Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Young's modulus and thermal conductivity of model materials with convex or concave pores – from analytical predictions to numerical results

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ARTICLE INFO

Keywords:
Porous ceramics
Pore shape (convex, concave)
Microstructure
Elastic properties
Thermal conductivity

ABSTRACT

The effective Young's modulus and thermal conductivity of porous materials can be rigorously bounded from above via micromechanical bounds (upper Wiener–Paul bounds and upper Hashin–Shtrikman bounds), and several model relations are commonly used as tentative approximate predictions (Maxwell-type, Coble–Kingery-type, power-law and exponential relations). Based on numerical calculations on computer-generated digital model microstructures, both periodic and random, it is shown that these model relations provide rough approximations that are more or less appropriate for microstructures with essentially convex pores, but are not suitable for microstructures with concave pores. On the other hand, the Pabst–Gregorová cross-property relation provides a very accurate (better than 0.04 relative property units) analytical prediction for the relative Young's modulus of isotropic porous materials with isometric pores, both convex and concave, when the relative thermal conductivity is known. It is shown that this cross-property relation is the best prediction currently available for isotropic porous materials with isometric pores.

1. Introduction

The estimation of the effective properties of heterogeneous materials, especially multiphase materials (e.g. composites and porous materials), is one of the most important problems in materials science and the theory of materials. In particular, the prediction of the effective properties of porous materials is a key problem, because porosity is a ubiquitous feature in virtually all classes of natural and man-made materials, i.e. the artificial products of most processing techniques. While for dense composites many effective properties, e.g. elastic moduli and thermal (or electrical) conductivity, can be predicted with satisfactory accuracy by rigorous micromechanical bounds, when the volume fractions and phase properties are known (at least as long as the phase property contrast, i.e. the ratio of the phase properties, remains sufficiently close to unity) [1–3], the difference between upper and lower bounds increases as the phase property contrast deviates from unity. In the extreme case of porous materials, where the pore phase property values are negligibly small compared to those of the solid phase, the lower bounds become zero for all finite pore volume fractions and therefore inefficient. In this case it is common practice to invoke model relations, when a more concrete prediction of the effective properties is needed. The most popular model relations for the purpose of prediction are effective medium approximations, such as Maxwell-type, self-consistent and differential models [1–3], as well as our (Pabst–Gregorová-type) exponential relations [4–6] and Coble–Kingery-type relations [7–9]. For low porosity all these relations reduce to the exact solution of the corresponding single-inclusion problem (i.e. the solution for infinitely low porosity, corresponding for real materials to the so-called linear or non-interaction approximation [3], e.g. for spherical pores [10–12]), and for high porosity the form of these relations ensures that the corresponding upper bounds (e.g. the upper Wiener bound for the conductivity of isotropic or anisotropic porous materials [13], the upper Paul bound for the elastic modulus of isotropic or anisotropic porous materials [14] or the corresponding upper Hashin–Shtrikman bounds [15,16] for isotropic porous materials) are not exceeded.

Now it is well known that apart from porosity, i.e. the volume fraction of pores (or, more generally, the volume fraction of the pore space), also other microstructural features determine the effective properties. There are several approaches to take these microstructural features into account, i.e. to quantify them and implement them into rigorous bounds (e.g. three-point bounds [1–3]) or model relations (e.g. cluster expansions or effective medium approximations [1–3]). While the correlation function approach [1,2] is systematic and general, but laborious to realize, difficult to implement and not without practical limits, a more pragmatic approach consists in identifying and

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https://doi.org/10.1016/j.jeurceramsoc.2018.01.040
Received 5 November 2017; Received in revised form 23 January 2018; Accepted 27 January 2018

subsequently quantifying key features of the microstructure that are likely to have a stronger influence on the effective properties than others. It is well known, for example, that the shape of pores has a significant influence on the effective elastic moduli and conductivity of porous materials, and there are many reasons to surmise that the influence of pore shape overshadows other influences on these properties, such as pore size, pore size distribution, pore distance, spatial pore distribution etc. (Numerical results underpinning this conjecture will be given in a subsequent paper.) It is also known that large deviations from spherical pore shape can strongly affect the effective properties even at low porosity. Of course, for anisometric pores that can be approximately considered as rotationally symmetric, e.g. elongated (prolate) or flattened (oblate) pores, spheroids are the model shape of choice, because the shape of spheroids (biaxial ellipsoids) can be uniquely described by a single aspect ratio and exact single-inclusion solutions of the Eshelby type [17] are available (the latter are available also for triaxial ellipsoids, but these require two aspect ratios for a unique description of their shape). These single-inclusion solutions for the effective elastic moduli and conductivity of materials with ellipsoidal or spheroidal pores are well known [1–3,18], and their implementation into effective medium approximations is straightforward [19–27], so that it can be expected that the effective elastic moduli and conductivity of porous materials with ellipsoidal or spheroidal voids can be roughly predicted, in a similar way as for materials with spherical pores and to a similar degree of approximation, according to one or another effective medium approximation.

Unfortunately many porous materials, e.g. powder compacts obtained by pressing or partially sintered ceramics, have pores that are neither spherical nor spheroidal or ellipsoidal. In this case the absence of the “Eshelby property” [28–34] principally precludes any analytical modeling of the porosity dependence of the effective properties. In particular, so-called “minimum solid area models ”(also called “minimum contact area models”), which have been often invoked for tentatively predicting the porosity dependence of effective elastic moduli and thermal conductivity of porous materials materials with concave pores [35–49], have recently been shown to be useless [50], because they yield completely misleading conclusions even in the simplest case for which these models have been originally designed and for which a minimum solid area can be well defined and easily calculated, i.e. for monosized grains (initially spherical particles with point contacts) in a simple cubic array [50]. Indeed, in the field of partially sintered materials, so-called minimum solid area models have misled many authors and have resulted in considerable confusion in the literature, including repeated statements of an allegedly “possible presence of (simple) cubic packing in the initial as-pressed powder compact” [41]. Therefore, numerical modeling is currently the only way to calculate the effective properties of porous materials with concave pores. Only this type of modeling can be expected to correctly predict the well-known and frequently observed fact, well documented by experimental data on powder compacts and partially sintered materials [35–49,51–55], that materials with concave pores (e.g. interparticle voids between spherical particles) exhibit effective Young’s modulus and conductivity values that are (for the same porosity) significantly below those of materials with convex isometric (e.g. approximately spherical) pores. In order to obtain results that are unaffected by undesired microstructural defects, e.g. microcracks or other defects resulting from specific material processing issues, it is useful to perform these calculations on computer-generated digital model microstructures, which are free of such bias. Although numerical calculations of this type have been performed by several authors in the past, mainly by Roberts and Garboczi [56,57], these previous papers focus either on conductivity or on elastic properties, but there is no work in the current literature that compares both elastic moduli and conductivity for the same microstructures and compares them with the predictions of our cross-property relation [58]. Therefore this work investigates, by numerical calculations on computer-generated digital microstructures, the porosity dependence of the Young’s modulus and thermal conductivity of cubic and isotropic porous materials with isometric pores *vis-a-vis* the upper Wiener–Paul bounds, the upper Hashin–Shtrikman bounds, the power-law predictions, the Coble–Kingery relations and our (Pabst–-Gregorová-type) exponential predictions. This paper reports, for the first time, the remarkable fact that even in the case of concave pores, for which all effective medium approximations fail, the relative Young’s modulus can still be predicted with great accuracy via our cross-property relation [58], when the relative thermal conductivity is known, and *vice versa*.

2. Theory: rigorous bounds, predictive models and cross-property relations

2.1. Rigorous micromechanical bounds

Depending on the microstructural information available (e.g. one-point, two-point, three-point correlation functions and parameters [1–3]) rigorous bounds of higher order (theoretically up to fourth order [1]) can be applied to delimit the possible effective property values. However, when the only microstructural information available are one-point correlation functions (i.e. volume fractions), only the one-point bounds (for microstructures of arbitrary symmetry, i.e. isotropic or anisotropic ones) and the two-point bounds for isotropic microstructures remain. Moreover, in the case of porous materials with negligible pore phase property values the phase property contrast is infinitely high, and all lower bounds (at least all classical, so-called “contrast bounds ”[1]), tend to be zero. Defining the relative thermal conductivity k_r and Young’s modulus E_r as

$$k_r = \frac{k}{k_0}, \tag{1a}$$

$$E_r = \frac{E}{E_0}, \tag{1b}$$

respectively, where k and E are the effective thermal conductivity and Young’s modulus of the porous material and k_0 and E_0 the corresponding values of the dense (i.e. pore-free) solid, the one-point upper bounds (upper Wiener bound [13] for the thermal conductivity and upper Paul bound [14], often called Voigt bound, for the Young’s modulus) are

$$k_r \leq 1 - \phi, \tag{2a}$$

$$E_r \leq 1 - \phi, \tag{2b}$$

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).

The relative thermal conductivity and Young’s modulus of isotropic porous materials with zero pore phase property values are bounded from above via the upper two-point bounds (upper Hashin–Shtrikman bounds) [8,9] in the form [6]

$$k_r \leq \frac{1 - \phi}{1 + \phi/2}, \tag{3a}$$

$$E_r \leq \frac{1 - \phi}{1 + \phi}, \tag{3b}$$

respectively. The inequality for thermal conductivity, Eq. (3a), is valid for isotropic porous materials without any restriction, while the inequality for Young’s modulus, Eq. (3b), corresponds to the upper Hashin–Shtrikman bound exactly only when the Poisson ratio is 0.2 or 1/3 [59]. Nevertheless, as long as the solid phase is non-auxetic, it is an excellent approximation to the upper Hashin–Shtrikman bound also for other Poisson ratio values, at least in the range 0.1–0.4.