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**PROPERTIES AND SHAPING OF LIGHTWEIGHT CERAMICS BASED ON
PHOSPHATE-BONDED HOLLOW SILICA MICROSPHERES**

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Résumé - Les valeurs du module de Young's, de la résistance, de la ténacité et de la conductivité thermique de céramiques légères à base de microsphères creuses de silice, agglomérées par un phosphate, sont données en fonction des conditions de traitement. Elles sont comparées aux données correspondantes d'autres céramiques composite légères. Le formage par pressage ou par usinage au tour est décrit brièvement.

Abstract - The values for the Young's modulus, strength, fracture toughness and thermal conductivity of lightweight ceramics based on phosphate-bonded hollow silica microspheres are reported as a function of the processing conditions. They are compared with the relevant data for other lightweight ceramic composites. The shaping by either pressing or lathe machining is briefly discussed.

I - INTRODUCTION

Hollow microspheres are a relatively new material. They are available in the form of glasses, e.g. borosilicate glass or vitreous silica, and also in crystalline form e.g. alumina or zirconia. The hollow glass spheres can be bonded either by sintering or by using a bonding agent such as phosphate. In the case of glass spheres, compacts have been reported which were prepared by sintering (1) and, in the case of vitreous silica microspheres, the phosphate bonding process yields homogeneous, easily manageable ceramics (3). Some theoretical work has been done on the prediction of the Young's modulus (2,3) and fracture toughness (2) of these composites. In this paper we present a further characterisation and some measurements of the mechanical properties of phosphate-bonded ceramics based on hollow silica glass microspheres. Furthermore we present some examples of machined and pressed plates of complex shape.

II- EXPERIMENTAL

Hollow silica microspheres were chosen as raw material (Emerson and Cuming Inc., ecospheres SI). The diameter distribution was determined using a digital planimeter. The ceramics were made by the phosphate bonding process as described (3). The concentration of the mono-aluminium phosphate (MAP), the firing time and the firing temperature were varied. Densities, ρ , were measured on large flat specimens, of which the outer part had been removed by machining, using weight and dimensional data. Mercury intrusion porosimetry (MIP) was used to study the pore structure of the composites (Carlo Erba macro-pore unit 120). The thermal conductivity was measured using a thermal comparator (TC-1000, Lafayette Instruments Company). Young's modulus, E , was determined by deflection measurements on 3-point bending specimens. The fracture toughness, K_{IC} , as well as strength, S_f , were

determined in a similar way using generally 3 specimens of size $3 \times 9 \times 45 \text{ mm}^3$. A small notch of relative depth 0.15 was sawn in the K_{IC} specimens with a diamond saw. The notch was sharpened by cutting with a razor knife. The compliance was calculated according to the formula derived by Brown and Srawley (4). The fracture surfaces were examined by scanning electron microscopy (SEM).

III - RESULTS

From the diameter analysis it was revealed that the average diameter of the spheres was $49 \mu\text{m}$ with a rather large standard deviation of about $21 \mu\text{m}$. This figure is somewhat lower than the $80 \mu\text{m}$ (weight basis) indicated by the manufacturer. The size distribution appeared to be bi-modal and rather wide, in agreement with the manufacturer's data. A typical microstructure of the formed ceramic is shown in fig. 1a. From the MIP measurements it was clear that the average pore diameter and width of the pore size distribution in the various composites were relatively constant at about $10 \mu\text{m}$ and $1 \mu\text{m}$ respectively and independent of the processing conditions.

Fig. 1. Fracture surface of the hollow silica microsphere composite as-fired at 600°C for 3 hours using 4 wt % MAP (left) and after 3 hours at 1000°C (right).

The thermal conductivities of the composites are 0.09 W/m.K and 0.1 W/m.K at densities of 180 kg/m^3 (8 % q_r) and 240 kg/m^3 (11 % q_r) respectively. For quartz foam ceramic (7% q_r) a value of 0.07 W/m.K was reported (5). Good agreement is thus observed. For comparison, the thermal conductivity of hollow spheres under self-loading conditions in N_2 under atmospheric pressure was reported to be 0.026 W/m.K (6) while the manufacturer claims 0.05 W/m.K for 'loosely packed material'.

The results of the mechanical measurements are collected in fig. 2. In fig. 2a the influence of the firing temperature is depicted. The influence of this processing parameter on density, Young's modulus, strength and fracture toughness is only slight. A more or less constant density of about 0.18 g/cm^3 , a Young's modulus of about 0.4 GPa and a fracture strength of about 0.8 MPa are found. On the other hand the fracture toughness rises from about $16 \text{ kPa.m}^{1/2}$ at the lower firing temperatures to about $35 \text{ kPa.m}^{1/2}$ at the highest temperature of 700°C . This rise in K_{IC} is accompanied by a slight increase in density.

The influence of the MAP concentration is given in fig. 2b. The values of all mechanical properties increase with the MAP concentration as does the density. This increase is thus not unexpected. At the highest density (240 kg/m^3) an S_F value of 2.0 MPa , a K_{IC} value of $44 \text{ kPa.m}^{1/2}$ and a Young's modulus of 0.8 GPa were obtained.

Fig. 2a. Dependence on firing temperature at constant time (3 hours) and MAP concentration (4 wt %).

Fig. 2b. Dependence on MAP concentration in wt % at constant firing temperature (600°C) and time (3 hours).

Fig. 2c. Dependence on firing time at constant firing temperature (600°C) and MAP concentration (4 wt %).

Finally in fig. 2c the influence of firing time is shown. Although the density remains approximately constant, the fracture toughness and strength decrease with increasing time from their starting values of 30 kPa.m^{1/2} and 1.6 Mpa to 20 kPa.m^{1/2} and 0.4 Mpa respectively. Young's modulus shows a much smaller decrease from about 0.6 GPa to 0.3 GPa. As was shown with X-ray techniques, the silica microspheres devitrify during the longer firing times.

IV - DISCUSSION

Inspection of the fracture surfaces of the various composites reveals that the fracture mode is of mixed nature. The majority of the bonded spots in the ceramic fracture through the spheres themselves, but a small proportion of them fracture at the necks. In general it appeared to be impossible to locate the fracture origins in the S_f specimens.

From the strength and fracture toughness data an estimate of the critical flaw size can be made. The main problem is now to estimate the compliance factor Y since the shape of the fracture origin (critical flaw) is unknown. The usual assumption of a flaw with semi-circular surface (7) yields $Y = 1.26$. Other assumptions lead to values between 1 and 2. Calculation of the flaw size with $Y = 1.5$ gives values of several hundreds of micrometers. Since the pore diameters were about $10\text{ }\mu\text{m}$ a single pore channel cannot be responsible for failure. Processing defects such as air bubbles or inhomogeneous filling of the available space by the microspheres are probably the fracture origins. If this is true it means that the strength of the composites can still be increased fivefold or sixfold by introducing a better processing route that yields more homogeneous ceramics. In one or two cases the fracture origin could indeed be identified as a large pore.

In general the strength follows the fracture toughness behaviour quite closely. There are two apparent exceptions. Firstly, in fig. 2a at 700°C the value for S_f is much lower than can be expected from K_{IC} . In this material on average somewhat larger pores appeared to be present. Secondly, in fig. 2c a somewhat steeper decrease in S_f than in K_{IC} is shown. The increasing crystallisation of the silica (and the MAP) is probably responsible for this.

It is interesting to compare the present results with the recent findings of Green (1) on sintered glass microspheres. He obtained materials in the relative density range of 0.08 to 0.25 and examined the E , K_{IC} and S_f behaviour as functions of density. Non-linear behaviour of E as well as K_{IC} and S_f was observed: a rather rapidly rising value of the property in question with density at the lower densities and a much slower increase at the higher densities. This behaviour was also theoretically described (2). The curves for higher densities could be interpreted in terms of existing micromechanical models, but for the lower densities a new theory was developed which fitted the K_{IC} behaviour well and the E behaviour satisfactorily (2). For foam glass with relative densities of about 0.08 the values of the measured properties can be found on the curve extrapolated from the high density part of the glass composites curve. Other light-weight ceramics such as the space shuttle tile material have lower values of fracture toughness and strength at the same density but much higher values than the glass composites. The values for our phosphate-bonded silica spheres are similar to the values for the strong direction of these (anisotropic) tiles but with the advantage of isotropy. Since we obtained only a limited density range, a critical comparison of the experimental results for our composites with the theoretical predictions is rather difficult.

In fig. 3 various shapes that are fabricated from this ceramic are depicted. The large plates (diameter 16 cm, thickness either 1.0 cm or 2.7 cm) were made in order to be able to cut test specimens for mechanical measurements. The ribbed plates were made either by pressing a granulated mass directly in a mould (weight typically 10 grams) or by normal lathe machining (weight typically 13 grams). Typical machining conditions were: cutter diameter 6 mm, speed 350 mm/min, 5000 revolutions/min, feed 1 mm. By both techniques quite detailed structures with height to width ratios ranging up to 5 were produced easily.

The ribbed plates were intended to be loudspeaker membranes. For the pressed plates a flat frequency response curve with no clearly detectable resonances was obtained while for the machined plates a strong second harmonic was present but at the rather high frequency of 3.1 kHz. The latter fact is due to the presence of the ribs which increase the resonance frequency by a factor of 1.9 as compared with a flat plate with the same weight. In both cases the basic resonance was at about 470 to 490 Hz but this resonance is completely suppressed by the fixation of the plate to the driver coil. Another possible application of the material is as flame-

Fig. 3. Examples of as-prepared plates, test specimens and ribbed plates cut from them and as-pressed ribbed plates.

retardant core material in sandwich constructions in which this core also contributes to the strength and possibly to noise damping. Fig. 1b shows the microstructure of the material after 3 hours at 1000°C. Although obviously degraded, the characteristics of the microstructure are still present. Moreover, no chlorine or fluorine is produced during this process. Various other applications of the material can be envisaged.

V - CONCLUSIONS

Phosphate-bonded hollow silica microsphere composites can be produced with a low density (180 kg/m^3) and relatively high values of Young's modulus (0.6 GPa), strength (1 MPa) and fracture toughness ($30 \text{ kPa}\cdot\text{m}^{1/2}$). Substantially higher values, in particular for the strength, can be obtained at somewhat higher densities. A rather low value of thermal conductivity of about $0.1 \text{ W/m}\cdot\text{K}$ is found. Together with the rather high compressive (crushing) strength of about 15 MPa, as reported earlier (3), and the good machinability, as demonstrated in this paper, these factors make the material a promising lightweight construction material.

VI - ACKNOWLEDGEMENTS

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