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Original article

Modeling of Young's modulus and thermal conductivity evolution of partially sintered alumina ceramics with pore shape changes from concave to convex

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ABSTRACT

Numerical calculations of the effective (relative) Young's modulus and thermal conductivity have been performed for porous model materials on computer-generated digital microstructures with a transition from concave to convex pore shape. The results are compared to the case of purely concave and convex pores (isolated or overlapping). It is shown that the Pabst-Gregorová cross-property relation for isotropic porous materials with isometric pores gives an excellent prediction of effective (relative) properties for materials with a transition from concave to convex pore shape. With accuracy better than 0.010 relative property units (RPU) this prediction is far better than the prediction by any other cross-property relation currently known. For the intermediate (concave-convex) microstructures the accuracy of this cross-property relation is better than that for microstructures with purely concave pores (accuracy better than 0.034 RPU) and, surprisingly, even better than for purely convex pores (accuracy better than 0.011–0.013 RPU).

1. Introduction

Partial sintering is one of the many methods that can be applied for fabricating porous ceramics (or other materials, e.g. metals or glasses) from powder compacts [1–10]. It is mainly used for single-phase materials, where sintering occurs by diffusion processes without a liquid melt (solid state sintering [11]), and is realized by firing the material at a temperature that is lower (or a time that is shorter) than required for full densification. The initial powder compact (e.g. after pressing) or the green body (e.g. after slip casting, dewatering and drying) consists typically of convex particles in point contact, the average number of contact points (coordination number) being 7 for random close (dense) [11] or maximally random jammed [12] packing of monodispersed spherical particles. The pore space between these convex particles (intergranular void space) is fully connected and exhibits a purely concave surface. During sintering the point contacts become area contacts, first (in the initial stage of sintering) in the form of sinter necks, with a cross section dictated by the particle shape (circular if the particles are spherical), and then (in the intermediate and final stage of sintering) in the form of grain boundaries, whose shape becomes polyangular (with five edges on average [11]) and whose number increases to an average of 14 faces per grain [11], when full densification is approached. At the same time the pore space transforms from its fully connected, purely concave state (powder compact before sintering), through a state with essentially concave pore space surface and convex singularities in the form of sinter necks (intial stage of sintering) to an interconnected network of pore channels along the grain edges (intermediate stage of sintering) and finally to a state in which the pores are convex and isolated (final stage of sintering) [11]. In principle, the sintering process can be stopped at an arbitrary stage of this sequence by rapidly cooling down. Then the resulting microstructure is that of a partially sintered material.

The determination of the effective properties of partially sintered materials is a long-standing and still largely unsolved problem of materials science and technology, although the first attempts to solve this problem date back almost six decades ago [13]. They are related to the so-called minimum contact area or minimum solid area approach [14–20], which has recently been shown to be highly misleading [21]. What has become universally recognized through decades of research is the fact that the effective property values, in particular strength (compressive, flexural, tensile etc.), elastic moduli (Young's modulus, shear modulus, bulk modulus) and conductivities (thermal conductivity, electrical conductivity), of partially sintered materials are lower than those of their isoporous counterparts fabricated in another way, e.g. by using pore formers or foaming [10]. The obvious reason for this difference is pore shape: for sufficiently high porosity, partially

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sintered materials exhibit a pore space with essentially concave surface curvature. Unfortunately, due to the absence of exact single-pore solutions for other than ellipsoidal shapes [22] and the fact that the pore space of partially sintered materials is fully connected initially (bicontinuous microstructure) and retains its bicontinuous character down to rather low porosities, individual concave pores are neither amenable to analytical modeling (not even in the case of periodic arrays) nor very interesting from the practical point of view. Therefore, numerical modeling is the only way to calculate the effective properties of materials with essentially concave pore space surface curvature.

While the case of convex (spherical or spheroidal) pores, isolated or overlapping, has been treated previously by many authors, and also numerical calculations for materials with a concave pore space surface curvature (intergranular void space) are available [23,24], all these calculations have been performed either for elastic properties or for conductivity (thermal or electrical). We are not aware of any work that compares results for elastic moduli and conductivity for materials with concave pores, although the application of cross-property relations would represent a major progress in this field. Moreover, as explained above, real sintering processes usually do not result in purely concave pores. Therefore it would be interesting to investigate the effective properties of materials that exhibit intermediate microstructures with a transition from a fully connected pore space with purely concave surface (bicontinuous microstructure) to purely convex isolated pores (matrix-inclusion microstructure). It can be expected that even a crude approach that takes into account this transition would yield results that are much more realistic for partially sintered materials and much more representative for real sintering processes than an approach that takes into account only concave pores. Therefore, the present work reports recent results of numerical property calculations (Young's modulus and thermal conductivity) based on digital microstructures that exhibit intermediate microstructures with both concave and convex pore surface features. Based on these results the accuracy of cross-property relations is tested and compared

2. Theoretical

For many purposes porous materials can be considered as two-phase composites, consisting of a solid phase and a pore phase. When the property values of the pore phase are negligibly small compared to those of the solid phase, it makes sense to define relative properties, e.g. the relative Young's modulus and relative thermal conductivity [25,26],

$$k_r = \frac{k}{k_0}, \quad E_r = \frac{E}{E_0}, \tag{1a,b}$$

respectively, where k and E are the effective thermal conductivity and Young's modulus of the porous material as a whole and k_0 and E_0 the corresponding values of the dense (i.e. pore-free) solid phase. Irrespective of the microstructure (which can even be anisotropic), these relative properties are bounded from above by the upper bounds (upper Wiener bound [27] for the thermal conductivity and upper Paul bound [28], often called Voigt bound, for the Young's modulus)

$$k_r \le 1-\phi, \quad E_r \le 1-\phi, \tag{2a,b}$$

where ϕ is the porosity (i.e. the volume fraction of the pore space) and the equality sign applies to materials with translational invariance in the direction of the applied field (stress field or temperature gradient field). For isotropic microstructures we have the upper Hashin-Shtrikman bounds [29,30],

$$k_r \le \frac{1-\phi}{1+\phi/2}, \quad E_r \le \frac{1-\phi}{1+\phi}, \tag{3a,b}$$

where the equality sign holds only for very special types of microstructures [31,32]. This is essentially all that can be said without adopting model assumptions. The simplest assumption on which analytical modeling can be based is that of spherical pores. For this case the single-inclusion solutions are [33–35]

$$k_r = 1 - \tfrac{3}{2}\phi, \quad E_r = 1 - 2\phi, \tag{4a,b}$$

where the former is always exact and the latter is exact for solid Poisson ratios of 0.2 and 1/3, but remains an excellent approximation for all Poisson ratios, as long as the solid is non-auxetic. Albeit exact for the case of a single spherical pore in an infinitely extended solid, from the viewpoint of real materials these are just linear approximations, for which validity can be expected only for very low porosities. Under this circumstance also the well-known non-linear model relations [36]

$$k_r = (1-\phi)^{3/2}, \quad E_r = (1-\phi)^2, \tag{5a,b}$$

(power-law relation) and [37,38]

$$k_r = \exp\left(\frac{-\frac{3}{2}\phi}{1-\phi}\right), \quad E_r = \exp\left(\frac{-2\phi}{1-\phi}\right). \tag{6a,b}$$

(exponential relation) reduce to the aforementioned linear approximations.

Materials exhibiting a certain type of behavior (linear, power-law, exponential etc.) for one property (e.g. thermal conductivity), exhibit the same type of behavior, but with another numerical coefficient, also for another property (e.g. Young's modulus). Based on this fact, and the complete analogy of the porosity dependences reflected by Eq. (2) through (6), the following cross-property relations (CPRs) can be derived [26,39]:

$$E_r = k_r, \tag{7}$$

$$E_r = \frac{3k_r}{4-k_r}, \tag{8}$$

$$E_r = \frac{4k_r - 1}{3}, \tag{9}$$

$$E_r = k_r^{4/3}. \tag{10}$$

For reasons of convenience these CPRs will be denoted as WP-CPR (Wiener-Paul), HS-CPR (Hashin-Shtrikman), lin-CPR (linear) and PG-CPR (Pabst-Gregorová) in the sequel. Althougth their derivation is based on spherical pore shape, preliminary experience has shown that CPRs in the present form are suitable for isotropic porous materials with isometric pores of any shape. Moreover, based on the Eshelby solution for ellipsoidal inclusions [40–43], these CPRs can even be generalized to isotropic porous materials with anisometric (spheroidal) pores [44]. Since the present paper does not deal with anisometric pores, this possibility of generalization is not used here.

3. Experimental

3.1. Generation of digital microstructures

The digital microstructures in this work have been generated and all numerical calculations have been performed using the GeoDict® software package [45] in boxes (representative volume elements) with 200 × 200 × 200 cubic voxels (the voxel edge length being set to 1 μm). The pore diameters of the convex pores (spherical, isolated or overlapping) were chosen to be 15 μm (monodisperse). Microstructures with randomly arranged concave pores (i.e. intergranular voids between convex isometric grains) have been obtained using the GrainGeo® module by creating a maximally random jammed packing (with packing density 64%) of 15 μm spherical particles and letting the particle diameters grow uniformly via the GeoDict® "sedimentation algorithm", thus transforming point contacts into contact areas and reducing the porosity down to values approaching zero. The algorithm ensures that the pores remain concave until full densification is achieved. On the other hand, microstructures with a transition from