Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 34 (2014) 3897–3916

www.elsevier.com/locate/jeurceramsoc

High-precision green densities of thick films and their correlation with powder, ink, and film properties☆

R. Mücke[a,*], O. Büchler[a], N.H. Menzler[a], B. Lindl[b], R. Vaßen[a], H.P. Buchkremer[a]

[a] *Institute of Energy and Climate Research, IEK-1, Forschungszentrum Jülich GmbH, Germany*
[b] *cyberTECHNOLOGIES GmbH, Ingolstadt, Germany*

Received 13 November 2013; received in revised form 1 April 2014; accepted 6 April 2014
Available online 28 May 2014

Abstract

A precise geometrical method employing optical profilometry for green density measurements of thick films is presented that provides a typical reproducibility of 0.1–0.2% theoretical density (TD) and a measurement uncertainty of 0.2–0.4% TD for layer thicknesses of around 50 μm. The procedure can be applied for all thick films with a dried thickness of 10 μm or greater. In a case study, the green densities of screen-printed zirconia layers were investigated as a function of the starting powders (grain sizes from 0.1 to 0.4 μm), the solid content, the chain length of ethyl cellulose as binder and its concentration, and two different dispersants and their concentration. Rheological ink properties, surface roughness, drying stresses from deflection measurements, the mechanical properties of green films, and the equivalent compaction pressure were measured and correlated with the green density data. Compressive binder forces and lubrication effects dominated the packing of the particles.

Keywords: Green density; Rheology; Residual drying stress; Mechanical property; Ethyl cellulose

1. Introduction

The green density of a ceramic powder compact or film not only determines the amount of shrinkage required for its densification but is also of major importance for the microstructure and macroscopic properties of the final product. A low packing density can prolong the sintering time necessary to achieve the final density[1] or may limit the final density achievable after sintering.[2–5] This was attributed to entrapped pores during grain growth, and is significantly amplified for ceramics with a low packing density.[1,2,6,7] Larger starting pores or a lower coordination number of the grains results in a larger mean pore size during sintering.[7–11] Comparing equal relative densities, this implies that a smaller number of pores impeding grain growth by pore pinning are present in ceramics starting with lower green densities.[10] Therefore, not only the density-related but also the grain-size-related (e.g. mechanical and electrical) properties of the final product depend on its green density. Furthermore, low green densities often imply that agglomerates are present in the green body,[12] which not only retard densification,[9,13] but also increase the risk of crack formation during film drying.[14] During constrained sintering of films, the sintering potential and the viscous properties govern the process.[15,16] These strongly depend on the grain size evolution (sintering trajectories) and therefore also on the green density. For alumina compacts, Guillon et al.[17] found that a lower green density yields a higher viscosity during sintering and a lower absolute value of the sintering stress, both of which retard densification. Therefore, a high packing density is always of advantage for achieving dense ceramic layers for gas separation membranes, solid oxide fuel cells, and many other applications.[18] The necessary green density depends on the grain size and is typically lower for finer starting powders.[19] In any case, precise knowledge of the green density is important (both for research and quality control), even if the final ceramic component is to be porous as in catalysts or filters.

The green density (dried bulk density) of bulk materials is typically measured by one of the following methods: (1) geometric method by sample dimension and weight, (2) hydrostatic weighing (Archimedes' principle), (3) powder pycnometry,[20]

☆ Part of the work has been published in: Ref. [31].

* Corresponding author. Tel.: +49 2461614066.
E-mail address: r.muecke@fz-juelich.de (R. Mücke).

http://dx.doi.org/10.1016/j.jeurceramsoc.2014.04.012

(4) mercury intrusion porosimetry,[21] (5) quantitative image analysis of scanning electron micrographs or computed tomographs, and (6) X-ray radiography[22]. However, many of these methods are not suitable for measuring precise densities in layers with a thickness of approx. 50 μm. Powder pycnometry and mercury intrusion porosimetry require relatively large sample volumes and compact dimensions in order to achieve good reproducibility (e.g. 300–400 mm^3 volume to achieve a reproducibility of approx. 1% of the measured volume value[23,24]). Mercury intrusion porosimetry was reported to yield a statistical variation of 0.5–1% TD.[25] However, the dried (binder-free) films had to be mechanically removed before measurement, which is not possible for all coatings and is rather complicated. If binders are used which close pores after drying, intrusion methods may yield inaccurate results. The hydrostatic weighing method suffers from the large surface-to-volume ratios in rather thin layers: air entrapment and partial infiltration cannot be compensated completely by additionally weighing the wet sample in air. In a preliminary test, we obtained errors as large as 10% for free-standing layers 80 μm in thickness.[26] Furthermore, contact with the liquid may affect the integrity of the layer. Similarly, in X-ray radiography rather thick structures are required in order to obtain an adequate signal (1.6% deviation was reported for cylinders of iron compacts 8 mm in height[22]). Image analysis for separating solid and pores spaces, on the other hand, is not capable of investigating complete macroscopic samples, but only individual spots. Furthermore, image acquisition is very time-consuming and, for instance, the preparation of cross-sections without grain pull-outs is almost impossible for green bodies made of fine ceramic powders.

Somalu et al.[27,28] measured the layer thicknesses by SEM (approx. 10 μm) and, by employing the geometric method, provided green densities of screen-printed films with an average error of approx. 1.3% TD. Ji et al. utilized a magnetic thickness gauge and obtained a reproducibility of 3% for 100–170 μm thick layers.[19] These accuracies might not be sufficient in all cases, in addition, local variations in thickness, edge effects etc. can hardly be included in microscopic or other classical thickness measurement. Therefore, an enhanced geometric method for the determination of the green density was developed and used in this work measuring the volume of complete layers with high precision by optical profilometry. The following compensations were taken into account: (1) waviness of the substrate by differential scanning (substrate with/without a layer); (2) deformation due to drying stresses by polynomial compensation of the uncoated margin of the substrate; (3) open pores on the surface of the porous layer (similar to the "external void volume" in Ref. 29), which will decrease the appropriate layer volume, and interaction of the laser beam with the opaque particles by determining an effective penetration depth. In previous preliminary work,[30] we did not consider the penetration effect resulting in an error of about 0.5–2% TD. The achieved accuracy was, however, sufficient to test the suitability of binders for a specific powder/solvent system identifying an increase or decrease of the green density with augmented binder concentration.[31] The glass substrates previously used were replaced by polished stainless steel supports as glass is prone to electrostatic charge which affected the weight measurement slightly. A reproducibility of 0.1–0.2% TD and a typical measurement uncertainty of 0.2–0.4% were now achieved, which is approx. one third of the older measurements.

The work was motivated by the question of how ceramic screen-printing inks can be optimized with respect to the dried film density by varying the ink parameters. Terpineol-based inks with ethyl cellulose binders and yttria-stabilized zirconia are commonly used for electrolytes for solid oxide fuel cells (SOFC)[18,32–34] and are required to densify fully during sintering for proper cell operation. The ink vehicle is, furthermore, widely used in screen printing for electronic applications as it displays a low boiling point, low vapor pressure, good solvent compatibility with the polymer binder, and satisfactory safety.[35] There are only a few reports in the literature concerning the green density of such dried films. Recently, Somalu et al. studied nickel oxide/zirconia inks for SOFC anodes and found an increasing green density for an augmented solid[27] and binder content[28], which they explained by the formation of an elastic network supporting densification revealed by an increase of storage modulus, yield stress, and creep compliance. Sumita et al.[36] studied the green density of alumina sediments as a function of the type and content of the dispersant, and found an increase with rising dispersant content and a maximum at some optimal concentration. The present work investigates the influence of the parameters of raw materials and ink formulation such as grain size (from 0.1 to 0.4 μm), solid content, binder type and content, and the effect of dispersants on the green density and correlates the findings with rheological and roughness data. Zürcher and Graule[37] found Solsperse 3000 (a commercial pentastearic acid oligomer) to be the most suitable dispersant for binder-free YSZ suspensions with respect to their rheological properties. We compared it with a phosphoric acid derivative whose functional groups exhibit similar or even higher affinity for the surface of metal oxides.[38] Focusing on binder-free suspensions and sol-gels, e.g. Scherer et al.[39] explained the drying process on the basis of capillary and osmotic pressure. In screen-printing inks, the ethyl cellulose binder is known to graft directly onto the ceramic surface[38] and is thought to bridge multiple particles by bridging flocculation.[33] Therefore, additional factors such as the intrinsic shrinkage of the ink vehicle can be assumed to be one of the driving forces of densification during drying.[41] It will be shown that the binder both lubricates the particles and also drags them actively together. For a further, preliminary understanding of the particle packing process inside such inks, the intrinsic shrinkage of the ink vehicle, the residual drying stresses, and the mechanical properties of screen-printed dried films were analyzed. Their correlation to the green density during the systematic variation of the ink composition allowed us to identify the parameters which are most critical for yielding high green densities. Cold compaction of dies was used to determine the compaction pressure that yielded the same green density as the films. This equivalent compaction pressure was used to describe the efficiency of the packing in the dried films. A simple binder bridge model was proposed to explain the observed particle size effects.