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Short communication

Extrusion processing of dense $MgAl_2O_4$ spinel honeycombs with low relative density

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Abstract

Honeycomb structures were extruded from $MgAl_2O_4$ spinel dough with optimum rheological properties. Extruded honeycombs are sintered at 1700 °C followed by hot isostatic pressing (HIP) to achieve close to theoretical densities. Honeycombs have shown a density of 3.57 g/cc along with the cellular properties such as wall thickness of 90 μm, cell opening of $350 \times 350\ \mu m^2$, cell density of 900 channels per square inch and relative density of 0.45.

Keywords: A. Extrusion; D. Spinel; A. Sintering; A. Hot isostatic pressing

1. Introduction

Cellular materials are receiving a renewed attention as structural and functional components in recent years [1]. Unlike solids they are composites in which one phase is solid made up of inter connected network of struts or plates and other is filled with air. Properties of honeycombs are based on three major variables such as (i) relative density (ρ^*/ρ_s where ρ^* is the density of the cellular material and ρ_s that of the solid of which it is made) (ii) cell wall material and (iii) geometry of the cells. Flexibility in tailoring these variables offers the possibility to engineer the honeycombs to exhibit a very high stiffness-to-weight ratio in combination with unique thermal, acoustic and energy absorbing properties. Potential applications [2–8] of the honeycombs ranges from high surface area supports for heterogeneous catalysis especially for environmental control, high temperature molten metal filtration, energy conservation and heat transfer, solar and fuel cell and aerospace etc. $MgAl_2O_4$ spinel is one of the well known technologically important ceramics due to their inherent thermo-mechanical properties such as high melting point of 2135 °C, moderate strength (180–200 MPa) and hardness (13.5 GPa) in combination with high chemical inertness [9–10]. In spite of the advantages of spinel as a candidate material for extreme environments because of the above attributes, efforts to fabricate spinel ceramics as honeycombs to explore for versatile application are limited [11]. Hence, this paper presents the extrusion processing of high cell density $MgAl_2O_4$ spinel honeycombs. Various important parameters such as rheological properties of the dough, drying and sintering are found to primarily dictate the defect free shaping. Physico-chemical and cellular properties of the developed honeycombs are estimated and included in the paper.

2. Processing of honeycombs

2.1. Dough preparation and characterization

$MgAl_2O_4$ phase pure spinel powder (Baikowski, France) having average particle size of 200 nm was blended with 2.5 wt% of methylcellulose binder to obtain a homogeneous mixture. The mixture was subsequently kneaded in a vacuum sigma kneader with 1 wt% of polyethylene glycol as the plastisizer and 35–40% water. The homogeneity of the dough thus prepared was tested by debindering specimens collected from multiple points employing TGA/DSC analysis. The dough was characterized for their rheological properties using an indigenously designed and fabricated capillary extrusion

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rheometer as per the measurement procedures described elsewhere [12,13]. Extrusion pressures, *P*, required for maintaining stable flow through the capillary die were calculated from the steady state load values corresponding to the plateau region of the load displacement curve, as load per unit cross sectional area of the barrel

$$4F/\pi D^2 \quad (1)$$

where F is the load and D is the diameter of the barrel. Similarly, the extrusion velocities, *V*, corresponding to these pressures were calculated from the ram rates scaled for the relative change in the cross sectional area from the barrel to the capillary, as

$$v(D^2/d^2) \quad (2)$$

where v is the ram rate and d is the diameter of the capillary die.

Viscoplastic formable spinel dough prepared above was extrusion formed through a specially designed die which is the most common technique employed for the manufacture of cordierite based honeycombs [14]. Extruded honeycombs after shaping are dried and sintered at various temperatures of 1600–1700 °C. The samples pressure less sintered (PLS) at 1700 °C with no open porosity (> 98% TD) are hot isostatic pressed (HIP) to achieve the densities close to 100% of TD. Density values are further confirmed using Archimedes principle (ASTM 792). Cellular properties such as cell density, relative density and surface to volume ratio were calculated using the unit cell dimensions of the honeycombs using standard equations depicted in Table 1.

3. Results and discussions

Extrusion pressure versus extrusion velocity data obtained from the capillary extrusion rheometry was translated as shear rate vs. shear stress data using the Eqs. (1) and (2) and the apparent viscosity was calculated as $\eta=\tau/\gamma$. Fig. 1(a) shows the variation of viscosity with shear rates for two (*L*/*d*) ratios of 15 and 25 calculated from the extrusion data for the spinel dough. The trend is clearly non-linear, suggesting that the mix exhibits a shear thinning behavior. Such shear thinning behavior can be analyzed using the power law model

$$\eta = m\gamma^{n-1}$$

where, *η—viscosity*, *m—consistency constant*, *γ—shear rate and n—shear rate exponent or power law index* from the plot of $\ln\eta$ vs. $\ln\gamma$ (Fig. 1(b)).The deviation of flow properties from the Newtonian behavior can be estimated based on the deviation from the shear rate exponent "*n*". A shear rate exponent of "*n*" 0.74 corresponds to a strong non-Newtonian behavior (Fig. 1(b)). For defect free extrusion of honeycombs

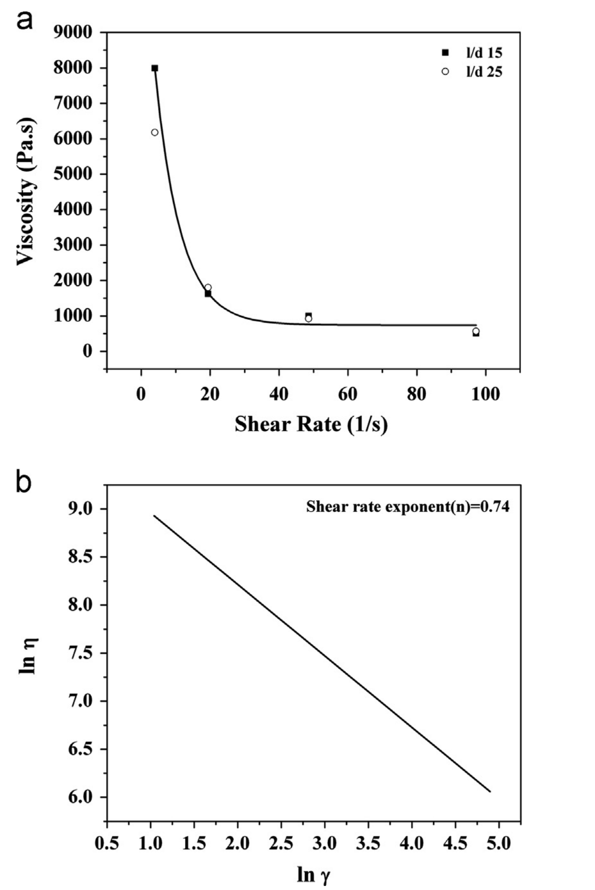

Fig. 1. (a) Variation of viscosity as a function of shear rate using capillary dies of two l/*d* ratios 15 and 25 and (b) plot of $\ln\eta$ vs. $\ln\gamma$ showing an *n* value of 0.74.

especially with thin walls, it is essential that the dough satisfies a non-Newtonian flow characteristic and further should have sufficient strength to maintain the integrity of the green honeycomb structure. Extruded and sintered honeycomb is shown in Fig. 2 demonstrating the suitability of rheological properties adaptable for optimal extrusions.

The properties of PLS followed by HIP honeycombs are shown in Table 1. Sintered honeycomb samples exhibited a density of 3.54 g cm^{-3} which on simultaneous application of temperature and pressure on HIPing enhanced to 3.57 g cm^{-3}eliminating even the residual porosity. Cellular properties have exhibited only negligible change in cell parameters of wall thickness and unit cell length. Relative density of the samples was found to be corresponding to cellular nature and hence exhibits high surface to volume ratio. Spinel honeycombs on account of their high refractoriness (melting point: 2135° C), theoretical densities in combination with low relative density of 0.45 offers potential to explore for high temperature structural applications.

Table 1
Cellular properties of sintered +HIP honeycomb samples.

Honeycomb density (g cm^{-3})	Relative density (ρ^*/ρ_s)	Cell density (Channel/in.^{2})	Surface area/unit volume (cm^2/cm^3)
3.54	0.45	900	3.61

4. Conclusions

Thin walled (90 μm) $MgAl_2O_4$ spinel honeycombs were successfully fabricated through extrusion followed by PLS and HIP. Structural integrity of the structures even with low relative

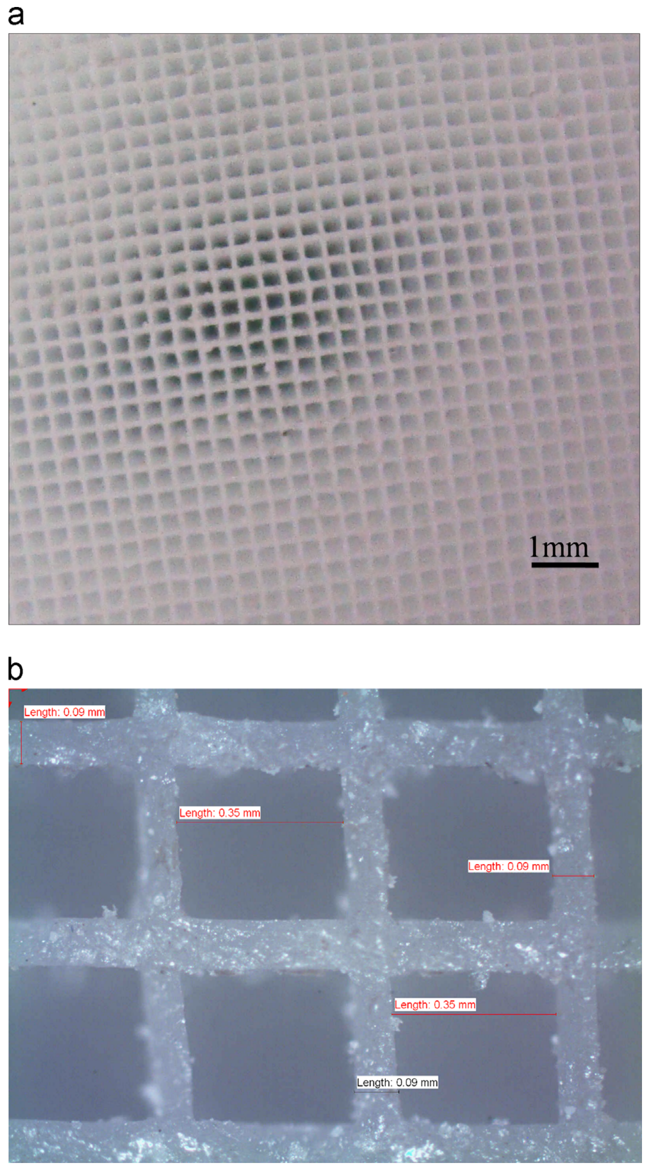

Fig. 2. (a) Sintered honeycombs and (b) optical micrographs of the channels showing wall thickness of 90 μm and unit cell length of 350 μm.

density of 0.45 can be attributed to the optimal parameters employed for processing. In view of the inherent high melting point of 2135 °C and density values of 3.57 g cm^{-3} and low relative density of 0.45, spinel honeycombs provide opportunities for high temperature and chemical corrosion resistant applications.

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