



Cellular ceramics processed by paraffin emulsified suspensions with collagen consolidation

Nuno Vitorino^a, João C.C. Abrantes^{a,b,*}, Jorge R. Frade^a

^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

ARTICLE INFO

Article history:

Received 15 December 2012

Accepted 9 February 2013

Available online 16 February 2013

Keywords:

Cellular ceramics

Alumina

Emulsification

Paraffin

Collagen consolidation

Interconnectivity

ABSTRACT

Cellular ceramics were prepared by emulsification of liquid paraffin in aqueous alumina suspensions, with sodium lauryl sulphate as a surfactant, and with or without collagen as a suspension shape stabilizer. Solidification of the paraffin droplets halts coarsening of this dispersed phase, and collagen-based gelling facilitates drying without coarsening of organic droplets and their subsequent thermal elimination without collapse of the green ceramic skeleton. Firing at 1550 °C, for 2 h, yielded the expected cellular ceramics. Cellular cell sizes and other microstructural features were changed by modifications in emulsification, namely addition of collagen and additions of defloculant, to adjust viscosity. These factors also play important effects on interconnectivity of cells.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Highly porous ceramics find applications in a wide variety of technologies such as filters for hot liquids or gases, supports for catalysts, bioreactors, biomaterials, porous supports for batteries or fuel cells, etc. The performance of these applications usually depends on specific requirements in terms of pore sizes, their distribution and connectivity, and often also thermal shock resistance, refractoriness, resistance to hot liquids or reactive gases, etc. [1,2]. Cellular materials with closed cells are required for thermal isolation whereas filters require high cellular connectivity for suitable permeability. Bimodal porosity may be needed for other prospective applications such as fixed-bed catalysts or active biomaterials, requiring high activity and permeation of fluids. These microstructural characteristics depend on processing [2]. Processing costs, flexibility and reproducibility of relevant parameters are, thus, key factors to extensive applications of cellular ceramics in many strategic technologies [3–6].

Processing routes for cellular ceramics often start from ceramic powder slurries, which are transformed to solid ceramic foams by a suitable method, with emphasis on:

- (i) infiltration of a reticulated polymeric sponge or replica, which is then pyrolysed before high temperature consolidation of the resulting cellular ceramics [7,8];

- (ii) gel casting, in which a ceramic suspension is foamed by adding a suitable agent under mechanical action [9,10];
- (iii) coating of different organic or polymeric shapes with ceramic slurry to yield hollow beads or bulk macroporous bodies [11];
- (iv) emulsification of a ceramic suspensions with a volatile organic liquid, followed by its slow evaporation [12].

In the present work one proposes an alternative method based on emulsification of a ceramic suspension with a suitable paraffin, at temperatures well above room temperature and below boiling of water; this adds flexibility to subsequent steps of stabilization of the emulsified system, drying of the ceramic suspension and corresponding consolidation at temperatures below the melting point of paraffin. The resulting self-supported body can be reheated to a plateau temperature well below the boiling point of the paraffin and below self-ignition, to allow its slow elimination without disruption of the green body, and subsequent firing to obtain the resulting cellular ceramics.

2. Methods

Alumina suspension (Alcoa CT3000) with 50% vol. of solids content was stabilized at viscosity ≈ 600 cP, using Dolapix PC – 67 (10% vol.) as dispersion agent. This was combined with paraffin (Merck 1.07337.2500), with reported melting temperature ≈ 58 °C, to form emulsion with dispersed paraffin droplets. The paraffin was melted at 80 °C, prior to addition of the alumina suspension in volume ratio paraffin:suspension=2:1, followed addition of an anionic surfactant (sodium lauryl sulphate, Sigma-Aldrich L-6026) as emulsification agent (6% related to the

* 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: nuno.vitorino@ua.pt (N. Vitorino), jabrantestg@estg.ipv.pt (J.C.C. Abrantes), jfrade@ua.pt (J.R. Frade).

emulsion volume), with or without simultaneous addition of collagen (OXOID LP0008) as a potential shape stabilizer. Emulsification was promoted by mechanical stirring at 1000 rpm for 10 min, while maintaining temperature at 80 °C, to avoid solidification of the paraffin. Further additions of Dolapix were used to lower the viscosity of the ceramic suspension, with corresponding effects on emulsification and microstructural features of resulting cellular ceramics. Viscosity of ceramic suspensions and corresponding suspension-paraffin emulsions was measured by a Sheen ERV8 Brookfield viscometer.

The resulting emulsion was cooled to room temperature, for 24 h, to promote solidification of isolated paraffin droplets and to induce gelling of the surrounding ceramic suspension containing collagen. These samples were dried slowly for 3 days, at ≈ 50 °C, below the melting point of paraffin, to prevent coarsening of the dispersed paraffin droplets during the drying step. One sample was dried at 80 °C, to demonstrate main differences between drying at temperatures below and above the melting point of paraffin.

The thermal cycle was programmed to allow non-disruptive elimination of the paraffin, based on simultaneous differential thermal analysis (DTA) and thermogravimetry (TGA) (Netzsch STA 409EP). The first endothermic peak in Fig. 1A (≈ 63 °C) is observed near the expected melting point of the paraffin phase, and a broad exothermic contributions in the range 250–450 °C with simultaneous weight losses can be ascribed to elimination of the paraffin; this was confirmed by DTA/TGA results for paraffin. The earlier steps of heat treatment were, thus, programmed to ensure slow heating (2 °C min^{-1}) from room temperature up to 200 °C, followed by one isothermal plateau at 200 °C for 3 h. Low heating rate (2 °C min^{-1}) was also used for up to 500 °C, when nearly complete weight losses are expected, and the sample was then heated at 5 °C min^{-1} to the final sintering temperature (1550 °C), and kept at this temperature for 2 h. This thermal treatment minimizes risks of disruption by sudden release of gases, and yields the intended cellular ceramics. Note also that the actual conditions may be easily modified to promote slow volatilization of the liquid paraffin rather than exothermic combustion. It suffices to replace the actual air atmosphere by a suitable inert atmosphere, such as N_2 or CO_2 , possibly performed at lower heating rate, to allow slow volatilization before reaching the boiling temperature, as illustrated in Fig. 1B. Therefore, the actual method should also be suitable for recycling the paraffin by volatilization and condensation.

Scanning electron microscopy (SEM – Hitachi SU1510) was used to confirm the cellular microstructures, and to examine other microstructural features such as connectivity between

individual cells. Stereology [13] was used to determine cell size distributions and average size (Table 1). The Archimedes method [14] was used to obtain information on open (x_o) and total porosity (x_t). Prismatic samples with length:width ratio of 2:1 were used for compressive mechanical strength testing (Lloyd LR30K), with cross head speed of 15 mm min^{-1} . Ten samples were used to determine the mechanical strength of sample D1C, and to evaluate its standard deviations (≈ 3 MPa). The remaining samples were screened with sets of four samples to confirm that compressive strength was also within an acceptable range.

Overall assessment of constrictions to percolation between adjacent cells was estimated by impedance spectroscopy measurements, after impregnation of the cellular ceramics with a collagen solution, gelatin. Major differences in electrical conductivity between gelatin and alumina allow one to trace current constrictions between adjacent cells, by analogy with the a method proposed by Moreira et al. [15]. The impregnating gelatin was prepared with a typical 5:100 weight ratio, by heating at 50 °C for 10 min, to obtain a liquid gelatin, suitable for impregnation of cellular ceramic samples. These impregnated samples were cooled to room temperature, to promote gelling, and Al foil were used as electrodes to obtain impedance spectra in the frequency range 20– 10^6 Hz; this allows de-convolution of contributions ascribed to the samples and to electrode processes, based on differences in relaxation frequencies.

3. Results and discussion

Fig. 2 shows a good distribution of dispersed paraffin droplets within a continuous green ceramic skeleton, obtained by solidification of the paraffin phase, collagen consolidation, and then drying at temperatures below the melting point of paraffin. Previous

Table 1

Preparation conditions for paraffin emulsified suspensions, and corresponding cell size D , open porosity x_o , total porosity x_t , constriction factor f_c and s_c compressive mechanical strength. V_d/V_e denotes defoluculant to emulsion volume ratio, Col, collagen content and h , the absolute viscosity.

Samples	Preparation			Results				
	V_d/V_e	Col. (wt%)	η (Pa s)	D (μm)	x_o	x_t	f_c	σ_c (MPa)
D0	0	0	2.9	57.3	0.67	0.68	0.112	38.7
D0C	0	5	19.0	16.5	0.66	0.67	0.023	23.0
D1C	1/30	5	7.0	17.4	0.69	0.71	0.085	21.8
D2C	2/30	5	6.1	17.9	0.71	0.73	0.094	19.4
D3C	3/30	5	5.2	19.3	0.73	0.73	0.251	14.5

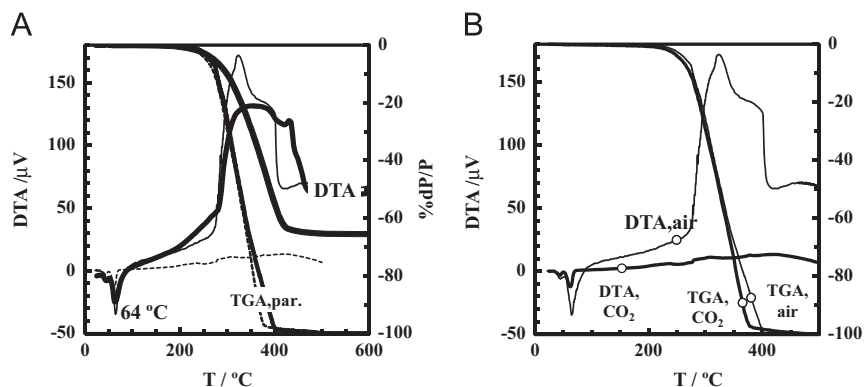


Fig. 1. Differential thermal analyses and thermogravimetry of pure paraffin wax (thin line) and sample D0 (broad line), at 5 °C min^{-1} and in air (A), and corresponding thermal analyses for paraffin performed under CO_2 atmosphere, at 1 °C/min (B).

Download English Version:

<https://daneshyari.com/en/article/1645467>

Download Persian Version:

<https://daneshyari.com/article/1645467>

[Daneshyari.com](https://daneshyari.com)