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Influence of stearic acid on suspension structure and green microstructure of injection-molded zirconia ceramics

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Abstract

The effect of stearic acid (added as a surfactant and/or a lubricant) on powder dispersion and particle packing of a zirconia ceramic/binder system has been investigated. Microstructural examination revealed that the addition of stearic acid prevented the particles from making a direct surface-to-surface contact. Contrarily, an insufficient coverage of the acid onto the powder surface resulted in a formation of particulate networks and led to an increase in suspension viscosity. A significant reduction in the most frequent pore size of the thermally debound samples was found as the fraction of stearic acid exceeded 3 wt% on the basis of powder loading. This corresponds to a nominal >90% of surface coating by the adsorbed acid before being blended with the wax/polymer as a binder. The acid adsorption gradually reached a plateau as the acid increases above 3 wt%. High acid quantities (>5 wt%) are detrimental to the molding integrity as cracks were observed during thermal removal of the binder. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

Keywords: Ceramic injection molding; Zirconia; Stearic acid; Particle packing; Rheology; Agglomeration

1. Introduction

Ceramic injection molding (CIM) is a fabrication process capable of mass-producing geometrically complex components with thin sections cost-effectively. This process involves blending polymeric binders with distinct attributes with ceramic powders to form a flowable, uniform suspension so that the mix can be shaped into a prescribed mold cavity at a given set of temperature and molding conditions [1]. A subsequent debinding process removes the binder vehicle. The binder chemistry has been reported to not only influence the suspension rheology but also critically affect the integrity and shape retention of moldings [2–8]. Defects such as voids [5,6,8] warpage [3,4] and even cracks [5–8] were found in the injection-molded parts and were believed to be related to the binder formulation [3,4,7], mixing uniformity [7,9], molding parameters [3,5,6] and the nonuniform shrinkage during part cooling [5,8]. The binder formulation, in particular, has received much attention in the literature mainly because an ideal binder system suited for all different powder characteristics is still impossible to attain. This imposes an inevitable restriction onto the process window for the selection of binder compositions. In fact, the success of CIM would largely depend on the binder system used.

The binder used in CIM usually consists of a major binder, a minor binder, a plasticizer/lubricant, and a surfactant for wetting ceramic particles. A binder system should at least provide a satisfactorily low level of viscosity at sufficiently high solid loadings to ensure a complete cavity filling without introducing defects. Therefore, low molecular weight organic polymers and waxes are frequently used as the base for the binder. Since particle agglomerates are frequently observed in ceramic starting powders, additives such as oleic acid and stearic acid are often used to improve powder dispersion during mixing [10–12]. A complete dispersion of given powder system in the binder is most desirable. Recent findings have revealed the flow behavior of an alumina suspension could be altered by stearic acid over a relatively low temperature range [11] and the effective powder loading was accordingly enhanced [12,13]. This resulted in a more homogeneous binder distribution

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within the molded compacts. Likewise, dispersants such as stearic acid could preferentially adsorb onto zirconia particle surfaces and effectively reduced the suspension viscosity by breaking up existing particle networks [12]. A uniform particle packing is believed to be one of the most critical factors in obtaining a homogeneous sintered microstructure [14]. The understanding of stearic acid in this respect was not yet exclusive, and this led to the investigation of the current study.

2. Experimental procedure

A commercially available zirconia powder containing 3 mol% yttria (HSY3.0, Daiichi Kigenso Kagaku, Japan) with an average particle size of 0.25 μm and a specific surface area of 6.9 m^2g^{-1} was used in this study. The zirconia powder has a narrow size distribution, has relatively spherical particles and was apparently agglomerated (Fig. 1). The powder was first treated by surface adsorption of differing amounts of stearic acid (Reagent grade, Showa Chemicals Inc., Japan) by ball milling in toluene. The powder was then annealed at 130°C for 24 h to ensure the powder surface was coated by the acid, presumably by chemical adsorption as asserted by Novak et al. [15]. Thermal gravimetric analysis (Netzsch, Model 309A) of samples was conducted over a temperature range from room temperature to 500°C to determine the amount of adsorbed acid before blending with paraffin wax and vinyl acetate polymer (Gin-Ming Chemicals, Taiwan) in proportions listed in Table 1 was made. The weight loss from the adsorbed acid during heating started at about 150°C in air (heating rate 10°C min^{-1}) and the acid was completely removed before temperature reached 280°C. No desorption of the stearic acid was assumed to occur during the further compounding process. Feedstocks with a nominal stearic acid ranging from 1 to 5 wt% (on the basis of powder loading) were then prepared. Notice that the solid loading was fixed at 50 vol% and the volumetric ratio of wax:polymer was held constant at 60:40 for comparison reasons. The rheological behavior of feedstocks at 160°C (resembling the melt temperature in the injection barrel) was determined by a capillary rheometer (CFT-500D, Shimadzu Inc., Japan) over a shear rate range of 300–15,000 s^{-1}.

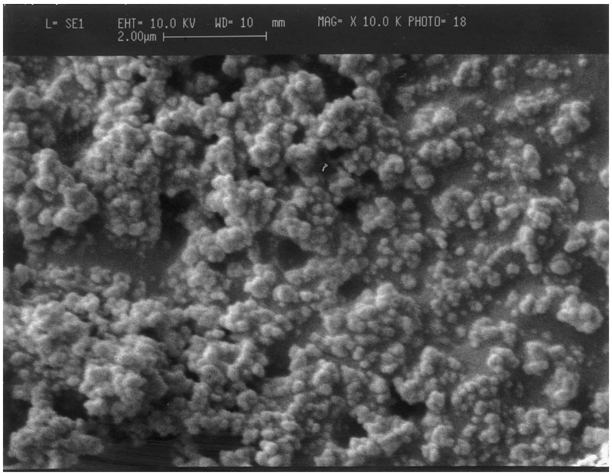

Fig. 1. Particle morphology of the zirconia powder.

The ceramic feedstocks were then fed into an injection molding machine (Battenfeld BA 250/50 CDC, Austria) to form parallelepiped bars of dimensions 4 mm × 5 mm × 60 mm. The molding parameters are shown in Table 2 and were unchanged for all operations in this study. The molded samples were thermally debound over a temperature range up to 600°C in air without an isothermal holding. A constant heating rate of 30°Ch^{-1} was used. The pore-size distribution of partially debound samples (samples were heated to 450°C at which only minor fractions (< 5%) of the binder phases of the samples were remained in the moldings to provide a sufficient strength required for the pore analysis) was determined through mercury porosimetry (Autopore 9220, U.S.A.). Fractured microstructure was examined by scanning electron microscopy (Cambridge Instrument, S360).

3. Results and discussion

Fig. 2 shows the rheological behavior of the zirconia suspensions containing various amounts of the stearic acid (SA) at the working temperature of 160°C. At the

Table 1
Composition of zirconia/binder mixtures

Stearic acid fraction	Composition (wt%)			
(wt%, with respect to powder loading)	Zirconia	Stearic acid	Paraffin wax	Vinyl acetate polymer
1	86.7 (50.0)	0.9 (3.3)	7.0 (28.0)	5.4 (18.7)
2	86.7 (50.0)	1.7 (6.7)	6.5 (26.0)	5.1 (17.3)
3	86.7 (50.0)	2.6 (10.0)	6.0 (24.0)	4.7 (16.0)
5	86.7 (50.0)	4.3 (16.7)	5.0 (20.0)	3.9 (13.3)

Volume per cent in parentheses.

Table 2
Molding variables used in this study

Molding variables	Value
Barrel temperature	90–140–150–150°Cfeed to nozzle
Mold temperature	35°C
Injection pressure	60 MPa
Hold pressure	100 MPa
Hold pressure time	10 s
Cooling time	25 s

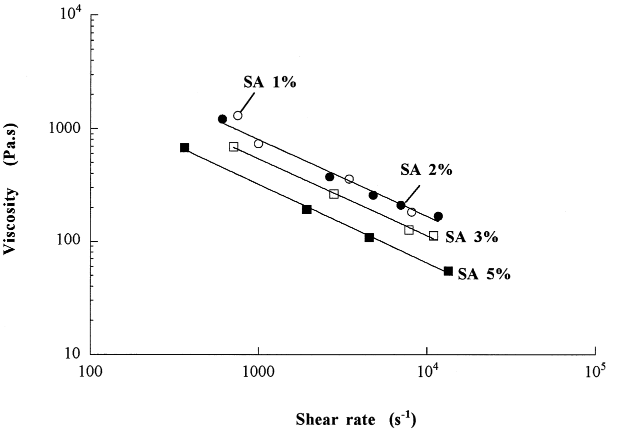

Fig. 2. The viscosity of zirconia suspensions with varying fractions of the stearic acid (SA) over a shear range of 300–15,000 s^{-1} at a temperature of 160°C.

chosen temperature, ceramic suspensions exhibit a pseudoplastic flow over the shear rate range employed and their viscosity dependence on shear rate is quite similar. The flow behavior of the feedstocks containing 1 and 2 wt% of the acid is virtually identical; however, the viscosity reduces substantially as the stearic acid fraction rises above 3 wt%. This suggests that a certain critical level of the stearic acid in the model zirconia/binder system might exist for obtaining a more stable feedstock. Formation of an outside layer on each particle surface by the adsorbed stearic acid was reported to assist in achieving a certain degree of steric stabilization in zirconia/wax systems [12,16]. Varying degrees of the surface coverage of the particle surface by the stearic acid would give rise to different degrees of powder agglomeration. This deduction is further vindicated in this study by observing the green microstructure of the moldings containing various fractions of the stearic acid. In Fig. 3, the zirconia particles appear to present a more uniform packing structure as the amount of stearic acid increases. Individual particles are seen uniformly covered by the binder as the stearic acid exceeds 3 wt% of solid loading. For the suspensions containing stearic acid below 2 wt%, on the other hand, the particles cluster into agglomerates and the presence of these agglomerates tends to change suspension structure by suppressing the particle packing efficiency. The apparent similarity found in the molded green microstructure for the samples with 1 and 2 wt% of the acids is consistent with their similar viscosity dependence over the employed shear rate range. This once again stresses that the existence of a correlation between the suspension viscosity and the particle packing structure, and that the modification of the particle surface by the surfactant influences the mixture rheology and molded packing structure as well.

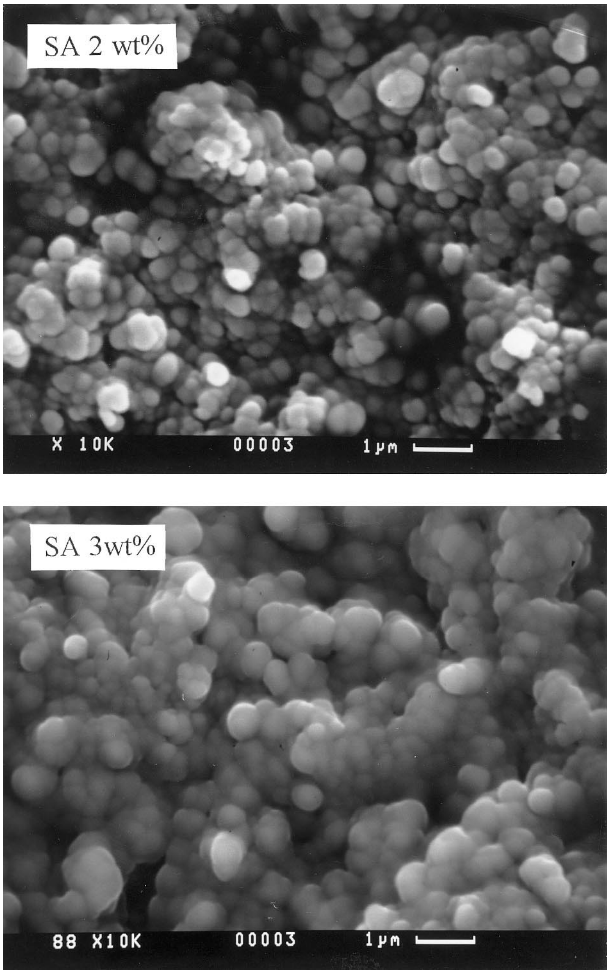

Fig. 3. The particle packing of green moldings containing various fractions of stearic acid (on the basis of powder loading).

The strength of the agglomerated network is expected to be dependent upon the stearic acid addition. From the adsorption isotherm (Fig. 4), we may find that the acid coverage on the particle surface exhibits a typical Langmuir behavior with a saturation reached at roughly 6 wt%, which is indicative of a monolayer coverage of the acid on the particle surfaces [16]. By arbitrarily choosing the specific adsorption at the 10 wt% addition as 1 (representing a full monolayer surface coverage), the respective surface coverage for differing surfactant amounts is expressed in parentheses shown in Fig. 4 The surface coverage rapidly rises as the acid fraction increases over the range up to about 2 wt% (corresponding to a nominal 84% coverage) and the particles reach steric "stabilization" as further addition of the acid only enhances the specific adsorption moderately. Correlating this result with the viscosity and microstructural observations, it appears that the steric layer formed on the particle surface by the stearic acid has to be relatively complete (exceeding nominally 90% of the bare surface), otherwise a particulate network may remain and the packing efficiency degrades. The strength of the agglomeration network might be evaluated from

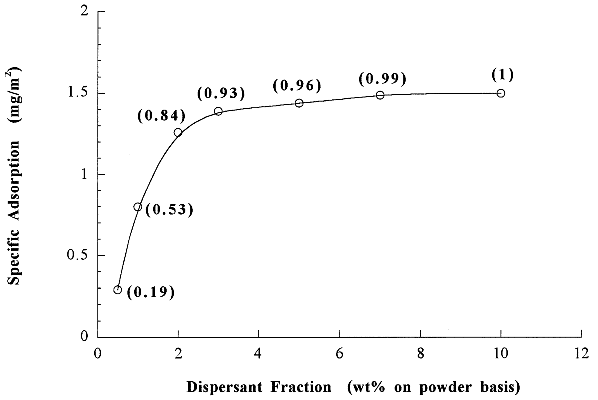

Fig. 4. The adsorption isotherm of zirconia powders with varying stearic acids as a dispersant.

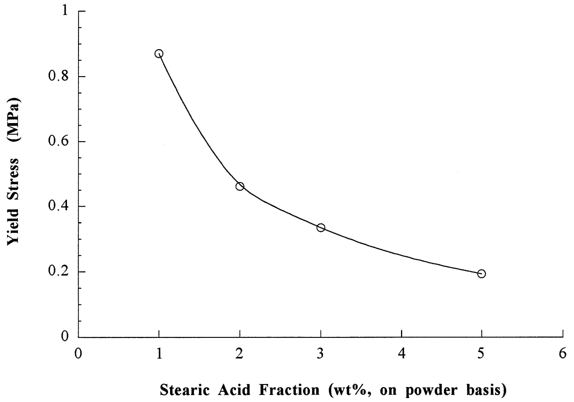

Fig. 5. The yield stress of zirconia suspensions containing various fractions of the stearic acid.

the yield stress (τ_y) of suspensions at a given temperature. For suspensions exhibiting a non-linear Bingham-type flow, the shear stress (τ) and the shear rate (γ) has been related by the equation proposed by Casson, [17]

$$\tau^{1/2} = \tau_y^{1/2} + c\gamma^{1/2} \tag{1}$$

The yield stress is determined by extrapolating the shear rate to zero and is shown in Fig. 5. As the amount of stearic acid increased, the yield stress decreased rather exponentially. This represents a reduced network strength as the surfactant increases and a relative ease for particles to roll over the neighboring particles in compliance with the applied shear in the suspension.

The resulting breakdown of powder agglomerate into smaller fragments under the prescribed shear force as the fraction of stearic acid increases seems to result in a reduction in peak pore-size (Fig. 6). Fig. 7 further reveals that the most frequent pore diameter substantially reduced from about 116 nm for the mixtures containing 1 and 2 wt% stearic acid to less than 100 nm as the acid fraction was increased over 3 wt%. Therefore, the surface modified particles not only exhibit a lower viscosity over the shear rate range measured but also lead to a more efficient packing structure accordingly.

The addition of stearic acid in our model zirconia/binder system is not without a drawback. As the acid fraction was increased to 5 wt%, cracks were often observed during thermal debinding at the heating rate used whilst moldings with an acid fraction from 1 to 3 wt% after the identical thermal process were free from any debinding defect. In fact, most of the cracks are apparent after the temperature was raised to about 250°C, a relatively low temperature for a substantial degradation of compositions other than the low-melting stearic acid and the wax to occur. At lower heating rates ($<30°\mathrm{Ch}^{-1}$) the cracks were avoided. It is suspected that rapid productions of such evaporation species coupled with the weakening molding integrity as temperature is raised the main reason for the cracking defect.

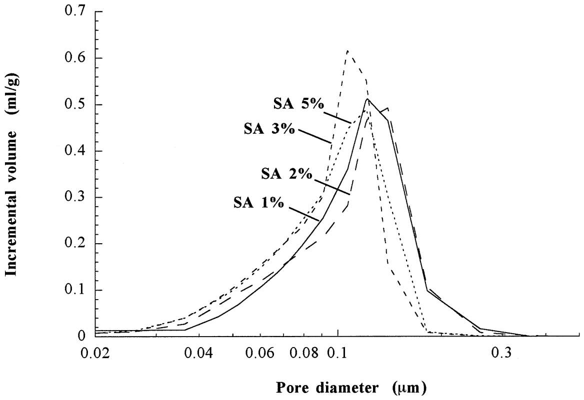

Fig. 6. The pore size distribution of zirconia suspensions containing various fractions of the stearic acid.

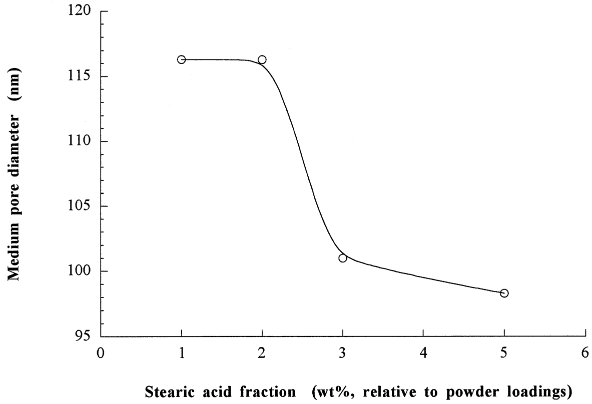

Fig. 7. The variation of most frequent pore diameter of thermal debound moldings containing various fractions of the stearic acid.

4. Conclusions

Zirconia powders with varying degrees of surface modification (by adsorption of differing amounts of stearic acid in a toluene medium in a ball mill before blending with given binder systems) were shown to lead to different suspension structures and green microstructure as well. The surface-coated acid acts as a dispersant which substantially reduces the clustering size of powder agglomerates as its fraction exceeds 3 wt% on the powder basis in our model system. The powder/binder suspensions decreased their viscosity proportionally to the stearic acid fraction. This reduced viscosity is correlated with the enhancement of the microstructural uniformity of particle packing. Reduction of the most frequent pore diameter from about 116 nm for the partially coated case to less than 100 nm for the fully acid-covered case (more than 90% coverage) is demonstrated. These results suggest that the feedstock rheology and the green microstructure of injection-molded ceramic-binder mixtures may be engineered by means of surface active additives.

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