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Burnout effects on cellular ceramics obtained from gelatine gelcasted emulsified suspensions

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Abstract

Differential thermal analysis, thermogravimetry and dilatometry were used to study burnout changes occurring during the earliest stages of firing of cellular ceramics obtained by gelcasting of emulsified suspensions. These analyses provide information on microstructural rearrangements during the initial burnout stages, and for the effects of heating rate, isothermal plateau and corresponding time on cell size distributions, average cell size and other microstructural features of resulting cellular ceramics. Compressive strength and its scattering were also related to those microstructural changes induced by burnout conditions.

Keywords: Cellular ceramics; Taguchi planning; Emulsification; Gelcasting; Heat treatment

1. Introduction

Gelcasting has raised increasing interest as a versatile method to process ceramics with different shapes,[1,2] and to yield strong bodies for green machining. Combination of gelcasting and foaming of ceramic suspensions[3,4] has also been used to process porous ceramics with wide range of relevant microstructural characteristics, often by co-addition of pore formers. Classical pore formers may be polymeric sponges,[5] natural products such as starch,[6] synthetic microspheres of suitable polymers,[7] graphite particles, etc.

Emulsification of ceramic suspensions is also a versatile method to process highly porous ceramics, with emphasis on cellular ceramics.[8] The use of highly volatile alkanes is attractive for its prospects to allow recovery and reutilization of these organics by low temperature volatilization and upon condensation, before drying the resulting green cellular ceramics. However, highly volatile alkanes are ill suited for gelcasting because gelling additives often require previous treatment at temperatures approaching 100 °C. Therefore, one proposed an alternative method based on emulsification of ceramic suspensions with molten paraffin, to allow subsequent gelcasting at temperatures below the melting point of this fugitive phase[9]; this allows solidification of paraffin droplets before gelcasting and drying, without undue coarsening, yielding relatively strong green bodies.

Burnout conditions must be controlled to avoid overpressure of burnout gases resulting from pore former (paraffin droplets), gelling additive (dried gelatine), tensioactive additives, etc. Otherwise, overpressure of burnout gases may lead to failure of very fragile green ceramics. In addition, the presence of molten paraffin is more likely to allow microstructural rearrangements, compared to solid pore formers. Thus, burnout conditions may play significant effects on shrinkage and microstructural features of resulting cellular ceramics, with corresponding impact on microstructure dependent properties,

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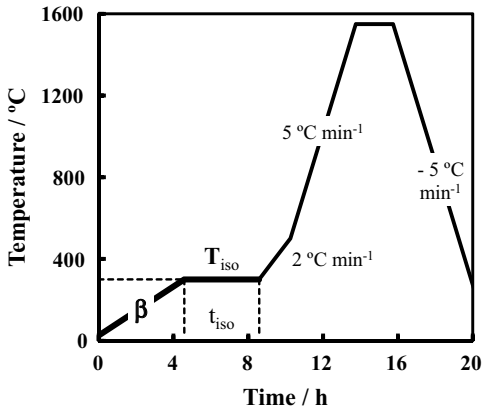

Fig. 1. Representative thermal cycle showing the burnout stage and subsequent sintering for a representative sample, E3 in Table 1.

such as mechanical strength,[10,11] permeability,[12,13] thermal or electrical conductivity,[14,15] etc. This is the main purpose of the present study. Cellular ceramics obtained by gelcasting of emulsified suspensions may be a model for other cellular ceramics when pore formers undergo melting before oxidation or thermal decomposition.

2. Experimental conditions

Alcoa CT3000 powder was used to prepare aqueous alumina suspension with a solid load of 50 vol%, with addition of Dolapix PC-67 for dispersion and stabilization. This suspension (prepared at room temperature) was emulsified with paraffin (Merck 1.07337.2500) above its melting temperature, with paraffin:suspension volume ratio = 1.5, by stirring at 1000 rpm (Brinkmann Heidolph Mechanical Overhead Stirrer RZR1) and with additions of sodium lauryl sulphate (Sigma–Aldrich L-6026) as tensioactive, and collagen (Oxoid LP0008) as a gelling additive. Further details about emulsification and subsequent drying can be found elsewhere.[9,16]

The initial stage of heat treatment was adjusted based on thermal analyses to avoid excessively fast weight losses, and risks of disruption by evolution of large volumes of gases resulting from burnout of paraffin and other additives. This stage is shown as thick lines in Fig. 1, and was adjusted by changing the heating rate (β), the isothermal temperature (T_{iso}) and time (t_{iso}). The remaining steps of the firing cycle were identical for every sample, with heating rate of 2 °C min^{-1} until 500 °C, followed by heating at 5 °C min^{-1} at temperatures above 500 °C and sintering at 1550 °C for 2 h. The cooling rate was −5 °C min^{-1} for every case.

Thermogravimetry (Netzsch STA409EP) was used to identify a relevant temperature range for relatively slow weight losses, and differential thermal analysis allowed one to distinguish endothermic phase changes from exothermic decomposition reactions. Dilatometry (Netzsch DIL402EP) was also used to monitor shrinkage or expansion during the initial burnout stages of heat treatment. These results were used to establish a Taguchi plan to study combined effects of initial heating rate, temperature and duration of the isothermal plateau, with three levels for each factor (Table 1). The relative impacts of a given factor on a relevant microstructural parameters (average cell size, etc.), and a related property (compressive strength) were assessed by averaging the results for experiments with this factor at the selected level. For example, the impact of isothermal plateau temperature on cell size was taken as the average of experiments $(d_{c,1} + d_{c,4} + d_{c,7})/3$ for the lowest level $T_{iso} = 200$ °C, $(d_{c,2} + d_{c,5} + d_{c,8})/3$ for the intermediate level $T_{iso} = 250$ °C, and $(d_{c,3} + d_{c,6} + d_{c,9})/3$ for the highest level $T_{iso} = 300$ °C.

The resulting cellular ceramics were used to assess the impact of burnout conditions on microstructural characteristics and relevant properties such as compressive strength. Scanning electron microscopy (SEM – Hitachi SU1510) was used to determine average cell sizes, size distributions and other microstructural features, using a suitable stereology code.[17] The Archimedes method was used to obtain information on total (x) and closed (x_c) porosity. A Lloyd LR30K equipment was used to measure compressive strength under crosshead speed of 15 mm min^{-1}, using nine prismatic samples with length:width ratio = 2:1.

3. Results and discussion

3.1. Thermochemical changes during the burnout stage

Weight losses of samples processed by emulsification with molten paraffin and gelcasting (Fig. 2) are mainly determined by elimination of pore former (paraffin). Thus, one performed thermogravimetry of a paraffin sample (p) at identical heating rate (5 K min^{-1}); this shows gradual increase in the rate of weight losses, reaching a peak at temperatures close to 300 °C, and approaching complete elimination (≈98%) at 400 °C. Thermal degradation of gelatine was also assessed by thermal analyses of gelatine gelcasted alumina samples (a + g in Fig. 2), showing peaks of weight losses at temperatures in the order of 100 °C and also in the order 300 °C, in agreement with literature results.[18,19]

Fig. 2 also shows the combined contributions of paraffin and gelatine (g + p). This sample was prepared by emulsification of molten paraffin in liquid gelatine, in the volume ratio 1.5:1. This sample was cooled to room temperature, causing solidification of the paraffin droplets and inducing gelling, and then dried at about 50 °C; this sample shows an enhanced shoulder at temperatures in the range 200–300 °C, suggesting that burnout effects of paraffin and gelatine in previously emulsified samples may include a significant contribution which is not revealed for separate additives.

Fig. 3 shows differential thermal analysis of samples (a + g + p) obtained by emulsification of alumina suspensions with paraffin as pore former and gelatine as gelcasting additive. The relevant changes include the endothermic contribution ascribed to melting of paraffin droplets, the exothermic shoulder in the range 200–300 °C, ascribed to thermal degradation of gelatine, a double exothermic peak in the intermediate temperature range (300–400 °C), ascribed to combustion of paraffin, and the additional exothermic peak at temperatures above 400 °C, also ascribed to elimination of paraffin. Note that paraffin burnout does not show the initial shoulder. The DTA results for the