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Journal of the European Ceramic Society 35 (2015) 2823–2832

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Colloidal stabilization of cerium-gadolinium oxide (CGO) suspensions via rheology

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Received 16 March 2015; accepted 25 March 2015
Available online 16 April 2015

Abstract

A rheological method based on the analysis of the flow index is proposed for the optimization of ceramic suspensions with respect to dispersant-ceramic affinity, dispersant concentration, and ceramic loading. The single-flow index (SFI) feature was identified as the criterion defining the optimized colloidally stable state. The method was applied to explore the ability of four commercial dispersants (acidic affine, neutral, basic affine, and polyvinylpyrrolidone (PVP)) to disperse cerium-gadolinium oxide (CGO) in ethanol. Only the acidic affine and the PVP dispersants were found to efficiently disperse the CGO powder. The acidic affine dispersant was further demonstrated to impart superior packing properties due to the formation of a thinner monolayer around the ceramic surface. CGO suspensions using the acidic affine at optimized amount were prepared and processed via tape casting. The resulting green tapes exhibited uniform and high packing density, producing a theoretical density in the sintered tapes of ca. 97–98%.

Keywords: Cerium-gadolinium oxide; Ceramic suspensions; Colloidal stable state; Rheology; Flow behavior

1. Introduction

The dispersion of colloidal particles into a suspending continuous medium (either aqueous or organic solvent) is a focal issue in a wide host of industries including paints, pharmaceutical, cosmetics, and colloidal processing of ceramics [1–4]. The level of dispersion of colloids and their stability can be modulated to specific requirements by intently manipulating inter-particle (colloidal) forces [1,5]. This manipulation can result in three possible states: strongly flocculated, weakly flocculated, and colloidal stable systems [1]. Generally in ceramic processing, the colloidal stable state is preferred over the others as it produces superior properties such as higher average packing densities [6], highly homogenous arrangement of the colloidal units [6], and high reproducible conditions of shaping [6]. Additionally, this approach is of great practical importance, as it confers a superior long-term stability against any aging phenomena [6]. All these features are essential for developing robust and reliable ceramic processing routes [1–6]. The control over the inter-particle forces is obtained by the use of a dispersing agent, selected for its affinity to the ceramic surface, and whose concentration is adjusted to attain monolayer coverage of the ceramic surface [1,7–9]. The suspension resulting from the use of such an optimized dispersant is a colloidally stable system, characterized by high fluidity, and by an arrangement of the particles that is not altered throughout the entire process of shaping. Both features clearly refer to the flow behavior of the suspensions, which in turn emerges as critical factor controlling the shaping of ceramics into high quality green bodies. Among the different techniques proposed in literature to explore the properties of ceramic suspensions [7,10–17], rheology is the most relevant and extensively used [1,4,7,18–21], as it exactly offers the advantage of controlling the flow behavior of the system. In a conventional approach, the focus is on the determination of

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.03.043
0955-2219/

the dispersant concentrations that confer the required high fluidity, identified by low viscosity, negligible yield stress and a liquid-like internal structure [1,4,7]. However, none of these characteristics really account for the arrangement of particles when external forces are applied (e.g. during the shaping). Such an understanding of the flow behavior of the ceramic suspensions can be achieved by the analysis of the flow index. Indeed, the latter can be conveniently exploited to identify any possible change in the colloidal state of aggregation. According to this approach, systems characterized either by agglomerates (too low amount of dispersant) or flocculated structures (too high amount of dispersant) likely exhibit a multi flow index profile, due to the unstable arrangement of the colloidal units (agglomerates and flocks), whose size and distribution vary depending on the shear conditions. By contrast, a colloidally stable dispersed system is likely described by a single flow index profile, as no variations in the arrangement of the colloids (primary particles) is expected to be generated at increasing/decreasing shear conditions.

In this work, the use of the flow index is proposed for the optimization of ceramic suspensions. The approach adopted enables the identification of dispersants with high affinity to the ceramic of interest, the definition of their most appropriate concentrations, and the study of the effect of ceramic loading on the rheological properties of ceramic suspensions. The flow index is estimated via a power law model, and the single flow index (SFI) condition is proposed as an adequate criterion unequivocally defining the optimal conditions to achieve the colloidally stable state. Four commercial dispersants with different properties (acidic affine, neutral, basic affine, and the amphiphilic polyvinylpyrrolidone (PVP)) were investigated for their ability to produce colloidally stable gadolinium doped ceria (CGO) dispersions in ethanol solvent. Besides, the effect of the ceramic loading on the rheology properties was explored for the acidic dispersant and PVP-based suspensions. Subsequently suspensions were prepared using acidic affine dispersant, processed via tape casting and characterized for their microstructural features.

2. Experimental

2.1. Materials

All materials were reagent grade and used as received.

Commercial gadolinium doped ceria powder ($Gd_{0.10}Ce_{0.9}O_2$), (Rhodia, La Rochelle Cedex, France, 99% purity) was used as ceramic component. The powder specific surface area (SSA) determined by BET (Brunauer–Emmett–Teller; Autosorb 1-MP, Quantachrome Instruments, Boynton Beach, Fl, USA) was found to be 6.54 m^2/g. CGO powder, was degassed at 300 °C for 3 h and surface absorption was carried out with krypton gas. The primary particle size was in the range of 100–150 nm (estimated by SEM). The particle size distribution (PSD) (LS13 320 laser diffraction particle size analyser, Beckman Coulter, Fullerton, USA) analysis showed an agglomerate size of d_{50}: 0.622 μm (d_{10}) and d_{90}:1.313 μm. The CGO phase purity was verified by XRD and the results are not included in the article (Bruker D8, Germany).

Table 1
Dispersants properties.

Dispersant	Features	Supplier	M_w (kDa)	Density at 20 °C (g/ml)
D_1	Acidic affine	DisperByk	–[a]	1.06
D_2	Basic affine	DisperByk	–[a]	1.05
D_3	Neutral	DisperByk	–[a]	1.05
PVP	Amphiphilic	Alfa Aesar	10[b]	1.20

[a] Not provided by the supplier.
[b] Estimated via Gel Permeation Chromatography.

The three commercial dispersants investigated were purchased from DisperByk (Germany). The details about their characteristics are reported in Table 1. For the sake of simplicity, they were identified using the codes D_1, D_2, and D_3 (see Table 1) to refer to acid affine, basic affine, and neutral dispersant, respectively. The capital letter D stands for dispersant. The PVP used in this study was purchased from Alfa Aesar (Denmark) with an M_w of around 10 kDa (estimated by Gel Permeation Chromatography).

Absolute ethanol (Sigma Aldrich, Denmark) was used as solvent.

2.2. Ceramic suspension preparation

A series of suspensions at a ceramic loading of 28 vol%, containing increasing amounts of dispersant (expressed as mg of dispersant over m^2 of ceramic surface), were prepared for each dispersant. In a typical procedure, the dispersant was dissolved in the solvent in a PE bottle containing zirconia balls. CGO powder, typically 25–30 g, was gradually added to the solvent and dispersant mixture. The suspensions were left to roll for at least 72 h.

For D_1 and PVP, a series of suspensions at the optimal dispersant amount with a ceramic loading ranging from 10% to 48% in volume were prepared following the same procedure.

Samples were labeled as reported in Table 2, where CGO refers to the CGO powder. The first number, e.g. 10, refers to the ceramic loading expressed as percentage by volume, while the second number defines the dispersant content in mg over m^2 of the inorganic powder.

2.3. Rheological characterization

The rheological properties of dispersions were measured with a rotational rheometer (Anton Paar MCR302). A constant temperature of 21 °C was maintained during the experiments using a temperature control unit. The prepared suspensions were characterized running flow curve test experiments (in rotational mode) and sweep frequency test (in oscillation mode). To prevent the evaporation of the solvent during the experiments, a proper solvent trap was used. All rheological measurements were performed using a pre-shear at 0.1 s^{-1} for 2 min followed by 2 min at rest (0 s^{-1} shear rate), to remove any effects due to the sampling and loading of dispersions. Flow curve tests were conducted in step mode using 45 steps with a waiting time of 10 s. The step mode procedure allows the sample to reach equilibrium and