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Research paper

Extrusion of ceramic emulsions: Preparation and characterization of cellular ceramics

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ABSTRACT

Recently, much effort has been given to development and/or optimization of porous materials with requirements for intended applications in catalysis, filtration, isolation, etc. In this context, this paper presents processing conditions and the correspondent characterization of cellular ceramics processed by extrusion of ceramic emulsions, obtained by emulsification of red clay, kaolin and alumina suspensions, after sintering at different temperatures. The emulsification of the ceramic suspension in paraffin with a melting point higher than room temperature is the key for the success of this processing method due to the freezing of the organic droplets allowing good stability of matrix during the extrusion process. Experimental results show good microstructural stability, yielding cellular ceramics with mechanical strength up to 30 MPa, permeability up to 3×10^{-4} m s^{-1}, and thermal conductivity lower than 0.25 W m^{-1} K^{-1}, framed with mentioned applications.

1. Introduction

Cellular ceramics have been extensively studied due to their specific properties such as high permeability, low relative density, high specific area, low thermal conductivity and high thermal shock resistance. These properties are strongly dependent on microstructural features, namely porosity, shape, average cell size and size distribution, wall thickness and also connectivity between the cells (Acchar et al., 2008; Vitorino et al., 2013a), Table 1. According to their properties, cellular ceramics can be framed with specific applications like filters for hot liquids or gases, supports for catalysts, bioreactors, biomaterials, porous supports for batteries, fuel cells, etc. (Han et al., 2003a, 2003b; Vitorino et al., 2013a; Sanches et al., 2014).

The diversity of microstructural features is highly dependent on the preparation conditions used for cellular ceramics production (Studart et al., 2006). In this context, several strategies were proposed to prepare these materials, including: i) replication (Acchar et al., 2008; Nor et al., 2008), gel casting (Sepulveda and Binner, 1999; Bartuli et al., 2009; Luyten et al., 2009), emulsification of ceramics suspensions with volatile alkanes (Barg et al., 2009) or in melted paraffin (Vitorino et al., 2013a; Sanches et al., 2014), and correspondent processing methods such as tape casting, slip casting, gel casting, spin coating, extrusion or even screen printing (Isobe et al., 2006; Sarkar et al., 2012; Sanches et al., 2014).

Extrusion is a unitary operation widely used in industry (ceramics, metal, food, etc.), allowing large scale production of regular shapes with constant cross section such as tubes or rods, bricks, etc. (Ribeiro et al., 2005). However, the success of this operation is dependent on the plasticity of the material to be extruded, i.e. the material ability to be deformed without rupture, through the application of stress, and to retain the deformation, when stress is removed or reduced (Ribeiro et al., 2006). The role of plasticity on extrusion is well known (Andrade et al., 2011) and this property may be assessed by stress-deformation curves obtained by compression of extruded bodies. This method allows one to know, for each paste with a specific humidity, the stress required for plastic deformation and the amplitude of the plastic zone, i.e., the maximum deformation without cracking or other macroscopic defects in the extruded bodies (Vitorino et al., 2014, 2015).

In a recent work one evaluated the plastic behaviour of ceramic emulsions prepared by emulsification of ceramic suspensions in melted paraffin, in order to obtain some insights for upscaling, and concluded that the combination of emulsification of ceramic suspensions in melted paraffin with extrusion is a suitable strategy to produce cellular porous ceramic materials in a large scale with constant cross section (Vitorino et al., 2014).

The extrudability of ceramic emulsions has already been assessed in previous works. Nevertheless, some physical properties are mandatory

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Table 1
Summary of properties range typical from porous ceramics.

Property	Range	Reference
Cavity size, *D*	3–300 μm	(Sepulveda and Binner, 1999; Barg et al., 2009)
Compression mechanical strength, σ_c	<65 MPa	(Barg et al., 2009)
Flexural mechanical strength, σ_f	<30 MPa	(Sepulveda and Binner, 1999; Bartuli et al., 2009; Sarkar et al., 2012)
Porosity, *P*	45–95%	(Peng et al., 2000; Khattab et al., 2012)
Gas permeability	10^{-11}–10^{-14} m^2	(Innocentini et al., 2009)
Liquid permeability, α	10^{-4}–10^{-5} m s^{-1}	(Belouatek et al., 2008; Sarkar et al., 2012; Lee and Koo, 2014)
Thermal conductivity (20 °C), k	0.05–0.23 W m^{-1} K^{-1}	(Lo et al., 2011; Bourret et al., 2013)

from the application point of view. Thus, the purpose of this work is to take advantage of extrusion of emulsified suspensions of red clay, kaolin and alumina, emulsified with paraffin, to process ceramic materials with high porosity and corresponding permeability to gases and liquids based on the requirements of representative applications.

2. Materials and methods

2.1. Ceramic emulsion: preparation

Emulsified ceramic suspensions of natural red clay, natural kaolin and alumina (Alcoa CT3000) were prepared based on a methodology presented in previous works (Vitorino et al., 2013a; Sanches et al., 2014; Vitorino et al., 2014), and used to extrude cellular ceramic green bodies. The methodology was based on ceramic suspensions with solid load 50% vol., stabilized with Dolapix PC-67 (chemical basis: polycarboxylic acid and sodium salt), and emulsified in melted paraffin, under mechanical stirring (10 min at 1000 rpm).

2.2. Ceramic emulsion: extrusion

The emulsions were extruded through a cylindrical die (8 mm diameter) to obtain rods using a screw extruder (Netzsch, model 250.05), with 5 cm s^{-1} of extrudate velocity to ensure high (internal die) pressures during the extrusion process.

2.3. Consolidation of extruded green bodies

According to our previous works (Vitorino et al., 2013a; Sanches et al., 2014), the extruded rods were dried during 48 h at room temperature, and then consolidated in two steps. Elimination of organic phases was performed on heating at 2 °C min^{-1} until 200 °C, with a 2 h of dwell time at this temperature, followed by heating at 2 °C min^{-1} in the temperature interval of 200–500 °C, and then at 5 °C min^{-1} on heating from 500 °C to the upper firing temperatures shown in Table 2, with a final 2 h plateau for consolidation of the cellular ceramics.

2.4. Characterization of cellular ceramics

The assessment of prepared cellular materials was based on mechanical, physical and microstructural characterization. Average cell size measurements were performed by stereological analysis (Abrantes, 2001), based on scanning electron microstructures (Hitachi SU 1510), using three microstructures per sample, with 100 measurement lines per microstructure. Compression (σ_c) and flexural (σ_f) mechanical strength were measured in 12 samples for each condition, using a Loyd Instruments LR 30 K. Dilatometric behaviour was studied with a Netzsch DIL402EP at 5 °C min^{-1}, and permeability to liquids (3 times per sample) was performed as indicated in relevant literature references (Moreira and Coury, 2004). Thermal conductivity was measured as reported earlier (Vitorino et al., 2013b, 2013c), using a C-Therm thermal conductivity analyser (TCI), based on the modified transient plane source technique. These measurements were repeated 10 times, with accuracy better than 5%, within the equipment technical specifications.

3. Results and discussion

Dilatometry was performed to assess dimensional changes occurring in the cellular bodies, when submitted to heat treatment. The main shrinkage contribution for the green alumina bodies occurs at temperatures in the range of 250–350 °C, and is ascribed to partial relaxation of the green ceramic wall during the elimination of paraffin droplets, in agreement with literature results (Vitorino et al., 2013a; Sanches et al., 2014). Note that this step of shrinkage is not detectable in the green cellular ceramics of red clay and kaolin. In these cases, dimensional changes occurred at higher temperatures, i.e., under typical

Table 2
Consolidation conditions of the different extruded ceramic emulsion.

Ceramic emulsion	Organic phase elimination					Consolidation		
	Heat rate (°C min^{-1})	Plateau		Heat rate (°C min^{-1})	End Temp. (°C)	Heat rate (°C min^{-1})	Dwell time	
		Temp. (°C)	Time (h)				Temp. (°C)	Time (h)
Red clay							1000 1100 1200	
Kaolin	2	200	2	2	500	5	1100 1200 1300	2
Alumina							1350 1450 1550	