Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Full length article

Graphite and PMMA as pore formers for thermoplastic extrusion of porous 3Y-TZP oxygen transport membrane supports

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A R T I C L E I N F O

Article history:
Received 8 June 2016
Received in revised form
28 September 2016
Accepted 3 October 2016
Available online xxx

Keywords:
Porosity
Gas permeability
Thermoplastic extrusion
Oxygen transport membranes
YSZ

A B S T R A C T

A gas permeable porous support is a crucial part of an asymmetric oxygen transport membrane (OTM). Here, we develop feedstocks for *thermoplastic* extrusion of tubular, porous 3Y-TZP (partially stabilized zirconia polycrystals, $(Y_2O_3)_{0.03}(ZrO_2)_{0.97}$)) ceramics, using graphite and/or polymethyl methacrylate (PMMA) as pore formers. The influence of pore former content and type, 3Y-TZP particle size and support sintering temperature on the microstructure, porosity and gas permeability were studied. Using at least 40 vol% pore former, consisting of graphite and PMMA in the volume ratio 2:1, tubes with gas permeability exceeding the target of 10^{-14} m^2 are obtained. In the temperature range 1250–1400 °C the support gas permeability is insensitive to the sintering temperature, and the feedstocks shrink more than 15% during sintering, making them ideal for co-sintering with functional OTM layers. This demonstrates the suitability of thermoplastic extrusion for fabrication of porous 3Y-TZP OTM supports, or for other technologies requiring porous ceramics.

1. Introduction

Pure oxygen gas supplied by ceramic oxygen transport membranes (OTM) can facilitate more efficient gasification processes and easier CO_2 capture and storage [1]. The oxygen flux is inversely proportional to the thickness of the membrane [2], and thin OTMs are therefore necessary to obtain commercially interesting oxygen fluxes. An asymmetric OTM design is therefore common, where the active membrane is reduced to 10–20 µm in thickness and supported on a 0.5–1 mm thick porous substrate necessary for mechanical integrity [3]. This support must in addition to good mechanical properties also have a sufficient gas permeability to avoid concentration polarization losses. A tubular OTM design is generally preferred due to simpler sealing and higher tolerance to thermal gradients than planar modules [1]. This work demonstrates how such support structures can be prepared by thermoplastic extrusion through the optimization of the extrusion feedstocks.

Thermoplastic feedstocks differ from the more common solvent-based feedstocks [4,5] in the way that they obtain their plasticity from warm thermoplastic polymers rather than a binder and a solvent. The thermoplastic feedstocks are compounded and extruded above the softening temperature of the polymer, and cool and harden immediately after extrusion. This process provides many advantages, for example [6]: 1) high green extrudate strength, 2) complex and thin-walled extrudates 3) low abrasion and wear of the equipment and 4) no complex drying step. A disadvantage is, however, the more complex de-binding process due to the large volume of polymer that must be removed. Thermoplastic feedstocks are commonly used for injection moulding, and have also been used to extrude dense ceramics [7,8], but are rarely studied for extrusion of porous ceramics [9].

So far, thermoplastic feedstocks that can provide porous ceramic support tubes of sufficient gas permeability and mechanical strength (>50 MPa) in a multilayer co-firing process for asymmetric OTM fabrication has not been reported. The required support gas permeability depends highly on the membrane material and operation conditions [10], but as a general guideline for a 1 mm thick support the Darcy permeability coefficient k should exceed 10^{-14} m^2. The gas permeability depends on the volume fraction of porosity (ϕ) and the pore diameter (D_p):

$$k = \phi D_p^2/32 \tag{1}$$

for the case of a simplified model with parallel pore channels (capillary permeability) [11]. Real porous structures with a more tortuous pore network will therefore have a lower permeability than predicted from Eq. (1). Still, Eq. (1) can provide guidelines for the

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.10.001

Please cite this article in press as: A.B. Haugen, et al., Graphite and PMMA as pore formers for thermoplastic extrusion of porous 3Y-TZP oxygen transport membrane supports, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.10.001

material engineering; e.g. that porosity above 40% and pore size above 1 μm should be aimed for to obtain gas permeability in the range of 10^{-14} m^2.

Sufficiently porous tubes have been obtained by solvent-based extrusion using partial sintering of coarse powders [12]. Our approach to introduce porosity in our thermoplastic feedstocks is using large pyrolyzable pore formers, combined with fine ceramic particles of high sintering activity. This allows co-sintering of the tubes with deposited thin films containing powders of similar sintering activity, without shrinkage mismatch between the layers [13]. For this, at least 15% linear shrinkage in the support tube is desired during sintering. The selected pore formers should be as isometric as possible, since anisometric pore formers will be aligned with the extrusion direction [14,15], and limit the desired pore connectivity in the radial direction. The high polymer content in thermoplastic feedstocks also limits the choice of pore formers; a completely polymer-based pore former might not be suitable due to the large gas volume developed if the pore former decomposes in the temperature range of the thermoplastic polymers. Furthermore, the introduction of the pore former should not compromise the feedstock's plasticity and extrudability. Previous work has shown that thermoplastic feedstocks with up to 20 vol% graphite pore former could be extruded, yielding MgO support tubes with 42.5% porosity and 4.7×10^{-16} m^2 gas permeability [9]. Pore former volumes up to 27 vol% was possible by combining spherical polymethyl methacrylate (PMMA) and graphite pore formers, increasing the gas permeability to $4.5 * 10^{-15}$ m^2 for MgO, but only demonstrated with small disc samples [16]. This work continues exploring this combination of PMMA and spherical type of graphite as pore formers in thermoplastic feedstocks, but now for extrusion of porous 3Y-TZP ($(Y_2O_3)_{0.03}(ZrO_2)_{0.97}$) tubes. This composition was chosen due to its transformation toughening mechanism, which should provide a support with high fracture resistance. We show how the pore former type and content – as well as the size of the 3Y-TZP powder and the sintering temperature – affect the microstructure and gas permeability.

2. Experimental

2.1. Thermoplastic feedstock preparation

Thermoplastic feedstocks were prepared with different amounts of ceramic powder, polymer and pore formers as shown in Fig. 1. The ceramic powder was $(Y_2O_3)_{0.03}(ZrO_2)_{0.97}$ (3Y-TZP) (40 nm primary particle size, product TZ-3Y-E, Tosoh, Japan) coated with 5.36 wt% stearic acid (Sigma-Aldrich, USA) as a surfactant. The stearic acid amount was calculated [17,18] to provide 1.5 monolayer coverage for sufficient wetting without excess stearic acid. For one feedstock, a slightly coarser 3Y-TZP powder (90 nm primary particle size, product TZ-3YS-E, Tosoh, Japan) was used. The polymer system, based on thermoplastic feedstocks for injection moulding [19], consisted of an ethylene-vinyl acetate copolymer (Elvax© 250, DuPont, USA) as the main binder and paraffin wax (melting point 53–57 °C, Sigma-Aldrich, USA) as a secondary binder/lubricant, always in the volume ratio 2:1. The pore former consisted of graphite and/or polymethyl methacrylate (PMMA), both shown in Fig. 1. The graphite was a "spherical" type with d_{V50} of 18 μm (FormulaBT SLA1518, Superior Graphite, USA), the PMMA a cross-linked (to avoid softening prior to decomposition) and polydisperse type with a d_{V50} of 9 μm (MR-10G, Esprix, USA).

Warm pressing has previously been found to provide similar microstructure as extrusion for thermoplastic feedstocks [8], and was therefore used as an initial shaping method during the screening of a large number of feedstocks. Feedstocks of 55 ml were mixed and compounded at 110–115 °C (Kneader 50N, Brabender, Germany), warm pressed to 1–2 mm thickness and cut into 24 mm diameter discs. A few selected batches (presented in Section 3.5) were scaled up to 500 ml in a larger kneader (Type BK20, Linden, Germany) and extruded into tubes (14 mm outer diameter, 1 mm thickness, length > 300 mm) at 110 °C using a single screw extruder (Model 19/20DN, Brabender, Germany). Sintering of all samples was performed in air with a slow heating rate to avoid binder and pore former decomposition defects: 10 °C/h to 250 °C (2 h hold), 10 °C/h to 400 °C (2 h hold), 10 °C/h to 650 °C (2 h hold), 30 °C/h to the sintering temperature (1250–1400 °C) (2 h hold) and finally cooling at 100 °C/h.

All samples are named as "composition" (vol% pore former/vol% ceramic/vol% polymers)-"pore former" (G for graphite, P for PMMA, GP for both (volume ratio 2:1 unless otherwise stated))-"sintering temperature" (°C). For example, sample 40/25/35-GP-1300 has the overall composition 40 vol% pore former, 25 vol% 3Y-TZP powder and 35 vol% polymers, the pore formers are graphite and PMMA in the ratio 2:1, and is sintered at 1300 °C. The coarser 3Y-TZP powder is used in samples marked with a "c" at the end, e.g. 40/25/35-GP-1300-c.

2.2. Characterization

Dimensions and weight of green and sintered samples were used to calculate the total density/porosity relative to the theoretical density of each green feedstock or 3Y-TZP, as well as the linear shrinkage after sintering. Hg porosimetry (Poremaster© GT, Quantachrome Instruments, USA) was used to measure open porosity and pore size distribution of sintered samples. The microstructure of polished sample cross-sections was studied by SEM (TM 3000, Hitachi, Japan). The gas flow through the samples upon application of a pressure gradient was used to calculate the Darcy gas permeability coefficient, k:

$$k = \frac{j\mu}{\nabla p}, \tag{2}$$

where j is the gas flux [$m^3/m^2\,s$], μ [Pa s] is the viscosity of the gas, and ∇p is the pressure gradient over the sample [Pa/m]. The measurements were performed with N_2 at room temperature and a total pressure difference of 200 kPa.

3. Results and discussion

For all samples the shrinkage, porosity, pore size, gas permeability and the torque during compounding are summarized in Table A1 in the Appendix A. The general observed trends within all the studied samples will be presented in the following subsections.

3.1. Influence of amount of pore former on 3Y-TZP support properties

Starting with the previously tested [16] 2:1 mixture of graphite and PMMA as the pore former, we first tried to optimize the relative amounts of 3Y-TZP powder, thermoplastic polymers and pore former in the feedstocks. The feedstock should contain enough pore formers for sufficient porosity, and at the same time enough polymers to provide defect-free and form-stable tubes. Several feedstocks with different amounts of pore formers (PMMA and graphite), 3Y-TZP powder and thermoplasts were studied (green crosses in Fig. 1). The torque during kneading, indicative of the feedstock's viscosity, generally increased with the pore former content (Table A1), but none of the feedstocks appeared too low in plasticity for extrusion (causing too high torque or pressure for the extruder). On the other hand, an upper limit for the polymer content was identified to be between 35 and 42 vol%, since feedstock 23/35/42-GP with 42 vol% polymer appeared too low in viscosity (torque 2.5 Nm)

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