental method

2.1. Preparation of the ceramic paste

Two alumina powders with different average particle sizes of 6.7 μm (large, L) and 0.13 μm (small, S) were used in this study. The powder was confirmed to be α-phase alumina without any second phase by XRD analysis. BET surface area of L-alumina and S-alumina was 0.933 m^2/g and 13.5 m^2/g, respectively. Fig. 1 shows the particle size distributions and morphologies of the L and S alumina powders.

An organic binder consisting of 40 wt% EA (Vinyl acetate content of about 28 wt% and number average molecular weight of 20,000–40,000. Melting point was 71 °C.) and 60 wt% stearic acid (SA, the SA consists of C18 of 69% and C16 of 30%. Melting point was 57–62 °C.) were used. EA and SA were mixed in a beaker at 120 °C for 2 h. The binder and either the L or S alumina powders were mixed at ceramic contents from 11 to 64 vol% using a kneader (PBV-01, Irie Shokai Co., Japan) at 120 °C for 20 min; the pastes are denoted L-*X*vol% and S-*X*vol%.

Torque value change depending on mixing time for S-59vol% at 120 °C was measured. With extending the mixing time the torque value decreased, and 12 min later the torque value became steady. Therefore, in this study the mixing time was decided to be 20 min to prepare the pastes.

The alumina powder of starting material and the fracture surface of the paste were observed using field emission scanning electron microscopy (FE-SEM; JSM-6335FM, Jeol, Japan). For the FE-SEM observations, a thin coating of Pt was deposited on the surface of the alumina or on the fracture surface of the paste.

2.2. Rheological measurements

The temperature dependence of the dynamic complex viscosity of the organic binder (40 wt% EA and 60 wt% SA) was analyzed using a rheometer (MARS-2, Haake, Germany) with a parallel-plate (35 mm diameter) at temperatures from 40 to 100 °C. The gap between the parallel-plate and the bottom of the measurement vessel was set to be 2 mm. After the parallel-plate approached 2 mm, the excess paste squeezed out was trimmed off.

The flow curves of L-19vol% and S-19vol% were measured using a parallel-plate (8 mm diameter) with a gap of 0.5 mm for shear rates from 0.01/s to 10/s at 70 °C. After the parallel-plate approached 0.5 mm, the excess paste squeezed out was trimmed off. Flow curve measurements of pastes with alumina contents over 19 vol% were unsuccessful due to their high viscosity.

Dynamic viscoelasticity was measured by the oscillation method using a parallel-plate (35 mm diameter) with a gap of 2 mm. Storage modulus (G') and loss modulus (G'') were measured at shear stress values from 5 to 20,000 Pa at a frequency of 0.5 Hz at 70 °C, known as stress sweep measurements.

G' and G'' are usually represented as:

$$G* = G' + iG'', \quad (3)$$

where

$$G' = G^* \cos\ \delta, \quad (4)$$

and

$$G'' = G^* \sin\ \delta, \quad (5)$$

when a viscoelastic fluid is characterized by the phase angle $0 < \delta < 90°$. G' is referred to as the elastic or storage modulus, which is a measure of the energy stored during the test, while