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Enhanced densification of thin tape cast Ceria-Gadolinium Oxide (CGO) layers by rheological optimization of slurries

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ABSTRACT

Optimized CGO-based slurries are formulated and shaped into thin dense layers via a tape-casting process. The formulation is adjusted with respect to the rheological behaviour. The internal structure and flow properties of slurries are explored with the aim of identifying the required conditions to obtain thin dense CGO layers at reduced sintering temperatures (1200 °C). We demonstrate a correlation between the rheological properties of the slurries, the sintering behaviour and the microstructure of the resulting tapes. Remarkably, a dense CGO layer less than 20 μm thick is obtained with a non-congested slurry, having optimized ceramic loading and liquid-like behaviour.

1. Introduction

Tape casting is one of the simplest and low-cost forming processes for producing high quality, flat, and large-area ceramic tapes [1,2]. It is an extremely versatile technique that enables the fabrication of either thin (below 100 μm) or thick (above 100 μm) tapes that can be further used either as single layers or multilayer structures [1,2].

In tape casting the rheological behaviour of the slurry is of utmost importance since to a large extent it determines the arrangement and packing of particles in the green body, that then dictate the sintering behaviour and the quality of the final product [3,4]. Essential processing demands on the rheology of the slurry are the shear thinning behaviour and the liquid-like character [3]. Indeed, when the casting blade is applied, the viscosity of the slurry is required to decrease to a sufficiently low value, and then quickly recover its initial high value when the shear forces are abruptly removed (after the passing blade). In this process, the shear thinning behaviour, originating from the alignment of the binder molecules at high shear rates, make the slurry extremely homogenous and ensure an easy processing (*e.g.* sufficiently low viscosity). The liquid-like character confers the required fast recovery to the high viscosity value, that preserves the homogenous structure of the slurry by reducing the mobility of its constituents and limiting the sedimentation of the particles during the solvent evaporation step.

Only an adequate tuning of the two rheological characteristics can ensure the processing of high quality tapes that can evolve in to fully dense ceramic layers. This requires the optimization of the formulation and an accurate understanding of the effect of the different slurry components on the rheological behaviour. Therefore, despite not being easy to observe, a strong correlation between the rheology and the sintering behaviour is expected [4].

Ceria-based oxides are key-compounds in many strategic applications [5–15]. Due to their relevance, growing attention has been recently dedicated to the processing of these materials, with specific interest on the sintering behaviour [16–23]. Full densification of ceria materials from a green body generally requires sintering temperatures as high as 1350–1600 °C [19–21]. This in turn causes the failure in co-firing of multi-layered ceramic structures [22] and determines high manufacturing costs [21]. Several alternatives have been proposed to lower the temperatures. Among others, either highly reactive nano-metric powders derived from wet chemical routes [24–26], or low melting-point sintering aids [27–33] have been investigated. However, these strategies give rise to further critical issues that likely influence the performances of the materials (*e. g.* alteration of the final composition [21]). Densification in reducing atmosphere has also been explored as possible alternative [18,34,35]. Yet, the large chemical expansion due to cerium reduction makes this unfeasible for multilayer components [21] or porous bodies [36].

A different approach, based on the engineering of particles packing in the green state, has been proven to promote full densification for CGO nano-metric (ultra-fine) powder [37,38]. Interestingly, it has been observed that only samples having low initial (green) density (lower

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than the geometrical limit of 63 vol% for random close packed sphere [37,38]) can be fully densified. This experimental result has been associated with a favourable rearrangement of nanometric particles in a non-congested network during the densification process. Recently, Glasscock et al. [21] further explored this approach by analysing the effect of forming stress on the initial microstructure (particles and pore arrangement), and on the resulting sintering behaviour for ultra-fine ceria-gadolinium oxide (CGO) powder. They observed that samples shaped with low stress forming techniques (*e. g*. tape casting) possess the lowest green density and a remarkable aptitude to fully densify.

In the light of this result, the use of rheology is herein proposed to control the sintering behaviour of nano-metric CGO, shaped via tape casting. The approach is to properly adjust the formulation of the slurry with the aim of attaining an arrangement and particle packing favourable for the full densification. Slurries with increasing ceramic loading are formulated, while keeping the ceramic loading of the corresponding green bodies constant and the loading (in the green bodies) was intentionally selected as high as possible (~54–56 vol%). A correlation between the flowing properties and the sintering behaviour of the resulting green tapes is demonstrated. The method adopted allows the optimization of the slurries with respect to the rheology to obtain dense thin CGO layers without the use of any sintering aids.

2. Experimental

2.1. Materials

All materials were reagent grade and used as received. Commercial gadolinium doped ceria powder ($Gd_{0.10}Ce_{0.9}O_2$, CGO), (Rhodia, La Rochelle Cedex, France, 99% purity) was used as ceramic component. The starting ceramic powder was characterized for its specific surface area (SSA) by BET (Brunauer-Emmett-Teller; Autosorb 1-MP, Quantachrome Instruments, Boynton Beach, Fl, USA), phase purity (X-ray diffractometer, Bruker D8, Germany), particles size distribution (PSD) (LS13 320 laser diffraction particle size analyser, Beckman Coulter, Fullerton, USA), and morphology (FESEM, Supra, Carl Zeiss, Germany).

A commercial dispersant (DisperByk, Germany) with acidic affine functions was used to disperse CGO particles into the solvent. A binder system based on polyvinyl-butyral (PVB, Butvar, Denmark) was used in combination with triethyleneglycol bis (2-ethyl hexanoate) (S-2075, Solutia, England). Porous layers were prepared by adding graphite (V-UF1 99.9, SSA 10.0 m^2g^{-1}; Graphit Kropfmühl, Germany) as pore former.

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

2.2. Slurries preparation (dense and porous)

The general procedure for preparing the CGO slurries consisted of a sequence of steps, where the first one was the preparation of a stable CGO suspension. Typically, the fixed amount of dispersant (5 mg/m^2) [39–42] was dissolved in ethanol in a PE bottle containing zirconia milling balls. The CGO powder was then gradually added and mixed with the dispersant and the solvent. The dispersion was then ball milled for 72 h. In the following step the binder solution was gradually added and the resulting slurry was homogenized by ball milling for further 72 h. Four slurries at increasing ceramic loading were prepared, keeping the ceramic loading of the green body constant (green density). Details are indicated in Table 1.

A CGO slurry formulation for tape casting porous layers was also prepared. A similar procedure was adopted, with the only difference that after 24 h of milling, the pore former (graphite) was added to the starting dispersion (solvent, dispersant and CGO). The obtained dispersion (solvent, dispersant, CGO, and graphite) was kept rolling for further 48 h, with a total milling time of 72 h. The final step was the addition of the binder system. The slurry was then ball milled for 72 h. Details on the formula are indicated in Table 1.

The slurry samples were labelled as reported in Table 1, 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 lower-case letters *d* and *p* at the end of the code refers to the dense and porous layers, respectively.

2.3. Rheological characterization

The rheological properties of the slurries 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. All the experiments were performed using a parallel plate of 50 mm in diameter (PP 50) at a gap distance of 0.6 mm. 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 the slurries.

All the slurries were characterized by running flow curve (in rotational mode), sweep amplitude and sweep frequency tests (in oscillation mode). Flow curve tests were conducted in the shear rate range of 0.1–100 s^{-1} in up and down shear rate ramps using the step mode procedure (45 steps with a waiting time of 10 s). The step mode procedure allows the sample to reach equilibrium and avoid possible transient effects. Frequency sweep tests were performed at a fixed shear stress of 0.5 Pa in the frequency range of 0.01–10 Hz. Prior to any oscillatory tests, the linear visco-elastic region was determined by performing sweep amplitude experiments in the shear stress range of 0.1–1000 Pa and at the frequencies of interest (0.01, 0.1, 1, and 10 Hz).

2.4. Tape fabrication and characterization

The thin dense CGO green layers were laminated with two thick porous CGO green layers in symmetrical configuration. Accordingly, the slurries were tape-cast into a green tape on Mylar® foil at constant speed (20 cm/min) in a controlled environment with a blade clearance varying from 400 μm for the fabrication of thick porous layers to 80 μm for the casting of thin dense layers.

Table 1
Sample labelling with the amount of each component indicated, both in the slurries and in the corresponding green tapes.

Samples	Slurry				Green Tape			
	Solvent (% vol)	Ceramic (% vol)	Organics (% vol)	Pore former (% vol)	Ceramic (% vol)	Organics (% vol)	Pore former (% vol)	Green Density (%)
CGO_18_d	61	18	21	/	46	54	/	54
CGO_15_d	67	15	18	/	47	53	/	55
CGO_12_d	74	12	14	/	46	54	/	54
CGO_10_d	77	10	13	/	46	54	/	54
CGO_12_p	59	12	22	7	29	55	16	42