Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 35 (2015) 2413–2425

www.elsevier.com/locate/jeurceramsoc

Three-dimensional shrinkage behavior of green tapes derived from spherical-shaped powders: Experimental studies and numerical simulations

Zongwen Fu [a], Pit Polfer [b], Torsten Kraft [b], Andreas Roosen [a,*]

[a] University of Erlangen-Nuremberg, Department of Materials Science, Glass and Ceramics, Martensstrasse 5, 91058 Erlangen, Germany
[b] Fraunhofer Institute for Mechanics of Materials IWM, Wöhlerstrasse 11, 79108 Freiburg, Germany

Received 13 August 2014; received in revised form 22 January 2015; accepted 30 January 2015
Available online 20 February 2015

Abstract

In tape-cast products a higher shrinkage is observed in the thickness direction compared to the in-plane shrinkage, which is attributed to an anisotropic green tape microstructure caused by shearing and drying during manufacturing. In the present study, cast tapes composed of spherical particles were investigated experimentally and numerically. The shrinkage behavior was analyzed after binder removal and sintering at different temperatures in all three spatial directions. The correlation between anisotropic shrinkage and microstructure concerning pore orientation and coordination number was discussed. Furthermore, it is shown that the anisotropic shrinkage during binder removal contributes strongly to the total shrinkage anisotropy.

Keywords: Tape casting; Anisotropic shrinkage; Ceramic sintering; Discrete element method; Simulation

1. Introduction

Dimensional control is one of the basic problems in ceramic processing, especially for tape cast sheets which are used to manufacture multilayer structures with highly integrated components.[1,2] In this technology, the exact positions, e.g., of vias or electrodes in different layers must be maintained during the entire thermal process.[2] Therefore, any uncontrolled shrinkage anisotropy during binder burnout and sintering can lead to device failure.[3–6] During tape casting, due to the shear flow gradient under the blade of the casting head as well as to the constrained drying process, non-spherical ceramic particles are predominantly oriented parallel to the casting direction.[7–15] Because of this anisotropic green tape microstructure, anisotropic shrinkage occurs:[8,13,14,16]

$$\varepsilon_z \gg \varepsilon_y \gg \varepsilon_x \tag{1}$$

where ε represents the linear sintering shrinkage and x, y and z denote the casting, transverse and thickness direction, respectively.

Not only tape-cast products exhibit an anisotropic microstructure; the shrinkage anisotropy could also be observed during the sintering of uniaxially pressed, extruded and three-dimensional printed ceramics.[17–19] During uniaxial pressing, extrusion and tape casting, it was found that non-spherical ceramic particles can be textured and that the largest and smallest shrinkages occur in the directions perpendicular and parallel to the particle orientation direction, respectively.[17] During rapid prototyping based on layer-by-layer assemblies via 3D printing, elongated pores perpendicular to the thickness direction as well as a layered microstructure could be found.[18,19] In all these cases a higher shrinkage in the z-direction was observed; the primary cause of anisotropic shrinkage in these systems is attributed to the orientation of anisotropic particles.[11,16,19–25] Wakai et al. simulated the shrinkage behavior of spherical particles, which are not oriented but which also exhibit anisotropic shrinkage behavior caused by particle rearrangement during sintering due to an inhomogeneous distribution of contact points.[26]

* Corresponding author. Tel.: +49 91318527540.
E-mail address: andreas.roosen@fau.de (A. Roosen).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.01.032
0955-2219/

According to the sintering theory, grain growth and pore elimination are the two most important mechanisms to describe sintering shrinkage.[27] In the present work, three-dimensional shrinkage behavior of tape cast alumina powders of spherical particle shape was investigated experimentally and numerically, and correlated with pore orientation and coordination number in the microstructure. Specifically, the reason for the higher shrinkage in z-direction compared to the lateral shrinkage is in focus. The study is based on experiments as well as on simulation of sintering behavior.

2. Experimental methods

2.1. Raw materials

Spherical alumina powders SP (Sumitomo Chemical Co., Ltd., Tokyo, Japan, d_{50}: ~3.0 μm) and DAW 05 (Denka Co., Ltd., Tokyo, Japan, d_{50}: ~4.2 μm) were used in the present study. The particle size distribution was measured by means of laser granulometry (Mastersizer APA 2000, Malvern Instruments, London, Great Britain).

2.2. Slurry preparation and tape casting

Tape casting slurries with a solid content of 28 vol.% alumina were prepared; powder dispersion was performed in a tumbling mixer (Turbula, Willy A. Bachofen AG, Swiss) with Al_2O_3 milling balls for 24 h in an azeotropic solvent mixture containing of 68 wt.% ethanol and 32 wt.% toluene; Menhaden Fish oil (Kellogg Co., Buffalo, USA) was added as dispersant. After 24 h of deagglomeration, binder (polyvinylbutyral, B-98, Solutia Inc., St. Louis, USA) and plasticizer (alkyl benzyl phthalate, Santicizer, Ferro Corp., Cleveland, USA) were added to the suspension. Subsequently, the slurry was homogenized for an additional 24 h, sieved through a 200 μm mesh screen and degassed (250 mbar, 30 min) to remove gas bubbles before casting. Table 1 shows the exact composition of the tape casting slurry used in this study and also the density of the components.

Tape casting was carried out on a tape-casting machine equipped with a fixed double-chamber casting head. A silicon-coated PET carrier film (Mitsubischi Plastics, Inc., Japan) with a thickness of ~100 μm was used as a tape carrier. The front and rear doctor blades were adjusted to a gap height of 900 μm and 1100 μm, respectively. Because increasing shear rates above ~12 s^{-1} did not result in an increased particle alignment,[8,12] the casting speed was kept at a constant value of 700 mm/min in this study. The filling height of the slurry reservoir was ~20 mm in all cases. Drying was performed at room temperature without additional air flow.

2.3. Sample preparation

The dried green sheets with a thickness between 240 and 280 μm, respectively, were removed from the PET carrier film and cut to the desired sample size of 30 mm × 30 mm with a hot knife (Groz-Beckert KG, Albstadt, Germany) at 60 °C. Debinding took place in air with a heating rate of 2 K/min up to 450 °C, followed by a holding time of 1 h. Subsequently, the samples were pre-fired at 1600 °C in air with a holding time of 1 h and a heating rate of 4 K/min on a high purity alumina setter (Kerafol GmbH, Eschenbach, Germany). In order to improve the densification, the pre-fired tapes were subsequently sintered at 1600 °C for 10 h as well as at 1730 °C for 5 h and for 15 h, respectively. Due to plastic deformation of alumina setter at these higher temperatures, porous mullite substrates were used as sintering support during these sintering experiments. The theoretical density of ceramic tapes before and after firing was calculated using the theoretical density values shown in Table 1. The bulk density of green tapes was determined by measuring the weight, the area by scanning of the surface geometry using a commercial scanner (Epson Perfection V500 PHOTO, Epson GmbH, Meerbusch, Germany, resolution: ~22 μm/pixel) and the height by means of micrometer screw. The bulk density after BBO and sintering was calculated according to mass loss and to measured shrinkage by laser scanning microscopy. The porosity was derived from the measured bulk and theoretical densities.

2.4. Analysis of shrinkage anisotropy

In order to determine the shrinkage anisotropy, the linear shrinkage in all three spatial directions was measured. For the measurement of the shrinkage in the casting plane, four hardness indentations in a distance of ~25 mm from each other were punched into the green tapes using a Vickers diamond pyramid (Zwick GmbH & Co. KG, Ulm, Germany).[8] The exact distance between these indentations was measured before and after firing by means of a laser scanning microscopy (UBM Messtechnik GmbH, Ettlingen, Germany) with an accuracy of 10 nm in z-direction and 1 μm in x- and y-directions. In order to measure the thickness shrinkage exactly, the average thickness along the two diagonals of small, non-warped specimens of about 1 mm × 1 mm in size was determined by means of laser scanning microscopy before and after debinding and pre-firing. The use of these two methods allowed an exact measurement of the shrinkage in all three spatial directions. Furthermore, the thickness before and after sintering was verified by micrometer screw gauge with an accuracy of 1 μm. Due to the relatively high surface roughness of the porous mullite setters used for sintering at higher temperatures above 1600 °C and holding times of 10 h, the beam of the laser scanning microscope was out of the measuring range of ± 500 μm. Therefore, the thickness had to be determined by micrometer screw gauge.

Average values of the shrinkage were calculated from measurements of at least ten different samples. Based on these data, the shrinkage anisotropy factors K in all three spatial directions were calculated according to the following equations:

$$K_{xy} = \left(1 - \frac{\varepsilon_x}{\varepsilon_y}\right) \times 100 \quad (2)$$

$$K_{xz} = \left(1 - \frac{\varepsilon_x}{\varepsilon_z}\right) \times 100 \quad (3)$$