Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 9045–9053

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effects of processing parameters on cellular ceramics obtained by paraffin emulsified suspensions

M.F. Sanches[a,c], N. Vitorino[a], J.C.C. Abrantes[a,b,*], J.R. Frade[a], J.B. Rodrigues Neto[c], D. Hotza[c]

[a]Department of Materials and Ceramic Engineering, CICECO, University of Aveiro, 3810 Aveiro, Portugal
[b]UIDM, ESTG, Polytechnic Institute of Viana do Castelo, 4900-348 Viana do Castelo, Portugal
[c]Graduate Programme of Materials Science and Engineering (PGMAT), Federal University of Santa Catarina (UFSC), Brazil

Received 16 July 2013; received in revised form 20 December 2013; accepted 25 January 2014
Available online 31 January 2014

Abstract

Cellular ceramics were processed by emulsification of alumina suspensions with melted paraffin. Stabilization upon drying was promoted by collagen additions and solidification of the paraffin droplets. Consolidation allows easy elimination of the paraffin droplets on heating at relatively low rate (1–5 °C min^{-1}), with a plateau at 200 °C, and then heating up to the firing temperature (1550 °C). A Taguchi plan was used to assess the relative impact of solids loading, paraffin to suspension volume ratio, ultrasound stirring time and heating rate on microstructural features of sintered bodies. Increasing solids loading suppresses the cellular size, with negative impact on total porosity, whereas increasing paraffin: suspension volume ratio contributes to enhance porosity with a slight increase in average cellular size. Ultrasound stirring yields a slight decrease in porosity and also average cellular size. The heating schedule in the early stages of paraffin elimination contributes to changes in cellular size distribution, with important effects on compressive strength.

Keywords: Cellular ceramics; Taguchi planning; Emulsification; Paraffin; Collagen consolidation

1. Introduction

Highly porous ceramics, mainly with cellular microstructures, have a wide variety of potential applications due to unique properties such as low density, high permeability, high specific area, low thermal conductivity and high thermal shock resistance, without undue effect on refractoriness or chemical resistance to harsh conditions [1]. Suitability for specific applications depends on total porosity and/or specific surface area, and possibly also on other microstructural features such as cellular size distribution, cellular shape, thickness of cell walls, size of interconnecting windows, as well as the ability to retain sufficient mechanical strength. Cellular ceramics with closed cells are suitable for thermal isolation whereas open cells are needed for filtration and many applications which require permeability to fluids. This variety of properties is highly dependent on processing methods and corresponding conditions [2]. Processing may also determine cost, reproducibility of microstructural features, related properties, and environmental impact.

Processing is, thus, a key factor for increasing the relevance and applicability of cellular ceramics in many technological fields [3–7], and highly porous ceramics have been prepared with average grain sizes from the micrometer to the millimeter range [2,8]. Changes in specific area were also achieved with a variety of pore formers [2,7,9] dispersed in the continuous green ceramic matrix. Representative examples of pore formers are polymeric spheres, fibers, natural seeds, starch, and carbon black [7,10], that are eliminated under controlled heat treatment. Combinations of different pore formers can also be used for gradient materials [2,11].

Microstructural characteristics of highly porous cellular ceramics can be adjusted by replication, based on geometric characteristics of pore formers, as well as foaming [12,13], gelcasting [14], emulsification of ceramics suspensions with

*Corresponding author at: UIDM, ESTG, Polytechnic Institute of Viana do Castelo, 4900-348 Viana do Castelo, Portugal. Tel.: +351 258 819 700; fax: +351 258 827 636.
E-mail addresses: marisanches85@gmail.com (M.F. Sanches), nuno.vitorino@ua.pt (N. Vitorino), jabrantes@estg.ipvc.pt (J.C.C. Abrantes), jfrade@ua.pt (J.R. Frade), jbrn.ufsc@gmail.com (J.B. Rodrigues Neto), dhotza@gmail.com (D. Hotza).

0272-8842/$ - see front matter © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2014.01.117

volatile alkanes [15] or melted paraffin [16]. Replication methods were reported by different authors, often based on impregnation of a polymeric sponge (typically polyurethane) with ceramic suspension [7,17,18]. The organic sponge is eliminated by heating at low rate, usually $< 1\ ^{\circ}C\ min^{-1}$, to ensure slow decomposition of the polymeric support, and to allow the escape of huge volumes of resulting gases, without undue stresses and risks of flaws or collapse of the green cellular ceramics [19]. High surface area combined with high permeability may be key requirements for important applications, such as catalysis [20].

Direct foaming is based on incorporation of bubbles and consolidation of the foamed system, followed by high temperature sintering [2,7], to yield cellular ceramics with closed or open cells, without excessive impact on mechanical strength. Windows connecting the open cells are needed to adjust the permeability of resulting cellular ceramics to fluids. Foaming can be performed by injection of a suitable gas, or addition of a volatile liquid as a bubble former.

Processing methods based on emulsification are highly dependent on interfacial energy between the immiscible components of the emulsified system, which cause thermodynamic instability. Thus, tensioactive agents such as surfactants, proteins, or other anfifilic additives are used to suppress the interfacial energy [17,21,22]. The hydrophilic:lipofilic ratio must be high to ensure that the ceramic suspension forms the continuous phase, as for oil in water emulsions [23].

Microstructural features of cellular ceramics obtained by emulsification of ceramic suspensions are also dependent on the volume ratio of continuous to disperse phases, stirring rate and on viscosity of continuous aqueous suspension [13,24], as predicted for the relevant conditions leading to rupture of the elongated discontinuous droplets. When the interfacial stress $2\gamma/D$ becomes smaller than shear stress $\eta_c v_s$ [15], where γ is the interfacial energy, D is the droplet size, v_s is the shear rate, and η_c is the viscosity of the continuous phase, i.e., the ceramic suspension; this yields:

$$D \propto \frac{\gamma}{\eta_c \nu_s} \tag{1}$$

Viscosity of the continuous aqueous suspension can be adjusted by controlling several factors, with emphasis on addition of dispersing agents, consolidation additives, and solid load. Collagen may exert a combination of tensioactive and consolidation effects [24]. Solids loading is most likely to affect mainly the viscosity of ceramic suspensions, as described by the classical Krieger–Dougherty equation [25]:

$$\eta_r = (1-\phi/\phi_m)^{-n} \tag{2}$$

where η_r is relative viscosity, ϕ is the volume fraction of solids, and ϕ_m and n are fitting parameters. The critical solids loading parameter ϕ_m is relatively high in alumina suspensions, i.e., in the order of 0.61 [25].

Solids loading may also affect subsequent steps of drying and elimination of the organic phase in the early stages of heat treatment. These steps must be controlled to avoid risks of collapse on heating the resulting green cellular ceramic ceramics.

The stability of emulsified or foamed suspensions may be significantly different from the corresponding oil in water emulsion, mainly if one considers the effects of nanometric powders or colloidal particles adsorbing at liquid/gas or liquid/liquid interfaces [26,27], with impact on interfacial energy [28,29]. For example, a very high energy of attachment of particles at liquid-gas interfaces (relative to thermal energy kT) may yield irreversible adsorption [30].

Mechanical stirring is most commonly used to obtain emulsified ceramic suspensions, and there is clear evidence that droplet size decreases with an increase in stirring rate [15,24], as predicted by Eq. (1). However, the emulsified suspensions may become unstable for excessive stirring rates.

Ultrasonic emulsification may also be considered to lower oil droplet sizes [31], and to minimize the incorporation of air bubbles, or to promote degassing. Sonication is easily implemented in an ultrasound bath or by inserting a transducer sonotrope in the emulsion, mainly for small emulsion volumes, to ensure uniformity at short distances from the sonotrope. Ultrasonic effects may combine an initial disruption of relatively large droplets (in the order of 0.1 mm), due to instable waves acting at the water–oil interface [32], and disruption into much finer droplets by cavitation in the continuous aqueous phase [33].

Emulsions obtained by sonication still show the expected effects of viscosity and interfacial energy on droplet size [34], and oil droplet size is expected to decrease with increasing ultrasound input energy, i.e., increasing power or increasing sonication time. However, this trend may be reverted with excessive input energy [33]. The input energy may be insufficient to counter the effects of coalescence mainly when high volume fractions of the dispersed oil phase are used. In addition, instable interfacial waves may not function on very viscous media, thus requiring an initial stage of pre-mixing. This may be the case for emulsified suspensions with very high solids loadings or when adding consolidating agents, such as collagen.

In a previous work [16] one assessed the roles of addition of collagen and different contents of defloculant to change viscosity. The main objective of the present work is, to explore other factors such as paraffin:suspension volume ratio (p) and solids loading (s), for their expected effects on viscosity ratio with direct impact on cell size (Eq. (1)), combined with additional effects of sonication time, to assess if increasing energy contributes to decrease droplet sizes, and also to changes in heating rate during the initial stage of heat treatment, when elimination of paraffin may still exert changes in the green ceramic bodies. However, one should seek a suitable planning to assess the contributions of these factors, without excessive experimental effort. The Taguchi method meets this requirement of a systematic approach for experimental optimization to seek enhanced quality with a minimum number of experiments [35,36]. The method is based on designed orthogonal arrays to evaluate the relative impact of two or more variables on characteristics of a particular product or process.

2. Materials and methods

A Taguchi plan was used to study the ability to adjust microstructural characteristics of cellular ceramics, by varying