Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 2173–2185

www.elsevier.com/locate/jeurceramsoc

Fabrication and characterisation of cellular alumina articles produced via radiation curable dispersions

Judit Wilkens-Heinecke [a,b], Yoram de Hazan [a,*], Sascha Populoh [c], Christos G. Aneziris [b], Thomas Graule [a,b]

[a] *Laboratory for High Performance Ceramics, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*
[b] *Institute of Ceramic, Glass and Construction Materials, TU Bergakademie Freiberg, Germany*
[c] *Laboratory for Solid State Chemistry and Catalysis, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*

Received 22 August 2011; received in revised form 25 January 2012; accepted 12 February 2012
Available online 8 March 2012

Abstract

A general and versatile method for the production of cellular materials from radiation curable solvent-free colloidal ceramic dispersions containing pore formers has been developed. By this technique cellular ceramic articles with a precisely controlled porosity, cell size and shape are obtained for compositions containing solid pore formers. Monolithic bulk samples are obtained by thermal curing, whereas thin films and multi-layered articles are advantageously produced by UV curing. In this work the influence of three different spherical pore former types, PE, PS and PMMA, on the processing and final properties of the porous materials using alumina as model material is studied. The effect of pore former type and concentration on rheology, curing behaviour, debinding and sintering steps as well as thermal conductivity and mechanical strength of the sintered cellular materials is presented. It is also shown that the choice of pore former type modifies the sintering behaviour and resulting properties.

Keywords: Al_2O_3; Photopolymerisation; Porosity; Thermal conductivity; Mechanical properties

1. Introduction

Cellular ceramics are used in a broad range of engineering applications such as filters for molten metals or particles in gas streams,[1–3] in catalysis and separation,[4] as load-bearing lightweight structures or for thermal and acoustic insulation applications.[3] Most of these applications have rather strict requirements in terms of the morphology, e.g. cell size, cell window size and interconnectivity between the cells, and total porosity. These can be achieved by selection of an appropriate fabrication method. A wide range of fabrication methods were developed in the past.[1,5,6] Three different major approaches can be differentiated: ceramic foams produced by the replication of a sacrificial foam template,[7] direct foaming of a liquid slurry[6,8] or burn-out of fugitive pore former.[9–12] A wide range of fugitive pore formers are available and have been investigated, such as starch,[9–12] wax,[13] polymer beads,[14] saw dust and carbon.[15] In this paper the production of alumina (Al_2O_3) foams by the burn-out of polymeric beads will be presented. Given a suitable ceramic feedstock, the pore size and shape replicated in the final cellular ceramic can be controlled by the characteristics of the pore forming agents.

It is found that such cellular articles can be obtained with a feedstock consisting of a solvent-free, high loaded (with simultaneously low viscosity), radiation curable alumina dispersion containing solid polymer beads.[16] Curing of these compositions can be performed by thermal or UV–vis radiation. Alumina is in this paper used as a model material to demonstrate the process, but also other porous materials like hematite, titania and hydroxyapatite can be produced by this technique.[16,17] Likewise the polymer beads used in this study are used as a model material to demonstrate the good reproduction of size and shape of the pore formers. Depending on the final application, different pore formers with a wide variety of shape and size could be also used. Shaping the compositions by UV curing offers

Abbreviations: PF, pore former; PE, polyethylene; PS, polystyrene; PMMA, poly(methyl methacrylate); RT, room temperature; NPC, nominal pore former content; TSL, total solid loading.

* Corresponding author. Tel.: +41 0 433059168; fax: +41 0 433059168.
E-mail addresses: judit_heinecke@gmx.de (J. Wilkens-Heinecke), ydehazan@gmail.com, ydehazan@bluewin.ch (Y. de Hazan).

0955-2219/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2012.02.014

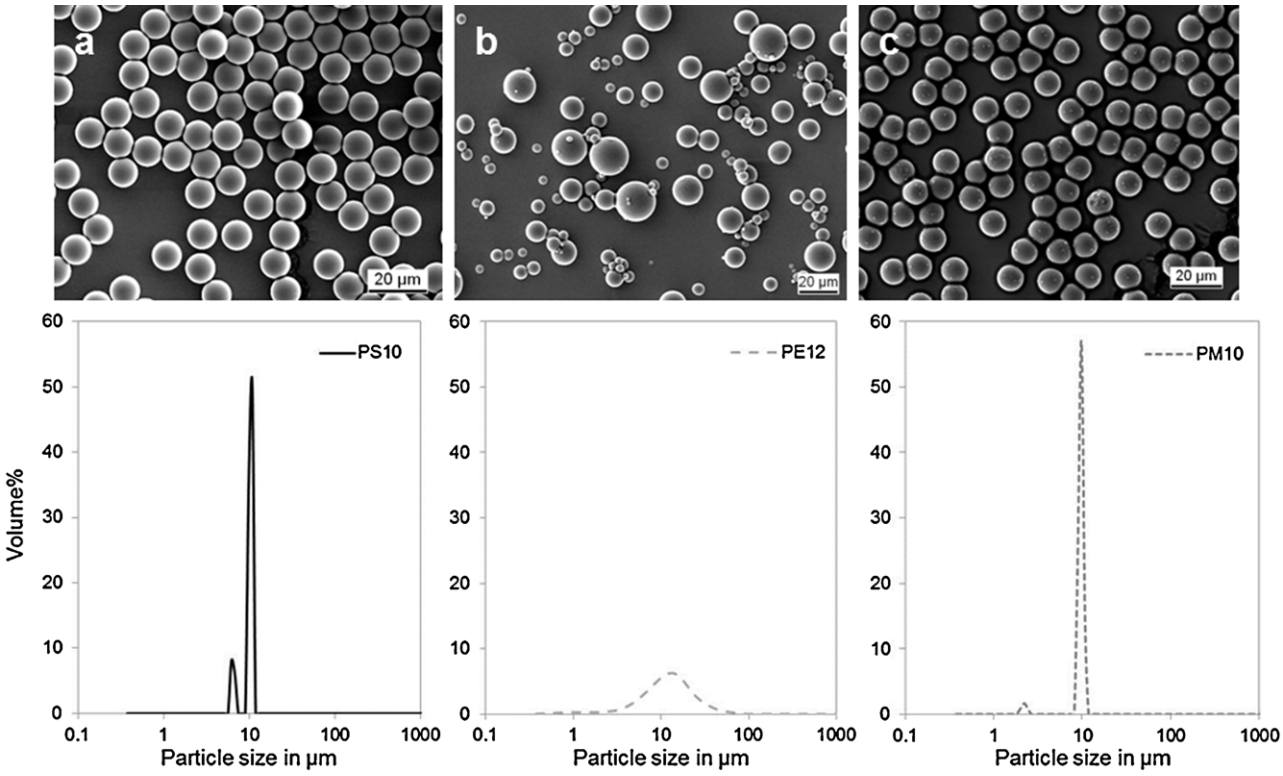

Fig. 1. SEM images and measurement of particle size distribution of pore formers used in this work: PS10 (a), PE12 (b), PM10 (c).

the possibility to lithographically pattern the pastes, similar to rapid prototyping/manufacturing.[18] By this near net-shape solidification method, which relies on solvent free dispersions and solid pore formers, complex cured samples can be obtained without stresses, due to low overall shrinkage.[18,19] Another advantage offered by UV curing of such pastes is the fast multi-layer shaping process, where in several minutes a shaped, solidified article is obtained at ambient conditions. Since no diluent is used, the interface between two cured layers is of high quality, which minimises defects, cracks and delamination. Nevertheless, shrinkage or deformation can still occur during the debinding process, therefore crosslinking of the matrix is necessary for shape retention during debinding.

The presented technique allows the production of cellular materials in a variety of shapes and with well-controlled cell morphology. In this paper the effect of different pore former types and concentration on the paste properties, shaping, the debinding and sintering processes is presented. The influence of pore formers on the resulting cell morphology, microstructure as well as mechanical and thermal properties is discussed.

2. Experimental

2.1. Materials

In this study TM-DAR (short TM), α-Al_2O_3 obtained from Taimei Chemicals Co., Ltd., Japan, was used. This powder has a mean particle size of 150 nm (according to measurements of particle size distribution by static laser light scattering with LS230, Beckman Coulter), a density of 3.98 g/cm^3 and a specific surface area of 12.5 m^2/g, measured by BET method with SA3100 (Beckman Coulter, USA). The alumina particles were sterically stabilised with MelPers4343 (MP), a commercial comb-shaped surfactant obtained from BASF, Germany.[20] This surfactant has a low charge density polycarboxylate backbone, polyether side-chain of 500 g/mole and a molecular weight of 20,000 g/mole. 4.5 wt.% per weight of alumina particle was used in this study for the stabilisation.

As UV curable media a mixture of 4-hydroxybutylacrylate (4-HBA; purity > 94%; from BASF, Germany) and poly(ethylene glycol) 200 diacrylate (PEG200DA; from Rahn, Switzerland) was used. This monomer mixture was used without any solvents or diluents and was mixed in the ratio 14:1 (4-HBA: PEG200DA). Chemical structures of the used monomers and also the photoinitiator LTM were already reported by Wozniak et al.[21]

Three different types of spherical polymer microbeads were used as pore forming agents (short PF), presented in Fig. 1. From Sumitomo Seika Chemicals Co., Ltd., Japan FLO-BEADS CL-2080 were obtained. These are polyethylene beads with a mean particle size of 12 µm (short PE12), a density of 0.92 g/cm^3 and a refractive index of 1.51. The second type of pore former were poly(methyl methacrylate) (Spheromers CA10) beads from Microbeads AS, Norway with a mean size of 10 µm (short PM10), density of 1.2 g/cm^3 and refractive index of 1.489 (non-cross-linked PMMA). PMMA beads are cross-linked and can contain up to 3% crosslinking agent which may increase its index of refraction. Polystyrene (PS) beads from Microbeads AS, Norway were the third type of used pore formers. They have a mean size of 10 µm and 40 µm (short PS10 respectively