

HIGH STRENGTH LIGHT WEIGHT FLY ASH COMPOSITES

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ABSTRACT

Fly ash is a valuable by-product of coal-fired power generation. After beneficiation to recover valuable minor constituents, a fine powder of spherically shaped, largely amorphous, calcium aluminosilicate particles is left, which is well suited for processing into useful shapes without further milling. With the addition of Portland cement or lime, the formed body may be autoclaved at near 200°C to form a pozzolanic bond between fly ash particles. Light weight is achieved by extruding honeycomb structures with parallel open channels. Maximum strength to weight ratio would be achieved for pore-free honeycomb walls. The strength to density ratio of the honeycomb structures is independent of weight, since both weight and strength decrease linearly with fractional channel volume.

INTRODUCTION

The long range objective of this effort is to utilize fly ash from coal burning power plants to manufacture lightweight construction materials. To this end, selected processing methods from advanced ceramics and advanced cement based materials were adapted, chief among them the extrusion of fine monolithic honeycomb structures. This technology was developed by the automotive industry for the manufacture of cordierite catalyst carriers. While high surface area and high thermal shock resistance are the principal attributes of interest in automotive exhaust catalyst carriers, high strength, low weight, thermal insulation and acoustic isolation are of primary interest in construction materials. Building components envisioned range from brick size blocks to 4x8 foot panels, as well as a variety of posts, beams and other configurations. The size of components which could be produced in this study was severely limited by the extrusion equipment.

Since the density of silicates is largely dominated by the silica network, which is the lightest component, achieving densities less than about 2.3 gm/cc in a silica rich composition such as fly ash or Portland cement can only be achieved by incorporating open space in the structure. The most obvious way of accomplishing this is to increase the porosity of the final body. The difficulty is that the strength of a ceramic body decreases exponentially with porosity according to the Ryshkewitch equation^{1,2}:

$$\sigma = \sigma_0 e^{-\beta P} \quad (1)$$

where σ_0 is the theoretical, pore-free strength of the material, P is the fractional porosity and β is an empirical constant for the material. Rewriting equation (1) for a honeycomb structure, the theoretical strength will be multiplied by the area fraction of the solid walls in cross section and the porosity in the equation will be replaced by the porosity within the solid walls:

$$\sigma = A_w \sigma_0 e^{-\beta P_w} \quad (2)$$

Defining the macroscopic bulk density of the honeycomb structure, ρ_b , as the weight of the honeycomb divided by its total volume, the area fraction of the walls perpendicular to the extrusion direction can be expressed as the ratio of this bulk density to the density of the walls, ρ_w . The pore fraction in the walls will be one minus the solid fraction in the walls. The solid fraction in the walls will be equal to the ratio of the wall density to the theoretical density of the fly ash. The Ryshkewitch equation may thus be expressed for a honeycomb structure as:

$$\sigma = \frac{\rho_b}{\rho_w} \sigma_0 e^{-\beta \left(1 - \frac{\rho_w}{\rho_0}\right)} \quad (3)$$

Rewriting equation (3) slightly, the macroscopic strength to density ratio may be related to the maximum, pore free, strength to density ratio and the fractional porosity of the honeycomb walls.

$$\frac{\sigma}{\rho_b} = \frac{\sigma_0}{\rho_0} \frac{e^{-\beta P_w}}{(1 - P_w)} \quad (4)$$

Equation (4) says that for zero porosity in the honeycomb wall, the strength to density ratio of the honeycomb will correspond to the pore free strength to density ratio. For a given wall porosity, the density of the honeycomb will be determined by the relative dimensions of the channels and walls in the honeycomb, which are fixed by die design. The strength will scale in exactly the same fashion.

Achieving any given macroscopic density requires fabricating honeycombs with specific numbers of channels and wall thicknesses. Assuming square channels of side d with wall thickness t , the

relationship between honeycomb dimensional parameters and macroscopic bulk density may be written:

$$\frac{t}{d} \left(1 + \frac{1}{n} \right) = \sqrt{\frac{1}{1 - \frac{\rho_b}{\rho_w}}} - 1 \quad (5)$$

where n is the total number of channels in the sample being tested. In the limit of large n , the bulk density may be expressed as a function of the wall density and the ratio of the wall thickness to the channel width.

$$\rho_b = \rho_w \left[1 - \frac{1}{\left(1 + \frac{t}{d} \right)^2} \right] \quad (6)$$

The fundamental approach to achieving high strength lightweight honeycomb structures is to develop the extrusion process to produce honeycombs with dense, thin walls, and to develop the curing process to further enhance the wall density in the final structure. Extrusion parameters, such as pressure and extrusion rate, affect the green density of the extruded body, which will be reflected in the final solidified product. Similarly, plasticizers, water and lubricants may be transient components of the green body. In leaving the body during firing or drying they leave behind void spaces in the structure which can affect the ultimate density. The relative fractions of these components added to promote extrudibility affects the ultimate wall density of the honeycomb structure, and thus the ultimate strength. Porosity in the green extruded body may be reduced during autoclaving by filling the pores with reaction products. In fired bodies, the porosity is reduced by normal vitreous sintering, with concomitant changes in sample dimensions. In autoclaved bodies, residual plasticizer and binder will affect both density and the hydration reaction.

SAMPLE PREPARATION

The minimum achievable wall thickness in the extruded honeycomb will be limited by the maximum particle size of the fly ash in the mix. The raw fly ash was therefore separated by sieving into fractions of particle size greater than 90 μm and less than 90 μm . The latter comprised greater than 98 weight % of the ash and was used exclusively in the extrusion of honeycombs.

Extrusion batches need to have sufficient plasticity to allow flawless knitting of the honeycomb walls during extrusion, with sufficient stiffness to support thin walls (0.05-0.13 cm). This required optimization of the water and binder additions, adequate shredding of the batch before extrusion to enable thorough de-airing, and optimization of the speed of extrusion. Methyl cellulose (MC), with additions of polyethylene oxide (PEO) to improve water retention during extrusion, was the initial binder studied, in the range of 0.5-5 weight % of solids³. Binders and plasticizers used in hydrothermally processed honeycombs had to be chosen to avoid adversely affecting the hydration reactions which are responsible for strength development. Methyl cellulose exhibits limited solubility in hot water, and appeared to impede the development of strength during autoclaving. In subsequent batches, the methyl cellulose was replaced by a mixture of hydroxyethyl cellulose (HEC) and polyethylene glycol (PEG), with small amounts of PEO again added. These exhibit higher solubility in hot water, and higher strengths were attained on autoclaving.

All specimens were extruded on a 40 ton, vacuum de-airing, piston extruder (Loomis Products Co.), with dies fabricated in house. A 2.54 cm square honeycomb with rounded corners and a nominal wall thickness of 0.16 cm, has evolved as the standard test piece, but different configurations have been fabricated. Fly ash samples containing 10-100 weight % Type I Portland cement (OPC, ordinary Portland cement) were hydrated at 60°C for 1-7 days after extruding, then autoclaved at temperatures from 150-210°C for 1-24 hours.

RESULTS AND DISCUSSION

Variables whose effects on strength were systematically measured included composition, reaction temperature and reaction time. Within very broad limits, the effects of each of these variables on strength mirrored their effects on sample porosity. Figure 1 shows the measured crushing strength as a function of fractional porosity of sintered samples, determined from density measurements on the samples. The data are plotted on a semilogarithmic plot in accordance with equation (1). Samples in Figure 1 were prepared by a variety of methods, and with a variety of compositions. Samples sintered at moderate temperatures (800-1000°C) contained up to 5% borax or boric acid as a sintering aid. Pure fly ash samples were sintered at temperatures above 1100°C. High porosity cast samples were foamed and contained 5-10% calcium lignosulfonate as a foam stabilizer⁴. Extruded cylinders contained from 1-5% methyl cellulose. The autoclaved honeycombs shown in the figure for comparison contained 40% OPC. The solid line in Figure 1 represents the linear regression fit of the data to equation (1). The empirical constants in equation (1) corresponding to this fit are: $\sigma_0 = 615 \text{ MPa}$, and $\beta = 6.6$.

The data on extruded honeycombs in Figure 1 are plotted as if the open channels in the honeycomb were ordinary porosity, and can be seen to exhibit as much as an order of magnitude greater strength for a given weight than the cast cylinders. This serves to illustrate the advantage of the honeycomb configuration for achieving high strength, light weight materials, but the

appropriate equation to compare these data qualitatively would be equation (4). Alternatively, the crushing force can be divided by the cross-sectional area of the wall to give the wall strength, which can be plotted against the wall porosity to compare directly with Figure 1. Figure 2 shows such a plot of wall strength vs. wall porosity, where the wall porosity was determined by mercury intrusion porosimetry. Included in the plot is the solid line representing equation (1) with the values of the empirical constants determined from Figure 1. Two different compositions are represented in Figure 2, 30% and 40% OPC, both autoclaved at 180°C, the former for 12 hours, the latter for 13 hours. The average strength of the latter is higher, as might be anticipated in light of the higher OPC content and longer curing time. The difference, however, can be attributed entirely to the difference in porosity of the two compositions. They both fall within the anticipated range for agreement with equation (1), with empirical constants determined from fly ash samples fired at high temperatures and containing no Portland cement. Mechanistically, this indicates that the strength of samples in both figures was determined by the strength of the fly ash framework. The mechanism of bonding between fly ash particles did not affect the strength achieved. The fact that in all autoclaved samples tested thus far the wall porosity has exceeded 20% is of major relevance to the direction of future work.

Figure 3 shows electron micrographs of fractured surfaces of autoclaved honeycomb samples containing 40 and 10 weight % Portland cement. In the former, the fracture is transgranular, passing through the fly ash grains. The transgranular nature of the fracture in Figure 3A is particularly notable when the fracture passes through hollow fly ash particles (cenospheres), as illustrated by the arrow (a) on the micrograph, but is also evident by the general planar character of the fracture surface, with little evidence that the body is made up of spherical fly ash particles. The fracture has the appearance of a typical ceramic fracture surface. In Figure 3B, by comparison, the fracture is clearly intergranular. The spherical fly ash particles are evident as the fracture proceeded between the particles, leaving many of the spherical surfaces unmarred. The 40 % OPC composition of Figure 3A exhibited about 8 times the crushing strength of the 10 % OPC sample of Figure 3B. In samples where the weakness of the bonding between particles permitted intergranular fracture, the strength was no longer represented by equation (1), at least not with the empirical constants determined from Figure 1.

Figure 4 shows an electron micrograph of the fracture surface of a sintered fly ash honeycomb, such as used to determine the empirical constants in equation (1) from Figure 1. Fracture is again clearly transgranular, and the only evidence of the spherical nature of the initial particles is the spherical pores observed where the fracture passed through the hollow cenospheres. The bonding mechanism in this case can be seen to be vitreous sintering, whereas the bonding in the samples of Figure 3 was the pozzolanic reaction of the lime in the Portland cement with the free silica at the surface of the fly ash particles to form tobermorite and other calcium silicate hydrates.

CONCLUSIONS

High strength light weight honeycomb composites can be formed by autoclaving a mixture of fly ash and Portland cement, as well as by typical ceramic firing of fly ash honeycomb structures at high temperatures. A comparison of strength and density of fly ash honeycomb samples with typical construction materials is presented in Table 1. Materials are listed in order of increasing strength to density ratio, which has been normalized to 1.0 for construction grade pine. Typical values for both autoclaved and sintered honeycombs from the present study are shown. Differences in the strength to density ratio of honeycomb samples is determined primarily by differences in the fractional porosity of the walls for honeycombs with very different compositional modifications, as well as processing variations. This is attributed to the fact that the fracture mechanism is the same and occurs through the fly ash grains. This indicates that the solid grains form the weak link in the system and that the strength is proportional to the cross sectional area fraction of the solid, which may be converted directly to density of the wall. When intergranular fracture was observed, as seen in Figure 3(B), the same strength-porosity relationship no longer held.

In no case was the wall density greater than 80% of theoretical for autoclaved honeycombs. With the experimentally determined value of $\beta = 6.6$, a wall porosity of 20% yields a strength to density ratio of only 33% of theoretical from equation (4). For the honeycomb samples in Table 1, the total porosity, as determined by mercury intrusion porosimetry, was about 25 and 18% respectively. These values would predict a maximum normalized strength to density ratio of about 5. There is clearly still much room for improvement. Future efforts will be concentrated on the attainment of greater wall densities, i.e., eliminating the porosity in the walls.

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Table 1. Strength/density comparison with typical construction materials

Material	Bulk Density (gm/cc)	Compressive Strength		Normalized Strength/Density Ratio
		(MPa)	(psi)	
Aerated Concrete	0.69	4.4	640	0.10
Concrete	2.2	35	5100	0.25
Clay Brick	2.3	45	6500	0.31
Steel	7.8	455	66000	0.91
Pine	0.48	30	4350	1.00
Autoclaved Honeycomb	1.13	95	14000	1.36
Fired Honeycomb	1.32	155	22500	1.89

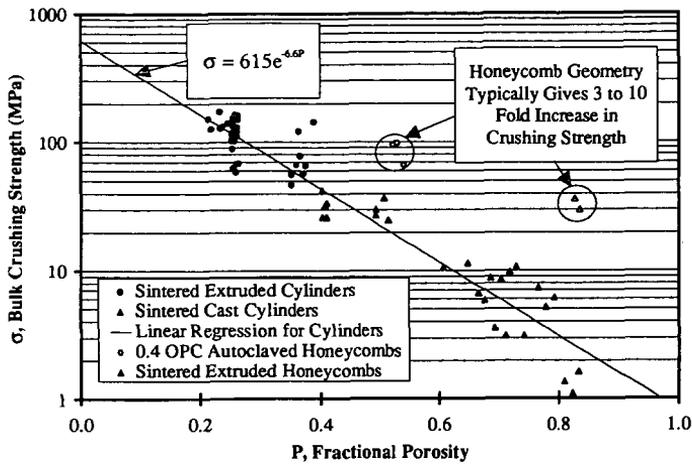


Figure 1. Crushing strength vs. fractional porosity for fired fly ash bodies.

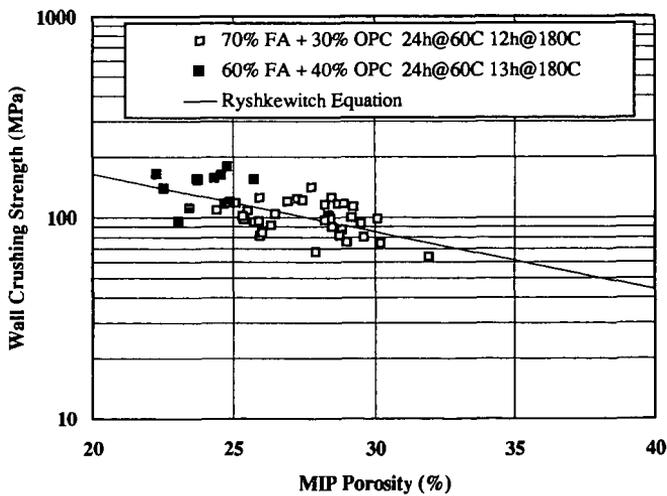
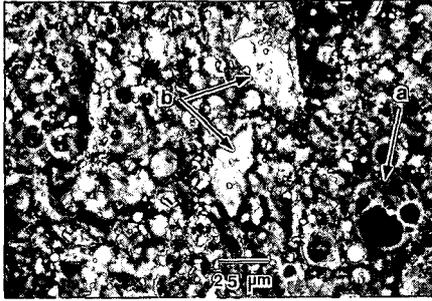
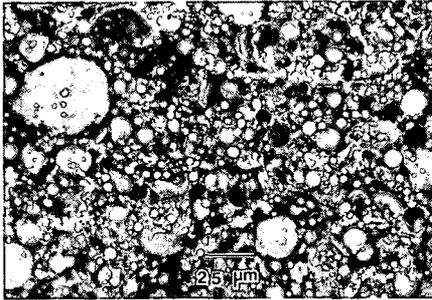


Figure 2. Crushing strength of the honeycomb wall vs. fractional porosity of the wall.



(A) SEM of 40 % OPC fly ash honeycomb illustrating transgranular fracture surface.
 (a) Cross section of hollow fly ash particle (cenosphere)
 (b) Unhydrated cement paste grains



(B) SEM of 10 % OPC fly ash honeycomb illustrating intergranular fracture surface. Note spherical morphology retained by fly ash particles in fracture surface.

Figure 3. Scanning electron micrographs of fracture surfaces of fly ash honeycombs illustrating (A) transgranular fracture in 40% OPC composition, and (B) intergranular fracture and pullout in 10% OPC composition.

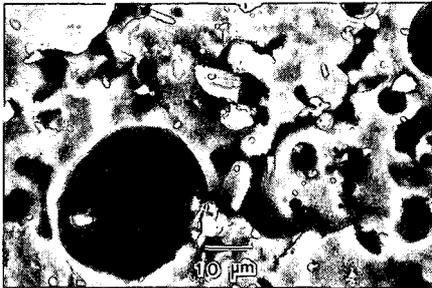


Figure 4. Scanning electron micrograph of fracture surface of pure fly ash honeycomb densified by firing at 1075 °C for 24 ho