Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 403–413

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of various pore formers on the microstructural development of tape-cast porous ceramics

Ayhan Sarikaya, Fatih Dogan*

Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409-0340, USA

Received 20 March 2012; received in revised form 6 June 2012; accepted 14 June 2012
Available online 21 June 2012

Abstract

Various types of pore formers have been used for the fabrication of ceramics with controlled porosity. This study addresses a detailed and systematic comparison of different pore formers (e.g. graphite, polymethyl methacrylate, sucrose and polystyrene) with distinct features such as size, distribution and morphology of particles and decomposition/oxidation behavior. Investigations also involve their effect on the rheological properties of the slurries and the microstructural development of laminated porous ceramic tapes.

Morphological features of the pore former particles were characterized using laser diffraction, B.E.T. surface area measurement and scanning electron microscopy (SEM) techniques as their thermal decomposition/oxidation behavior were determined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) methods. Tape compositions were developed and optimized in order to incorporate identical volumetric loadings of the materials in the tape formulations with different pore formers for a reliable comparison of their pore forming characteristics. Porous yttria stabilized zirconia (YSZ) ceramics were fabricated without macroscopic defects (e.g. cracks, warpage and delamination) by developing heating profiles based on the identified thermal properties of the pore formers. Characterization of the sintered porous ceramics by SEM and mercury intrusion porosimetry techniques revealed novel relationships between the physical properties of the utilized pore formers, processing parameters and final pore structures.

Keywords: A. Tape casting; B. Porosity; E. Fuel cells; Pore former

1. Introduction

Porous ceramics are essential for a wide range of engineering applications including separation membranes [1], filters [2], piezoelectric [3] and pyroelectric ceramics [4], lightweight structural materials [5], biomaterials [6], battery separators [7] and solid oxide fuel cell (SOFC) electrodes [8–10]. Controlling the features of the porosity in ceramic microstructures is crucial to satisfy the requirements of desired applications. For instance, uniform distribution of pores gives rise to the electrochemical performance of SOFC electrodes while their connectivity/percolation allows transport of the reactant and product gases efficiently [11–13].

Although there are numerous techniques to fabricate porous ceramics such as combustion synthesis [14,15], foaming [16], reactive infiltration [17], freeze drying [18] pyrolysis of polymeric precursors [19], electrophoretic deposition [20] and gel-casting [21], partial sintering of ceramic tapes [22,23] and incorporation of pyrolyzable pore formers to tape casting slurries [8,24,25] are commonly employed methods to fabricate tape-cast porous ceramics. In partial sintering, densification is retarded in order to obtain a certain amount of porosity. However, partial sintering has fundamental difficulties in controlling the essential features of porosity such as shape, size, distribution and connectivity of the pores. Moreover, a desired dense ceramic matrix cannot be formed since the ceramic particles are allowed only to form neck and create a skeleton. Thus, porous ceramics fabricated by partial sintering are poor in mechanical strength [8,26].

Pore former additions to the ceramic mixtures yield stable pores after the removal of the binder and the pore former particles. Formed pores are not removed at subsequent

---

*Corresponding author. Tel.: +1 573 341 7130; fax: +1 573 341 6934.
E-mail address: doganf@mst.edu (F. Dogan).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.06.041

sintering steps [26,27] and the final porosity of the ceramic microstructures resemble the features of the pore former particles even after sintering at elevated temperatures [26,28,29]. Considering that amount, size, shape and thermal properties of the pore formers can be controlled, this technique has more control over the features of the porosity as well as mechanical properties of the ceramic matrix. By controlling the properties of the pore formers, the ceramic microstructures can be also tailored by means of sintering shrinkage which is critical for the fabrication of multilayer tape-cast ceramics. Controlled sintering shrinkage and combination of tape casting with lamination also allow the fabrication of multilayer structures which involve graded porosity or integration of dense and porous ceramic layers [27].

In recent studies on the development of SOFCs, infiltration of polymeric precursors of catalytically active materials into porous 8 mol% yttria stabilized zirconia (YSZ) electrodes has been a critical step for fuel cell fabrication [30–32]. Porous YSZ electrodes are required to provide sufficient porosity to allow infiltration of the precursors and transport of the reactant/product gases while affording structural integrity to maintain conductivity of oxygen ions. Hence, the desired YSZ electrode microstructure involves a dense matrix with a controlled pore structure.

Electrode tapes are laminated on either side of an electrolyte tape and co-sintered prior to the infiltration steps. Formation of pores in the electrode tapes and densification of the adjacent electrolyte layer introduces challenges impairing the integrity of their multilayer structure due to their dissimilar shrinkages. Various pore formers can be utilized to control the development of the porous electrodes. However, each pore former results in a different shrinkage profile on the tapes due to its characteristic particle morphology while it requires a controlled removal with a specific heating profile due to its particular thermal decomposition/oxidation behavior. As a result, undesired macroscopic defects such as cracks, blisters, warpage and delamination were observed as the compositions of the electrode tapes were modified to improve the performance of the SOFCs by changing the type, size and loading of the pyrolyzable pore formers. Therefore, a systematic study was needed to understand the relations between the properties of the pore formers, the resultant pore structures and the dimensional changes upon their removal and sintering. The gained knowledge would allow developing fabrication routes for defect-free (e.g. cracks, delaminations, blisters and warpage) multilayer ceramics.

Pore forming materials were selected considering their desired properties. Selection criteria included particle size and shape for a better understanding of the effect of the pore former morphology on the final pore structure, and decomposition/oxidation of pore formers with a minimum amount of residual carbon and other trace impurities that can affect the sintering behavior and properties of the YSZ matrix [33]. Selected high-purity pore formers had distinct morphological features such as plate-like flake graphite, spherical PMMA and polystyrene, spheroidal graphite and random shaped sucrose. Moreover, they demonstrated dissimilar particle size distributions ranging from monodisperse to bimodal and polydisperse.

Even though numerous studies were conducted using graphite [8,28,33,34], PMMA [26,28,35], sucrose [36,37] and polystyrene [38–40] as pore formers, the processing conditions such as fabrication techniques, matrix materials, compositions and sintering profiles were not comparable and it was relatively difficult to draw any useful conclusions about their pore forming features with respect to each other. Moreover, the effect of the pore formers on the evolution of the final pore structures and the dimensional changes of the ceramics were not reported in sufficient detail towards processing of crack-free porous ceramic tapes. Therefore, a detailed comparative investigation of the pore formers is aimed by this study to reveal the relationships between their particle characteristics, processing conditions and effect on the pore structures of ceramics as well as dimensional changes during sintering of porous tape-cast ceramics.

Various techniques were employed for detailed analyses of the properties of the pore former particles such as size, shape, distribution, surface area and decomposition/oxidation behavior. The compositions of the ceramic slurries were developed for tape casting and lamination using identical volume fractions of the components for all of the pore formers for a consistent comparison. The analysis of their effects on the rheological properties of ceramic slurries in identical conditions provided additional information on their particle characteristics while characterization of their thermal properties allowed determining heating profiles for their defect-free removal from tape-cast multilayer ceramics. Detailed investigations on the final microstructures led to a better understanding of the pore former – microstructure relationships of the sintered porous ceramics.

2. Experimental procedure

Commercially available high purity powders of flake and spheroidal graphite (Superior Graphite, Chicago, IL, USA), spherical polymethyl methacrylate (PMMA) (Sekisui, Osaka, Japan), random shaped sucrose (Alfa Aesar, Ward Hill, MA, USA) and spherical polystyrene (Alfa Aesar, Ward Hill, MA, USA) were selected. Although various starch types are also common pore formers, they were not included in this study due to the swelling phenomenon at elevated temperatures which makes it difficult to predict the final porosity by considering the initial properties and loading of the pore formers [41–43]. All pore formers were characterized as received except sucrose. Since it was not supplied with a certain particle specification, it was sifted through a 325 mesh screen.

Pore former particles were dispersed in an ethanol (Sigma-Aldrich, St. Louis, MO, USA) and toluene (Sigma-Aldrich, St. Louis, MO, USA) mixture and lightly