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Young's modulus–porosity relations: an analysis based on a minimum contact area model

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The Young's modulus–porosity relation of porous ceramic materials has been analysed based on a minimum solid area of contact model. The minimum solid area of contact developed during sintering of an assembly of monosized spheres stacked in simple cubic packing is calculated by approximating the neck area by two sine-wave functions. The first function represents the shape of a sphere and the second function signifies the shape of the neck between neighbouring spheres. The model shows excellent agreement with 12 sets of relative Young's modulus, E/E_o, versus pore volume fraction, P, data from literature on five different polycrystalline ceramic oxides, namely Lu_2O_3, Sm_2O_3, Yb_2O_3, Al_2O_3 and ThO_2, whose porosities are reasonably represented by such idealized packing.

1. Introduction

In general, three approaches have been adopted to deal with mechanical property–porosity relations. These are: (i) mechanical strain analysis of bodies with generalized structure, (ii) premises of pore shape and resulting stress concentration effects (SCE), and (iii) consideration of actual geometrical load-bearing area. Recently, the last approach has been expanded by Rice in a series of papers [1–4] suggesting that most physical properties, including mechanical properties (e.g. elastic moduli, strength, etc.), are determined by the minimum contact area (MCA) fraction normal to the flux or stress. However, estimation of MCA, a difficult task to accomplish, will depend primarily on the initial geometry of particles in the compact and their packing pattern.

In a recent paper [5] a model has been proposed to describe the variation of electrical conductivity with densification during sintering of an as-pressed, porous ceramic green ware. Assuming a monosize particle diameter distribution, the model predicts the change in relative density, ρ/ρ_{th}, with progressive sintering. The gradual thickening of the neck area between neighbouring particles for a three-dimensional cubic array of equivalent spheres is calculated by approximating the neck area by two sine-wave functions.

Thus, the purpose of the present work is to use the same model [5] for developing a relationship between the normalized minimum contact area (NMCA) fraction of a solid and Young's modulus of porous ceramics. The applicability of the proposed relationship has been evaluated for 12 experimental relative Young's modulus, E/E_0, versus pore volume fraction, P, data sets from the literature on five different ceramic oxides, namely Lu_2O_3, Sm_2O_3, Yb_2O_3, Al_2O_3 and ThO_2. The selection of these data sets has been made on the basis that analyses by earlier investigators indicate that the behaviour of these materials closely resembles the cubic packing of the initial powder particles [6, 7].

2. Theory

The model is based on one given by Misuzaki *et al.* [5]. It considers the gradual change in the minimum solid area of contact between neighbouring grains with the progress of densification for an idealized simple cubic arrangement of equivalent spheres. To simplify the situation, a physical picture of sintering a simple cubic array of equivalent spheres has been considered. During sintering each sphere is welded to six nearest neighbours. This causes shrinkage and, hence, densification along the three mutually perpendicular axes. This makes the three-dimensional array turn parallel forming rectangular parallelopipeds, each of which contains a uniaxial string of spheres. The stages of shrinkage leading to further densification continue until each string of spheres becomes a compact square bar. The aggregation of these square bars generates the sintered compact. Now as suggested by Rice [4], the elastic–mechanical properties shall be determined basically by the relative density and the availability of a minimum solid area of contact at the neck between the particles along the direction of the externally applied stress. Therefore, consideration of only one string of spheres along the stress axis suffices. It is assumed that, before sintering, the cross-section of the string along the prospective stress axis is a series of circles with diameters a_i. On completion of sintering, the string turns to a rod of diameter a_f ($< a_i$). During sintering, the string can be expressed by the rotation of a wave function, $f(x)$, with a period $2a$ [5]

$$f(x) = f(x + 2na) \tag{1}$$

It can be asserted that shrinkage of the string both along and perpendicular to the x-axis can take place during sintering. Therefore, it follows that with progressive sintering parameter a becomes smaller, and so the maximum of $f(x)$, say a_t, decreases from its initial value, a_i, to the final value, a_f; consequent to development of densification during sintering in the porous ceramic green body. Mizusaki *et al.* [5] have shown from this premise that the relative density, ρ/ρ_{th}, can be expressed as

$$(\rho/\rho_{th}) = \int_0^{2a} [f(x)/a_t]^2 \, dx \tag{2}$$

Because a_t is the maximum of $f(x)$, it follows that

$$-1 \leqslant f(x)/a_t \leqslant 1 \tag{3}$$

The implication of Equation 3 is that the estimation of ρ/ρ_{th} requires only a change of relative form of $f(x)$ and not the time rate of change of a_t or a be considered. The change in shape of the neck area between two particles during the course of sintering has been modelled, as shown in Fig. 1, by a combination of the following two sine-wave functions [5]. For $0 \leqslant x \leqslant c$.

$$f(x) = (a_t)\{(1 + r_0)/2 + [(1 - r_0)/2][\sin(\pi x/c)]\} \tag{4}$$

and for $c \leqslant x \leqslant 1$

$$f(x) = (a_t)\{(1 + r_0)/2 + [(1 - r_0)/2] \times \sin[\pi(x + 1 - 2c)/(1 - c)]\} \tag{5}$$

The first expression above, Equation 4, represents the shape of a sphere. Equation 5 signifies the shape of the neck between neighbouring spheres. The factor r_0 stands for the ratio of the minimum diameter at the neck to the maximum diameter of the rotating body. Based on these assumptions it has been shown that the expression for relative density is [5]

$$\rho/\rho_{th} = 4c \int_0^{1/4} \{(1 + r_0)/2 + [(1 - r_0)/2] \sin 2\pi y\}^2 \, dy + 4(1 - c) \int_{-1/4}^{0} \{(1 + r_0)/2 + [(1 - r_0)/2] \sin 2\pi z\}^2 \, dz \tag{6}$$

where the quantities r_0 and c are explained in Fig. 1 and y and z are dummy variables. Now, substituting $a = (1 + r_0)/2$ and $b = (1 - r_0)/2$ and carrying out the integration analytically, rather than numerically as done in [5], we obtain from Equation 6

$$\rho/\rho_{th} = [a^2 - (4ab/\pi) + (b^2/2) + (8abc/\pi)] \tag{7}$$

Therefore, the pore volume fraction, P, is given by

$$P = 1 - (\rho/\rho_{th}) = \{1 - [a^2 - (4ab/\pi) + (b^2/2) + (8abc/\pi)]\} \tag{8}$$

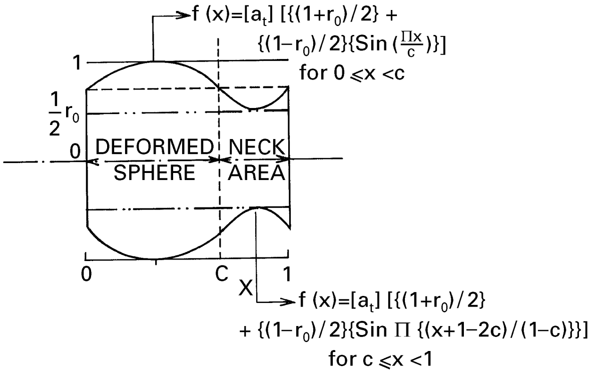

Figure 1 Sine-wave functions for the approximations of a partially deformed sphere and the developing neck area between two neighbouring spheres during sintering of simple cubic packed monosized spheres, along with the definitions of the parameters c and r_0, following the model of Misuzaki *et al.* [5].

Now, it follows from Fig. 1c that the minimum contact area (MCA) is at $x = (1 + c)/2$, i.e. at the mid-point of the neck between two neighbouring particles and, hence, from Equation 5 the diameter, $f(x)$, at $x = (1 + c)/2$ is given by

$$f(x) = a_t r_0 \tag{9}$$

The corresponding MCA becomes

$$\text{MCA} = (\pi/4) a_t^2 r_0^2 \tag{10}$$

Equation 10 shows that the MCA at any point of sintering is reduced by a factor r_0^2 from its maximum value, $(\pi/4)a_t^2$, at $r_0 = 1$, i.e. in the fully sintered condition. Therefore, the ratio of the normalized MCA (NMCA) fraction to the pore volume fraction, P, is given by the following expression

$$\text{NMCA}/P = [(r_0^2)]/\{1 - [\mathrm{a}^2 - (4ab/\pi) + (b^2/2) + (8abc/\pi)]\} \tag{11}$$

Equation 11 forms the basis for prediction of the NMCA fraction of a solid as a function of pore volume fraction, P, with c as the adjustable parameter.

3. Results

The materials investigated were Lu_2O_3, Yb_2O_3, Sm_2O_3, Al_2O_3 and ThO_2 [7–14]. The values of E/E_0 for different given porosities were calculated from the reported experimental Young's modulus, E, data, with the value of E_0, the Young's modulus of zero porosity material, suggested in the same references.

Fig. 2 shows the variation of E/E_0 with pore volume fraction, P, for three different data sets on Lu_2O_3 [8], Sm_2O_3 [9] and Yb_2O_3 [10]. A computer program was also run to calculate the variation of the normalized minimum contact area (NMCA) fraction with pore volume fraction, P, from Equation 11, with different values of the adjustable parameter, c, which provides the best fit to the trend in the aforementioned data of E/E_0 versus P. Thus, the variations of the NMCA fractions of the solids with P (for $c = 0.64$, 0.58 and 0.52 for Lu_2O_3, Sm_2O_3 and Yb_2O_3, respectively) are also plotted in the same Fig. 2. The excellent match between the predicted trend from the proposed NMCA

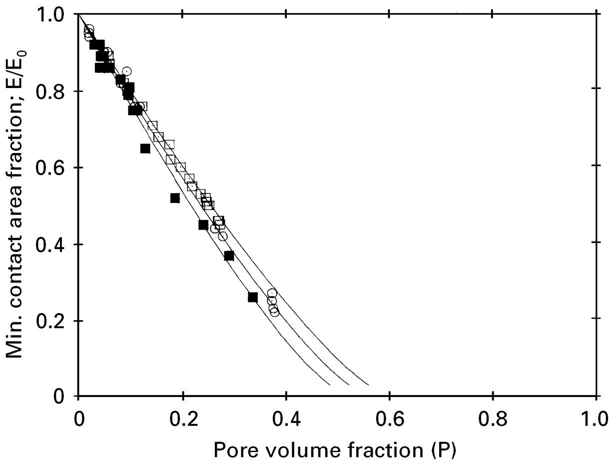

Figure 2 Variation of relative Young's modulus, E/E_0, and normalized minimum contact area (NMCA) fraction of solid with the pore volume fraction, P, of Lu_2O_3 (■), Sm_2O_3 (⊙) and Yb_2O_3 (⊡). The solid lines represent the best fits to the experimental data from the literature [8–10] according to the proposed relationship (Equation 11) between the NMCA fraction of the solid and P.

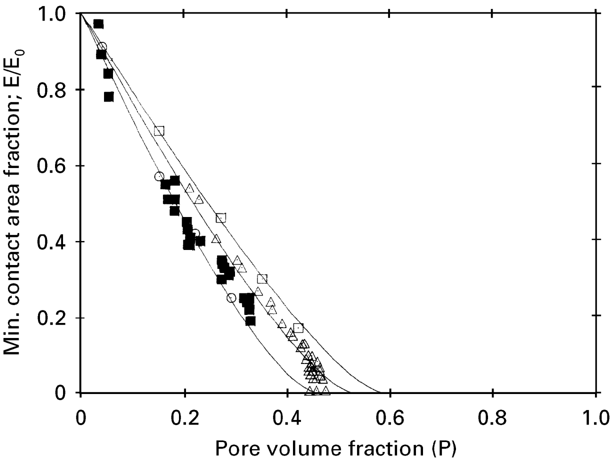

Figure 3 Variation of relative Young's modulus, E/E_0, and normalized minimum contact area (NMCA) fraction of solid with the pore volume fraction, P, of Al_2O_3. The solid lines represent the best fits to the experimental data from the literature [7 (■), 12 (⊙), 13 (△, ⊡)] according to the proposed relationship (Equation 11) between the NMCA fraction of the solid and P.

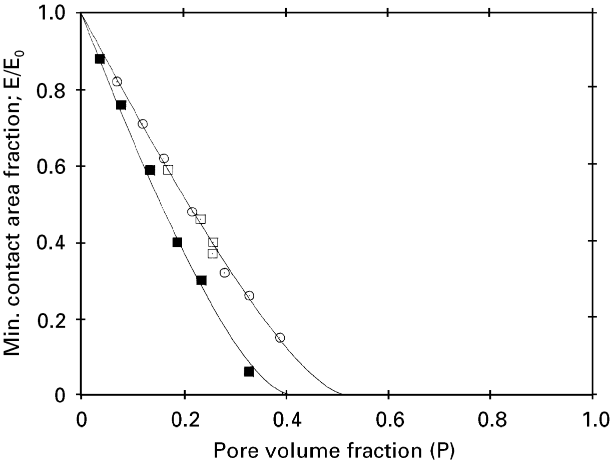

Figure 4 Variation of relative Young's modulus, E/E_0, and normalized minimum contact area (NMCA) fraction of solid with the pore volume fraction, P, of ThO_2 [(■) group I, (⊙) group II, (⊡) group III]. The solid lines represent best fits to the experimental data from the literature [14] according to the proposed relationship (Equation 11) between the NMCA fraction of the solid and P.

fraction concept (Equation 11) and the experimental data speaks for itself. The present observation also agrees with earlier suggestions, that the nature of packing for the initial powders was most likely cubic in these materials [6].

Fig. 3 presents the results of a similar analysis to that mentioned above for six sets of data on alumina taken from the literature [7, 12, 13]. Similar results for three sets of data on thoria [14] are presented in Fig. 4. The match between the trend predicted from the proposed relationship (Equation 11) and the experimental data is excellent in the case of thoria ($c = 0.65$ and 0.82, Fig. 4). Note that all the data sets for alumina fall within the predicted limits of $c = 0.55$–0.75, Fig. 3. In general, for alumina also the match between the trends predicted from the proposed NMCA fraction concept and the experimental data is quite good except at very low porosity, e.g. for the data of Green *et al.* [13], where the experimental data slightly deviate from the predicted trends. This may be due to two factors: (i) uncertainties in the experimental data at such high porosities ($P > 0.40$), or (ii) inherent limitations in the model for the assumptions of cubic packing of monosized particles. However, the excellent match between the predicted trend and the experimental data in most of the Al_2O_3 ceramics considered here strongly suggests the possible presence of cubic packing in the initial as-pressed powder compact, as was also suggested earlier by Wang [7].

The pore volume fraction, P, at which the Young's modulus becomes zero is termed the *critical pore volume fraction*, P_{cr} [6]. The results of the present work predict P_{cr} as 0.54 for Lu_2O_3, 0.58 for Sm_2O_3, 0.62 for Yb_2O_3 (i.e. an average of 0.58 for the rare earth oxides, Fig. 2), 0.46 and 0.60 (i.e. an average value of 0.53) for Al_2O_3 (Fig. 3), and 0.43 and 0.52 (i.e. an average value of 0.48) for ThO_2 (Fig. 4). The basis of the prediction is the porosity at which the NMCA fraction of the solid becomes zero for the respective c values which give the best fit to the corresponding experimental relative Young's modulus versus pore volume fraction data. These predicted P_{cr} values lie in the range $0.43 \leqslant P_{cr} \leqslant 0.62$, which tallies with the range $0.40 \leqslant P_{cr} \leqslant 0.53$ as observed by Lam *et al.* [12], as well as with the range $0.40 \leqslant P \leqslant 0.60$, typically found in practice, for as-pressed ceramic green ware [5].

The present results suggest that the proposed model, based on the minimum contact area concept suggested initially by Knudsen [15] and expanded by Rice [1–4], can predict the experimentally observed trend of variation in relative Young's modulus with pore volume fraction quite accurately. The inherent limitation of the model lies in the simplifying assumption that it considers the cubic packing sintering of monosized spheres. In practice, however, the particle shape may not be exactly spherical and the size distribution may not be monomodal. Moreover, the model does not consider the introduction of stress concentration effects due to reduction in neck area between neighbouring particles during the course of sintering.

In spite of these inherent limitations the model predicts the experimental data trend for several ceramic oxides quite well, thus confirming the observations made by Rice [1]: "neither basic concepts nor broad polycrystalline experience show any significant dependence of elastic properties on microstructural stress concentration *per se*".

4. Conclusions

A new relationship is proposed between the normalized minimum contact area (NMCA) fraction of a solid and the corresponding pore volume fraction, P, from considerations of modelling the change in neck area between two particles during sintering of an idealized assembly of monosized spheres stacked in simple cubic packing. The trends of variation in the NMCA fraction with P as predicted by the present model bear excellent agreement with 12 sets of experimental data from the literature on relative Young's modulus, E/E_0, versus pore volume fraction, P, of five different polycrystalline ceramic oxides, namely Lu_2O_3, Sm_2O_3, Yb_2O_3, Al_2O_3 and ThO_2.

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