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Strength and fracture of porous ceramic sintered from spherical particles

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Mechanical properties of ceramics obtained by the sintering of stabilized zirconia microspheres are investigated. Strength at compression and tension, elastic deformation and modulus of elasticity at compression, specific works of fracture, of fracture initiation, and stress intensity factor are determined. An expression is proposed to establish the dependence of strength on macrostructure parameters of brittle material sintered from microspheres, and its analysis is given.

1. Introduction

Mechanical properties of porous materials depend on peculiarities of macrostructure. Some expressions are known to establish dependence of materials strength on the volume content of pores [1, 2], the volume content of pores and the particles size [3], the volume content and the shape of pores [4], the strength and the number of contacts between particles [5]. Interesting investigations have been reported concerning the dependence of strength upon parameters of particles, size distribution, type of particle packing, specific volume of the dispersed phase [6], and strength of porous disperse structures by complex stress condition [7]. A review of some of the above mentioned and other expressions suggested for strength dependence on structure parameters is given in [8], for example. In known expressions, peculiarities of macrostructure and its effect on strength are as a rule, taken into account through empirical coefficients. However, some of them indicate the necessity to form structure elements in order to minimize the stress concentration.

According to Weiss [9], the stress concentration coefficeint in porous material of grain structure may be written as

$$K_\sigma = K_t K_b [\rho/(\rho + 2y)] \quad (1)$$

where K_t is the stress concentration coefficient in the contact region between grains, depending on the geometrical form of the contact; K_b is the coefficient of stress concentration occurring due to defects in the contact; ρ is the radius of curvature in the contact profile; y is the distance of the defect from the contact edge.

As can be seen from Equation 1, the value of K_σ is minimal when pores have a round shape and there are no defects in the contact. Such a type of macrostructure of a porous ceramic may be obtained, for example, by using grains of a spherical form.

The purpose of this paper is to present some experimental data on strength and fracture behaviour of a porous ceramic with model macrostructure obtained by sintering stabilized zirconia spherical particles (microspheres).

2. Experimental details

Microspheres of 20 to 200 μm diameter from technical grade purity calcia-stabilized zirconia (6 wt%) were prepared by melting particles in a high-frequency discharge [10]. Separation of microspheres on several fractions was accomplished by sieve analysis. Sintering of specimens from microspheres of monofractional composition, packed with vibration and pre-pressing, was accomplished in a gas–oxygen furnace at 2200° C over 4 h [11]. At the stage of sample formation, a fine dispersed binder of corresponding composition was added. The volume percentage of pores in the sintered body, defined by hydrostatic weighting, was 30 to 40%, depending on the granulometric composition of microspheres in the samples. Materials structure was investigated by scanning electron microscopy

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(Stereoscan S4-10) and X-ray analysis (Diffractometer DRON). The mechanical characteristics – compressive strength (σ_c), maximum elastic deformation at compression (ϵ_c), modulus of elasticity at compression (E_c), tensile strength (σ_t), fracture specific work (γ_F), stress intensity factor (K_{IC}), and specific work of fracture initiation (γ_c) – have been determined depending on the fractional composition of microspheres in the specimens. All mechanical tests were carried out using an Instron machine (Model 1115, UK) at room temperature and at a rate of deformation of 0.05 sm min^{-1}. Properties at compression were measured using cylindrical specimens (12 mm diameter, 24 mm height). The stiffness of the testing machine was taken into account when estimating ϵ_c and E_c.

The value of σ_t was determined by diametral compression tests of cylindrical specimens [12] of 12 mm diameter (d) and 12 mm height (h). σ_t was calculated using the following formula

$$\sigma_t = 2\xi Q/\pi dh \quad (2)$$

where Q is the load, and ξ is the coefficient of specimen stiffness. The latter has been determined in accordance with [13] from the ratio of compression and tensile strength. For the materials under consideration, ξ is equal to 1.1.

Values of γ_F, K_{IC} and γ_c were determined using beam samples ($b \times h = 7 \times 7$ mm) loaded by three-point bending. Span: height ration was 8:1. Notches were cut using a diamond tool. The notch width was ~0.1 mm, the depth was 5 mm. To minimize error in determination of γ_F, the preliminary investigation was carried out to define the effect of notch depth a on γ_F. It was found that when $a > 4.5$ mm, γ_F did not depend on a.

The value of γ_F was calculated using the formula

$$\gamma_F = U_F/2b(h-a) \quad (3)$$

where U_F is fracture work corresponding to the area under the load–deflection curve in the diagram.

The stress intensity factor is

$$K_{IC} = Y\sigma a^{\frac{1}{2}} \quad (4)$$

where Y is given by polynom of the form [14]

$$Y = 1.96 - 2.75\frac{a}{h} + 13.66\left(\frac{a}{h}\right)^2 - 23.98\left(\frac{a}{h}\right)^3 + 25.22\left(\frac{a}{h}\right)^4,$$

σ is the brutto-stress value ($\sigma = 3Ql/2bh^2$).

The value of γ_c is given by

$$\gamma_c = K_{IC}^2(1-\nu^2)/2E_b \quad (5)$$

where ν is Poisson's ratio ($\nu \simeq 0.2$); $E_b = Ql^3/4\delta bh^3$ is the modulus of elasticity determined by the bending of unnotched bars; l is span; δ, deflection.

3. Results

3.1. The structure of the material

A typical picture of the fracture surfaces observed with a scanning electron microscope is shown in Fig. 1. By sintering microspheres, contacts with smooth passage from one microsphere to another have been formed. The ratio of microspheres (R) and contact radii in its minimal cross-section (x) is equal to 3 to 4. The packing of microspheres is "free" packing with a co-ordination number of 6 to 8. X-ray investigations have shown that the main phase in the material is zirconia cubic solid solution. However, some quantities of monoclinic (< 3 wt%) and traces of tetragonal phases exist. Traces of "X-ray-amorphous" phase and zircon ($ZrSiO_4$) have been also found.

3.2. Strength and deformation

The dependence of σ_t and σ_c on the microspheres diameter is shown in Fig. 2 in logarithmic co-ordinates. It is evident that the dependence is linear with a tangent value of approximately 1. At $d = 20$ to 40 μm, the value of σ_c is 3.77×10^8 Pa, and σ_t is 4.6×10^7 Pa. The elastic deformation in compression tests is 0.36 to 0.60% and has no systematic dependence upon d. The dependence of

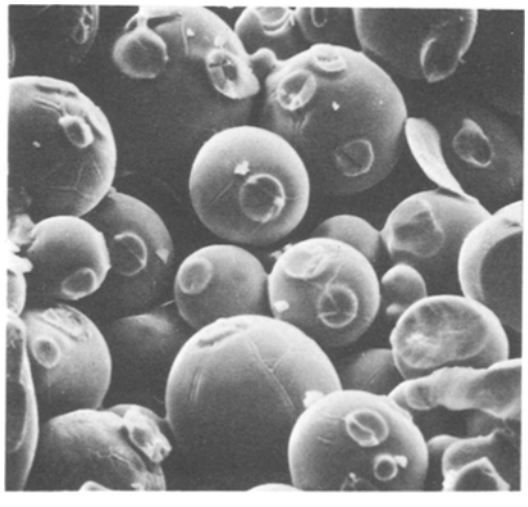

Figure 1 A typical microphotograph of material structure, × 200.

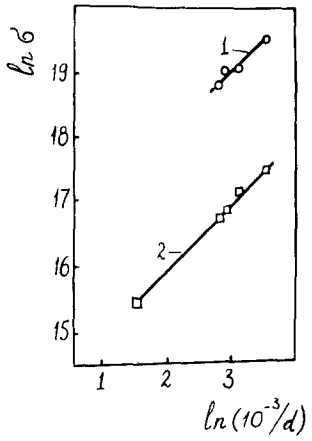

Figure 2 The dependence of σ_c (1) and σ_t (2) (in Pa) on d (m).

E_c on d is the same as for σ_c. The value of E_c decreases from 8.2×10^{10} Pa at $d = 20$ to 40 μm to 3.0×10^{10} Pa at $d = 56$ to 63 μm.

3.3. Fracture

The load–deflection curves of notched bars have expressive steps of uncontrolled (with the rate higher than $\dot{\delta}$ = const) and controlled crack propagation. The dependencies of K_{IC}, E_b, γ_F and γ_c on d are shown in Figs. 3 and 4. As may be seen, the values of K_{IC} and E_b decrease, γ_F and γ_c do not, with increasing microsphere diameter.

As has been shown by electron microscopy investigation of fracture surfaces, both the microspheres and the contacts are incorporated in the fracture process. About 30% of the fractured regions on the surface have the "petalar" fracture type: cleavage is propagated not only through the contacts, but occupies some part of the microspheres.

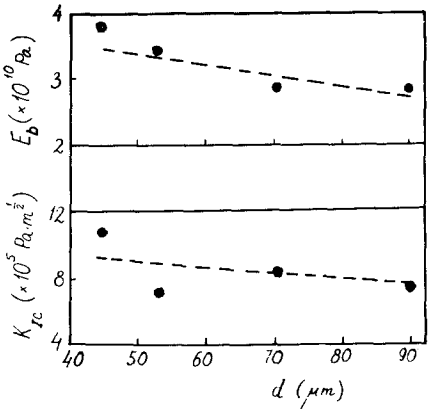

Figure 3 The dependence of E_b and K_{IC} on d.

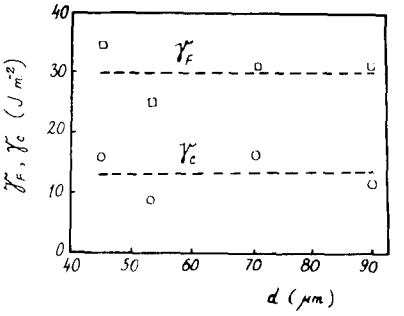

Figure 4 The dependence of γ_F and γ_c on d.

4. Discussion

A high degree of regularity in material structure obtained by sintering microspheres, as compared to traditional materials of "grained structure", allows one to give a more detailed analysis of the strength dependence upon the structure characteristics (volume content of open pores, P, radius of microspheres, R, radius of contacts x in its minimal cross-section, radius of curvature of contact, $\rho \simeq x^2/2R$, orientation of fractured contacts with regard to the loading vector, angle α).

The strength of material (σ) is proportional to the mean value of stress in the contact region cross-section (σ_m), the number of microspheres in the unit of surface area (N_s), the number of fractured contacts on each microsphere (N_f), and the area of fractured surface of a contact (S)

$$\sigma = \sigma_m \cdot N_s \cdot N_f \cdot S \tag{6}$$

In Equation 6

$$\sigma_m = \sigma_0 / K_\sigma \tag{7}$$

where σ_0 is the strength of the contact material.

The stress concentration coefficient on contact between microspheres at tension can be written, according to [9], as

$$K_t = (n(n-1)\sqrt{[n(n-1)+1]} + 0.8n(n-1) + 1.3\{\sqrt{[n(n-1)+1]}+1\})/\{n(n-1) + 0.6\sqrt{[n(n-1)+1]}+2\} \tag{8}$$

where $n = R/x$. Dependence of K_t upon n may be approximated by the following simpler formula

$$K_t = 1 + 0.15n^2. \tag{9}$$

It follows from geometry that the value of N_s may be approximately given by

$$N_s = \left[(1-P)\frac{3}{4\pi R^3}\right]^{\frac{2}{3}}. \tag{10}$$

Based on investigation of the fracture surfaces, it has been shown that N_f is $\sim 0.25N_c$, where N_c is the co-ordination number. The dependence of N_c upon porosity before sintering (P_0) in the range $0.3 < P_0 < 0.7$ may be approximated by the following expression [15]

$$N_c \simeq 11.6(1 - P_0) \tag{11}$$

and, consequently,

$$N_f \simeq 2.9(1 - P_0). \tag{12}$$

The mean value of angle between the normal to the surface of fractured contacts and the normal to the surface of specimen fracture is 30°, therefore

$$S \simeq \pi x^2 \cdot \cos 30°. \tag{13}$$

Thus, Equation 6 can be rewritten as

$$\sigma = \sigma_0 \frac{3(1 - P_0)(1 - P)^{\frac{2}{3}}}{K_\sigma \cdot n^2} \tag{14}$$

where $n = R/x$. In particular, as $n \to \infty$ (the case of "free filling") Equation 14 reduces to $\sigma \to 0$. In the other limiting case when densification of structure and the corresponding increase of co-ordination number have occurred ($n \to 1$, $P \to 0$, $1 - P_0 = 0.65$, $K_\sigma \to 1$, the case of "quasidense body") Equation 14 becomes $\sigma \to \sigma_0$.

According to Equation 14, the main parameter controlling the material strength is $n = R/x$. The value of n depends on sintering conditions. In general, the kinetics of the sintering process can be described by the relation [16]

$$(x/R)^\alpha = A_i \cdot R^{-\beta} \tag{15}$$

where A_i depends upon surface energy, viscosity, diffusivity of the material, and duration of the sintering process; coefficients α and β depend upon the sintering mechanism.

Substitution of Equation 15 into Equation 14 gives

$$\sigma = \sigma_0 \cdot B_i \cdot R^{-m} \tag{16}$$

where B_i involves A_i and some other parameters from Equation 14; m is the coefficient ($m = 1$ in the case of viscous flow, $m = 8/7$ in the case of surface diffusion, $m = 6/5$ in the case of volume diffusion [16]). In first approximation, it may be assumed that

$$\sigma \sim R^{-1}. \tag{17}$$

The experimental data represented in Fig. 2 are well described by Equation 17.

Another important parameter which is believed to determine material strength at constant porosity is σ_0. Because of defectivness of contact structure between microspheres, σ_0 has a statistical nature. It may thus be proposed that the distribution of contacts by strength value is described by Weibull's law in the form

$$w(\sigma) = 1 - \exp\left[-V\left(\frac{\sigma - \sigma_u}{\sigma^*}\right)^m\right] \tag{18}$$

where V is the contact volume, σ_u is the minimal strength of contacts, σ^* and m are the distribution parameters. It follows from condition $d^2w/d\sigma^2 = 0$ that the most probable value of contact strength is

$$\sigma_p = \sigma_u + \sigma^*\left(\frac{m - 1}{m}\right)^{\frac{1}{m}} V^{-\frac{1}{m}}. \tag{19}$$

The value of σ_p increases with increasing homogeneity of the contact material (parameter m), and the larger the volume, V, the lower the mean fracture stress.

It is evident from the suggested analysis that a strong material can be made using microspheres of small diameter only.

Experimental values of strength approach ~ 0.5 of the strength of dense ceramics of the same composition (under compression) and are much larger than these of "grained structure" porous ceramics which have been prepared by traditional technology [17] at appropriate porosity values. It should be noted that the elastic strain of the material (0.4 to 0.5% under compression) is also much larger than that of porous ceramics of "grained structure" (0.05 to 0.2%).

The effective work of material fracture is in the range 25 to 30 J m^{-2} and tends to increase at higher microsphere diameters. Some data of γ_F are known for dense ceramics: ~ 10 J m^{-2} for MgO [18], 15 to 48 J m^{-2} for Al_2O_3 [19–21], ~ 80 J m^{-2} for calcia-stabilized zirconia [22]. A comparison of these values may be made on the basis of a specific work of fracture normalized with respect to the area of specimen fracture cross-section. The fracture of microsphere material occurs mainly over the contacts between microspheres. The area of contact fracture surface is only 0.20 to 0.25 of the area of the specimen cross-section because the co-ordination number is 6 to 8. Consequently, the "normalized" value of γ_F (γ_F^*) is equal to 100 to 150 J m^{-2}.

The larger values of γ_F with respect to the values of γ_c indicate that the crack propagation process consumes more energy than the process of

crack initiation. This may, perhaps, be explained by subsidiary cracking in the fracture process. A similar effect is observed for graphite, for example, whereas fracture of glasses is of a different character: the limiting stage of the process is crack initiation [19].

5. Conclusions

It may be concluded from presented results that an ordering of brittle material of porous structure, for example, by designing a structure using microspheres, allows an increase in strength and maximum elastic deformation relative to those of traditional porous brittle materials. An optimum combination of properties may be reached for materials with fine-grained structure. This situation has been confirmed by theoretical analysis. It is also desirable to investigate the possibilities of increasing the fracture resistance of fine-grained structures. It may be possible to increase the fracture characteristics by introducing into the material structure elements which retard crack propagation, such as ductile fillers or more coarse grains.

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