EFFECTIVE ELASTIC PROPERTIES OF ALUMINA-ZIRCONIA COMPOSITE CERAMICS - PART 2. MICROMECHANICAL MODELING

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In this second paper of a series on the effective elastic properties of alumina-zirconia composite ceramics, principles of micromechnical modeling are reviewed and the most important relations are recalled. Rigorous bounds (Voigt-Reuss bounds) are given for the (scalar) effective elastic moduli (tensile modulus E, shear modulus G and bulk modulus K) of polycrystalline ceramics as calculated from monocrystal data (i.e. components of the elasticity tensor). Voigt-Reuss bounds and Hashin-Shtrikman bounds of the elastic moduli are given for two-phase composites. For porous materials, which can be considered as a degenerate case of two-phase composites where one phase is the void phase (with zero elastic moduli), micromechanical approximations (so-called dilute approximations, Dewey-Mackenzie formulae) are given. Apart from a heuristic extension of the dilute approximations in the form of so-called Coble-Kingery relations, semi-empirical extensions of the micromechanical approximations are given for the tensile modulus (Spriggs relation, modified exponential and Mooney-type relations, generalized / Archie-type power law relation, Phani-Niyogi / Krieger-type power law relation, Hasselman relation), including the new relation $E/E_0 = (1 - \phi) \cdot (1 - \phi/\phi_C)$, recently proposed by the authors, where E is the effective tensile modulus, ϕ the porosity, E_0 the tensile modulus of the dense (i.e. pore-free) ceramic material and ϕ_C the critical porosity.

INTRODUCTION

In Part 1 of this series of papers, the linear theory of elasticity has been summarized for anisotropic and isotropic materials in general [1]. In this theory, which is embedded in the general framework of rational mechanics and is known to be appropriate for brittle materials (e.g. ceramics at room temperature), the material is assumed to be a classical continuum, i.e. a single body (a one-constituent continuum) and not a multiple body (i.e. a superposition of several one-constituent continua) in the sense of rational mixture theory [2-5]. In other words, the material is considered from a macroscopic point of view, where microstructural heterogeneities are smeared out and reveal themselves only indirectly via the specific material properties.[1] In general these "properties" (i.e. the coefficients in the linear constitutive equations) have to be determined by direct measurement. It is the long-standing aim of research in rational mixture theory, however, to predict the mixture properties (and in general all mixture quantities) from those of the constituents by calculation only, without direct measurement. There are a few fortunate cases where this can be done with an accuracy sufficient for practical purposes. Such is the case for non-reacting multiphase mixtures or, more generally, materials with microstructure. These are the subject of the present paper. With regard to the purpose of this paper we confine ourselves to solid materials (linearly elastic, cf. [1]), with special emphasis on one-phase polycrystalline materials and two-phase materials (composites and porous materials).

Polycrystalline materials are one-phase materials with microstructure, usually uniform (in the absence of macroscopic gradients) but always heterogeneous (at the microscopic scale). They consist of small crystals (crystallites), isometric or anisometric (elongated / prolate or flat / oblate), held together by strong interaction forces (chemical bonds) and exhibiting random orientation or (a certain degree of) preferential orientation. Examples are densely sintered ceramic bodies. Polycrystalline materials with preferential orientation of anisometric crystallites are anisotropic. In a classical contribution [7,8] Voigt has shown, based on the isostrain assumption, that in the case of isotropic polycrystalline materials with a uniform and random microstructure the scalar elastic moduli can be calculated from the components of the elasticity tensor (stiffness matrix). In another classical paper [9], Reuss has proposed another result for this case, based on the isostress assumption and

using the components of the inverse elasticity tensor (compliance matrix), cf. [10-13]. In both approaches averaging is performed over all possible orientations of crystallites. Hill [14] was apparently the first to recognize that the Voigt and Reuss values were in fact the upper and lower bounds, respectively, to the property in question. Moreover, it turned out that for most practical purposes the Voigt and Reuss bound calculated for polycrystalline materials from monocrystal data are sufficiently close together to serve as a satisfactory estimate of the property value [13,14]. Comparison with experimental data has confirmed the validity of the Voigt-Reuss bounds and their usefulness for property prediction purposes. For further reference, the general procedure to calculate the Voigt and Reuss bounds for properties (elastic moduli) of polycrystalline materials is recalled in this paper.

The properties of multiphase materials with microstructure (= non-reacting multiphase mixtures) can in principle be predicted exactly when the properties of the constituent phases and all details of the microstructure are known. Of course the problem with this statement is the fact, that the microstructural details must be known quantitatively in order to properly formalize the abstract mathematical statement[2]

$$\text{Mixture property} = \text{Function} \atop (\text{phase properties, microstructure}). \qquad (1)$$

The theoretical framework to attack this task is called micromechanics. In micromechanics mixture properties are called effective properties. Effective properties of heterogeneous materials are the properties of heterogeneous media viewed from the macroscopic continuum level. The interested reader may consult one of the excellent monographs in this field [15-18], but the present paper is to a large degree self-contained. Micromechanics provides theoretical concepts for quantifying microstructural information to an arbitrary degree of precision and including it into the description of a material in the form of so-called correlation functions [17,18]. The lowest-order microstructural information (one-point correlation function) concerns only the volume fractions of the phases. Two-, three- and multi-point correlation functions involve information on the size, shape, orientation and mutual arrangement of the phases. Such higher-order correlation functions, however, are extremely difficult to determine. Evidently, for real materials[3] higher-order microstructural information is accessible only via tomographic techniques (direct 3D information) or, approximately, by image analysis of planar sections (3D information indirectly inferred from 2D information).

For the major part of the present paper we confine ourselves to the scalar effective elastic moduli M (where

M stands for the tensile modulus E, the shear modulus G or the bulk modulus K, respectively) as functions of the phase moduli M_i and microstructural information of the lowest order, the volume fractions ϕ_i. For this purpose we introduce the following basic assumption:

$$M = f(M_i, \phi_i) \qquad (2)$$

where M_i ($i = 0, 1, 2... n$) are the phase properties of all n phases and ϕ_i the volume fractions of the n phases. Note that the volume fractions of all n phases sum up to unity, i.e.

$$\sum_{i=0}^{n} \phi_i = 1 \qquad (3)$$

so that only $n - 1$ volume fractions are independent. Equation (2) is a widely accepted starting point of micromechanical modeling. At first sight it might seem sufficiently general to be of almost universal validity, since its only statement is that the effective property is a function of the phase properties and the phase volume fractions (existence of the function f). It might seem that further details of microstructure might only refine but not completely change this function. Consequently, the question of the validity or non-validity of equation (2) seems to be more or less an academic one. A simple example shows that this is not the case: an alumina suspension with 50 vol.% alumina can easily be prepared, but a porous alumina ceramic body containing 50 vol.% of (open, water-saturated) pores can also be prepared. In both cases the alumina volume fraction (or, alternatively, the water volume fraction or porosity) is 0.5, but the first system is a viscous suspension (E, G, K all zero, viscosity non-zero/finite), the second an elastic porous solid (E, G, K all non-zero/finite, viscosity infinite). Thus, equation (2) should be considered as a convenient working hypothesis only. Nevertheless, in the lack of more detailed microstructural information it is often the only feasible starting point for micromechanical modeling.

It is the main aim of the present paper to provide, on the basis of equation (2), the necessary micromechanical framework to model porous alumina, porous zirconia, dense alumina-zirconia composites and, finally, porous alumina-zirconia composites. However, many relevant relations will be given for the mathematical description of structure-property relationships in general.

Effective elastic moduli of polycrystalline materials

As detailed in Part 1 [1], the elastic behavior of anisotropic materials (monocrystals and anisotropic composites) is characterized by a fourth-order elasticity tensor, which can be represented, as a consequence of symmetry, as a (6 × 6) matrix. This matrix is again

symmetric with respect to its diagonal (due to energetic reasons), so that the maximum number of independent elements is 21 in the least symmetric case (triclinic monocrystal). For higher symmetries this number of independent elements is smaller.

When Hooke's law is written in engineering matrix notation as

$$\sigma_i = C_{ij}\,\varepsilon_j \qquad (4)$$

where σ_i is the 6-dimensional stress vector and ε_j is the 6-dimensional small strain vector, C_{ij} is called stiffness matrix. On the other hand, using the so-called compliance matrix $S_{ij} = C_{ij}^{-1}$ (the inverse of the stiffness matrix), Hooke's law can be written in the inverse form

$$\varepsilon_i = S_{ij}\,\sigma_j \qquad (5)$$

Note that the stiffness matrix and the compliance matrix have the same number of independent components (called elastic constants and elastic coefficients, respectively) and zero elements at the same positions, cf. [10,11]. The compliance matrix can be calculated from the stiffness matrix by matrix inversion as follows

$$S_{ij} = \frac{\text{subdet } (C_{ij})}{\det (C_{ij})} \qquad (6)$$

where subdet (C_{ij}) is the subdeterminant obtained by omitting the ith row and the jth column from C_{ij} and det (C_{ij}) is the determinant of C_{ij}. An analogous relation holds with the roles of S_{ij} and C_{ij} interchanged. For triclinic and monoclinic crystals the matrix inversion is lengthy and should preferably be performed by a computer. For materials of higher symmetry the matrix inversion simplifies considerably. E.g. for orthorhombic monocrystals and orthotropic polycrystalline materials or composites the number of independent components is 9 and we have [11]

$$S_{11} = \frac{\begin{vmatrix} C_{22} & C_{23} \\ C_{23} & C_{33} \end{vmatrix}}{\begin{vmatrix} C_{11} & C_{12} & C_{13} \\ C_{12} & C_{22} & C_{23} \\ C_{13} & C_{23} & C_{33} \end{vmatrix}} \qquad \text{etc.} \qquad (7)$$

$$S_{44} = \frac{1}{C_{44}} \qquad \text{etc.} \qquad (8)$$

For materials of even higher symmetry the inversion relations are as follows, cf. [11,13]:

● Trigonal monocrystals (6 independent components):

$$S_{11} + S_{12} = \frac{C_{33}}{K}\,,\; S_{11} - S_{12} = \frac{C_{44}}{K'}\,,\; S_{13} = -\frac{C_{13}}{K}\,,\quad (9a,b,c)$$

$$S_{14} = \frac{C_{14}}{K'}\,,\; S_{33} = \frac{C_{11} + C_{12}}{K}\,,\; S_{44} = \frac{C_{11} - C_{12}}{K'}\,. \quad (9d,e,f)$$

● Tetragonal monocrystals (6 independent components):

$$S_{11} + S_{12} = \frac{C_{33}}{K}\,,\; S_{11} - S_{12} = \frac{1}{C_{11} - C_{12}}\,,\; S_{13} = -\frac{C_{13}}{K}\,,$$
$$(10a,b,c)$$

$$S_{33} = \frac{C_{11} + C_{12}}{K}\,,\; S_{44} = \frac{1}{C_{44}}\,,\; S_{66} = \frac{1}{C_{66}}\,. \qquad (10d,e,f)$$

● Hexagonal monocrystals and transversely isotropic polycrystalline materials or composites (5 independent components):

$$S_{11} + S_{12} = \frac{C_{33}}{K}\,,\; S_{11} - S_{12} = \frac{1}{C_{11} - C_{12}}\,,\; S_{13} = -\frac{C_{13}}{K}\,,$$
$$(11a,b,c)$$

$$S_{33} = \frac{C_{11} + C_{12}}{K}\,,\; S_{44} = \frac{1}{C_{44}}\,. \qquad (11d,e)$$

● Cubic monocrystals (3 independent components):

$$S_{11} = \frac{C_{11} + C_{12}}{K''}\,,\; S_{12} = -\frac{C_{12}}{K''}\,,\; S_{44} = \frac{1}{C_{44}}\,. \qquad (12a,b,c)$$

In these relations K, K' and K'' have the following meaning:

$$K = C_{33}(C_{11} + C_{12}) - 2C_{13}^2\,, \qquad (13a)$$

$$K' = C_{44}(C_{11} - C_{12}) - 2C_{14}^2\,, \qquad (13b)$$

$$K'' = (C_{11} - C_{12})(C_{11} - 2C_{12})\,. \qquad (13c)$$

Totally analogous relations are valid with the stiffnesses C_{ij} interchanged by the compliances S_{ij}. Note, however, that for trigonal monocrystals, hexagonal monocrystals (including transversely isotropic polycrystalline materials or composites) and isotropic materials the elastic constant (stiffness) C_{66} is given by[4]

$$C_{66} = \tfrac{1}{2}\,(C_{11} - C_{12}) \qquad (14a)$$

cf. [1], while the elastic coefficient (compliance) S_{66} is given by [10]

$$S_{66} = 2\,(S_{11} - S_{12}) \qquad (14b)$$

Of course, for isotropic materials C_{66} and S_{66} are identical to $C_{44} = C_{55}$ and $S_{44} = S_{55}$, respectively [1], and therefore equation (12c) is redundant, since $S_{44} = \tfrac{1}{2}(S_{11} + S_{12})$:

● Isotropic materials (2 independent components):

$$S_{11} = \frac{C_{11} + C_{12}}{K''}\,,\; S_{12} = -\frac{C_{12}}{K''}\,. \qquad (15a,b)$$

Voigt [7,8] has shown that, under the assumption that the strain inside the material is uniform (isostrain assumption), the effective elastic moduli of a dense (i.e. pore-free) polycrystalline material composed of crystallites (i.e. small monocrystals) of arbitrary symmetry can be calculated from the 9 elastic constants (stiffnesses) C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{23}, C_{31}, when the material as a whole is statistically isotropic ("quasi-isotropic"), which requires random orientation of the anisotropic (and possibly anisometric) crystallites. Alternatively Reuss [9] has shown that, under the assumption that the stress inside the material is uniform (isostress assumption), the effective elastic moduli of a polycrystalline material composed of crystallites of arbitrary symmetry can be calculated from the 9 elastic coefficients (compliances) S_{11}, S_{22}, S_{33}, S_{44}, S_{55}, S_{66}, S_{12}, S_{23}, S_{31}, when the material as a whole is isotropic.[5]

According to Voigt the effective tensile modulus of a polycrystalline material is [7,8,11,12]

$$E_V = \frac{(A - B + 3C)(A + 2B)}{2A + 3B + C} \qquad (16)$$

the effective shear modulus

$$G_V = \frac{A - B + 3C}{5} \qquad (17)$$

and the effective bulk modulus

$$K_V = \frac{A + 2B}{3} \qquad (18)$$

In these expressions A, B, C are given by

$$A = \frac{C_{11} + C_{22} + C_{33}}{3} \qquad (19)$$

$$B = \frac{C_{12} + C_{23} + C_{31}}{3} \qquad (21)$$

$$C = \frac{C_{44} + C_{55} + C_{66}}{3} \qquad (21)$$

According to Reuss [9,11,12] the effective tensile modulus of a polycrystalline material is

$$E_R = \frac{5}{3X + 2Y + Z} \qquad (22)$$

the effective shear modulus

$$G_R = \frac{5}{4X - 4Y + 3Z} \qquad (23)$$

and the effective bulk modulus

$$K_R = \frac{1}{3(X + 2Y)} \qquad (24)$$

In these expressions X, Y, Z are given by

$$X = \frac{S_{11} + S_{22} + S_{33}}{3} \qquad (25)$$

$$Y = \frac{S_{12} + S_{23} + S_{31}}{3} \qquad (26)$$

$$Z = \frac{S_{44} + S_{55} + S_{66}}{3} \qquad (27)$$

Hill [14] has shown that the Voigt and Reuss values are the upper bound and the lower bound, respectively, of the effective elastic moduli M of statistically isotropic polycrystalline materials (Hill's theorem), i.e.

$$M_R \leq M \leq M_V \qquad (28)$$

Experience with the effective elastic properties of polycrystalline materials has shown that the Voigt bound and the Reuss bound are for practical purposes sufficiently close together. Therefore, the arithmetic average[6] of the Voigt and Reuss values,

$$M_{VRH} = \frac{M_V + M_R}{2} \qquad (29)$$

is often used as an estimate (approximate prediction) for the respective effective elastic modulus of dense polycrystalline materials ("Voigt-Reuss-Hill average", abbreviated "VRH-average").

We would like to close this section with a few words on the Poisson ratio. It is well known in elasticity theory (cf. e.g. [1,17]), that the Poisson ratio has several exceptional properties (e.g. in contrast to the elastic moduli E, G and K it can adopt negative values in principle). For the effective Poisson ratio of a polycrystalline or multiphase, possibly porous, material the situation seems to be still rather unclear and would need further investigation. According to our knowledge, neither explicit formulae in analogy to equations (16)-(18) and equations (22)-(24) are available for the effective Poisson ratio, nor is it known whether the effective Poisson ratio satisfes the Voigt-Reuss bounds or not. There is considerable confusion in the literature concerning this point. In the lack of a better alternative, it is often recommended e.g. to calculate the effective Poisson ratio of a composite via a simple mixture rule (arithmetic average of the end components weighted by volume fractions). This would correspond to a Voigt value and might, by analogy, suggest the possibility to calculate the effective Poisson ratio of an isotropic polycrystalline material via the standard formulae

$$\nu = \frac{E - 2G}{2G} = \frac{3K - 2G}{2(3K + G)} = \frac{3K - E}{6K} \qquad (30)$$

using the Voigt values E_V, G_V and K_V in place of E, G and K. It is known, however, that in the case of porous materials (degenerate case of composites where one phase is the void phase exhibiting zero elastic moduli) the mixture rule for the effective Poisson ratio evidently fails, since the effective Poisson ratio approaches a value of

0.2 for porosities approaching 100 % (e.g. in foams) and not 0 (as should be the case if the mixture rule would apply here). It would exceed the scope of this paper to discuss this paradoxical situation further. For further information the interested reader can consult [17] and [19,20].

Voigt-Reuss bounds for the effective elastic moduli of multiphase materials

When in a multiphase material the properties of the individual phases (constituents) are known, it can be expected that certain bounds on the effective property of the multiphase material (mixture) can be given without further microstructural information. This is indeed the case.[7] It is plausible e.g. that the value of the effective property of a multiphase material, whose carrier are the bulk phases and not the phase boundaries, should neither be lower nor higher than the value of that property for any of the individual phases.[8] Therefore it can be concluded that such an effective (mixture) property of the multiphase material, e.g. the effective elastic modulus M must be some kind of average value of all the phase (constituent) properties, e.g. the elastic moduli M_i. The most general average value is the general power mean (weighted by volume fractions):

$$\overline{M}_X = \left(\frac{\Sigma \phi_i M_i^N}{\Sigma \phi_i} \right)^{1/N} = (\Sigma \phi_i M_i^N)^{1/N} \qquad (31)$$

In this expression the summation extends over all n phases, the exponent N determines the type of mean value and the subscript X denotes this respective type. Setting e.g. $N = -1$ results in the harmonic mean $\overline{M}_H$, $N \to 0$ yields the geometric mean $\overline{M}_G$, $N = 1$ the arithmetic mean $\overline{M}_A$, $N = 2$ the quadratic mean $\overline{M}_Q$, and $N = 3$ the cubic mean $\overline{M}_C$ etc. For these types of averages the so-called majority relation holds:

$$... \overline{M}_H \leq \overline{M}_G \leq \overline{M}_A \leq \overline{M}_Q \leq \overline{M}_C ... \qquad (32)$$

This is a mathematical law, i.e. a proposition that can be rigorously proved. Interestingly, however, it has been found that in the case of multiphase materials with arbitrary microstructure (i.e. periodically ordered or randomly disordered and isotropic or anisotropic) the effective elastic moduli always lie between the arithmetic and the harmonic mean. This is a physical law, i.e. a finding based on model assumptions. Its applicability to reality is and remains in principle a question of experience.

The arithmetic mean (upper bound) is the Voigt bound M_V

$$M_V = \overline{M}_A = \Sigma \phi_i M_i \qquad (33)$$

and the harmonic mean (lower bound) is the Reuss bound M_R

$$M_R = \overline{M}_H = \left(\frac{\Sigma \phi_i / M_i}{\Sigma \phi_i} \right)^{-1} = (\Sigma \phi_i / M_i)^{-1} \Rightarrow \frac{1}{M_R} = \frac{1}{M_H} = \Sigma \phi_i / M_i \qquad (34)$$

In the case of two-phase materials one of the two volume fractions is redundant ($\phi_1 \equiv 1 - \phi$ and $\phi_2 \equiv \phi$, because of equation (3)) and the Voigt and Reuss bounds reduce to

$$M_V = (1 - \phi) M_1 + \phi M_2 \qquad (35)$$

and

$$\frac{1}{M_R} = \frac{1 - \phi}{M_1} + \frac{\phi}{M_2} \Rightarrow M_R = \frac{M_1 M_2}{(1 - \phi)M_2 + \phi M_1} \qquad (36)$$

respectively. When, additionally, one of the phases is the void phase (with zero elastic moduli $M_2 = 0$), and the elastic moduli of the solid matrix phase are denoted as $M_1 \equiv M_0$ as usual, the Voigt bound reduces to

$$M_V = (1 - \phi) M_0 \qquad (37)$$

and the Reuss bound, equation (36), degenerates to zero identically.

Hashin-Shtrikman bounds for the effective elastic moduli of isotropic two-phase materials with random microstructure

When the volume fractions are the only microstructural information available there are no other rigorous bounds than the Voigt-Reuss bounds. In contrast to the case of polycrystalline monophase materials (see above) the Voigt-Reuss bounds of multiphase materials are usually too far apart to be of any value for prediction purposes. For uniform[9] microstructures, however, these bounds can be specified more exactly using minimum energy principles and the Hashin-Shtrikman variational principle [21,22]. When, additionally, the microstructure is known to be (or can be assumed to be) isotropic and random, the so-called upper Hashin-Shtrikman bounds (upper HS bounds) for the shear modulus G and the bulk modulus K of two-phase materials can be written in the explicit form

$$G_{HS}^+ = G_1 + \left[\frac{1}{G_2 - G_1} + \phi_1 \cdot \frac{6 (K_1 + 2G_1)}{5G_1 (3K_1 + 4G_1)} \right]^{-1} \cdot \phi_2 \qquad (38)$$

and

$$K_{HS}^+ = K_1 + \left[\frac{1}{K_2 - K_1} + \phi_1 \cdot \frac{3}{3K_1 + 4G_1} \right]^{-1} \cdot \phi_2 \qquad (39)$$

respectively, when $K_1 > K_2$ and $G_1 > G_2$. The lower Hashin-Shtrikman bounds (lower HS bounds) G_{HS}^- and

K_{HS} are obtained by interchanging the subscripts 1 and 2, cf. [17,18]. In the special case where one of the phases is the void phase (with zero elastic moduli $G_2 = 0$, $K_2 = 0$), where $\phi_2 \equiv \phi$ is the porosity and the elastic moduli of the solid matrix phase are denoted as $G_1 \equiv G_0$, $K_1 \equiv K_0$ as usual, the upper HS bounds reduce to

$$G_{HS}^+ = G_0 + \left[-\frac{1}{G_0} + (1 - \phi) \cdot \frac{6\,(K_0 + 2G_0)}{5G_0\,(3K_0 + 4G_0)} \right]^{-1} \cdot \phi \quad (40)$$

$$K_{HS}^+ = K_0 + \left[-\frac{1}{K_0} + (1 - \phi) \cdot \frac{3}{3K_0 + 4G_0} \right]^{-1} \cdot \phi \quad (41)$$

and the lower HS bounds degenerate to zero identically. The HS bounds have been theoretically derived for the shear modulus G and the bulk modulus K. Approximate values of the corresponding HS bounds for the tensile modulus E can be obtained via the standard relation

$$E = \frac{9KG}{3K + G} \quad (42)$$

Dilute approximations for the effective elastic moduli of porous materials

In the case of porous materials the Voigt bound (for materials with arbitrary microstructure) of the effective elastic moduli is given by equation (37) and the upper HS bound (for isotropic materials) by equations (40) through (42). The Voigt bound is linearly decreasing with a slope of 1 and the upper HS bound is nonlinearly decreasing, cf. the porosity dependence of the relative tensile modulus M/M_0 (with M_0 being the tensile modulus of the dense ceramic material) in figure 1. For very low porosities ($\phi \to 0$) it is justified to assume a linear dependence of the relative elastic moduli on the volume fraction:

$$\frac{M}{M_0} = 1 + [M]\,\phi \quad (43)$$

where $[M]$ is the intrinsic elastic modulus defined as

$$[M] \equiv \lim_{\phi \to 0} \frac{(M/M_0) - 1}{\phi} \quad (44)$$

with M standing for the tensile modulus E, the shear modulus G or the bulk modulus K, respectively.

Exact solutions to the problem of non-interacting (i.e. a dilute system of) spherical inclusions have been obtained by Dewey [23] and Mackenzie [24], cf. also [17,25]. These solutions result in explicit formulae for the coefficients (intrinsic elastic moduli) in equation (43). Thus, for the relative shear modulus G/G_0, the relative bulk modulus K/K_0 and the relative tensile modulus E/E_0 we have the following formulae [17,23-27]:

$$\frac{G}{G_0} = 1 - \frac{15(1 - v_0)}{7 - 5v_0} \cdot \phi \quad (45)$$

$$\frac{K}{K_0} = 1 - \frac{3(1 - v_0)}{2(1 - v_0)} \cdot \phi \quad (46)$$

$$\frac{E}{E_0} = 1 - \frac{3(1 - v_0)(9 + 5v_0)}{2(7 - 5v_0)} \cdot \phi \quad (47)$$

Values of the intrinsic elastic moduli $[G]$, $[K]$ and $[E]$ are listed in table 1 in dependence of the matrix Poisson ratio v_0. For $v_0 = 0.3$ the intrinsic elastic moduli are -1.909, -2.625 and -2.005, respectively, whereas for $v_0 = 0.2$ all three intrinsic elastic moduli are exactly -2. Note that for the normal matrix Poisson ratios v_0 between 0 and 0.5 the intrinsic tensile modulus $[E]$ is between -1.917 and -2.005, i.e. a value of $[E] = -1.909$ is attained only for (slightly auxetic) materials with a (negative) matrix Poisson ratio v_0 close to zero. The limit values of $[K]$ and $[E]$ for (strongly auxetic) materials with a (negative) matrix Poisson ratio v_0 approaching -1 are -1, corresponding to the Voigt bound (values > -1 do not occur).
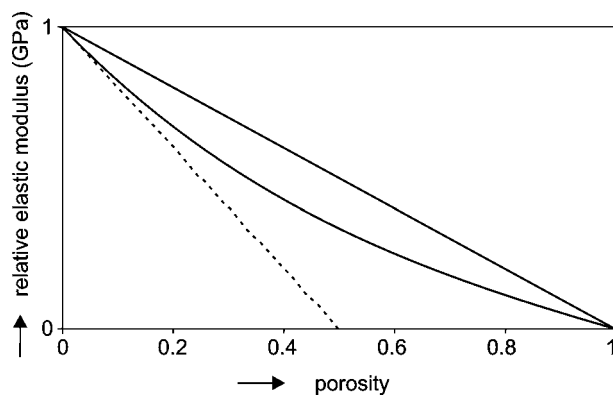

Figure 1. Voigt bound (full linear line with slope 1), upper Hashin-Shtrikman bound (HS upper, dashed nonlinear line) and Dewey-Mackenzie approximation (DM, dotted linear line with slope 0.5) for porous materials with a matrix Poisson ratio v_0 of 0.2.

Table 1. Intrinsic elastic moduli $[G]$, $[K]$, $[E]$ for different matrix Poisson ratios v_0.

v_0	$[G]$	$[K]$	$[E]$
-1.0	-2.5	-1	-1
-0.9	-2.478	-1.018	-1.115
-0.8	-2.455	-1.038	-1.227
-0.7	-2.429	-1.063	-1.336
-0.6	-2.4	-1.091	-1.44
-0.5	-2.368	-1.125	-1.539
-0.4	-2.333	-1.167	-1.633
-0.3	-2.294	-1.219	-1.721
-0.2	-2.25	-1.286	-1.8
-0.1	-2.2	-1.375	-1.87
0	-2.143	-1.5	-1.929
0.1	-2.077	-1.688	-1.973
0.2	-2	-2	-2
0.3	-1.909	-2.625	-2.005
0.4	-1.8	-4.5	-1.98
0.5	-1.667	$-\infty$	-1.917

Interestingly, the limit value of the intrinsic shear modulus $[G]$ for (strongly auxetic) materials with a (negative) matrix Poisson ratio of $v_0 = -1$ is -2.5, obviously the negative counterpart of the Einstein coefficient (intrinsic shear viscosity) in suspension rheology, cf. [28]. Note also that for the moderate matrix Poisson ratios v_0 between 0.1 and 0.4 the values of $[G]$ and $[E]$ are all relatively close to -2, while for $[K]$ this is not the case. For a matrix Poisson ratio of $v_0 = 0.5$ (corresponding to a totally incompressible matrix) the intrinsic bulk modulus diverges, i.e. a very small amount of pores would be extremely efficient (detrimental) in such a case. Finally, we note that all linear relations of the type (43) with $-1 > [M] > -2.5$ predict a critical porosity $1 > \phi_c > 0.4$, for which the effective elastic moduli become zero, i.e. the material looses integrity. Relation (43), with $[M] = -2$ for $v_0 = 0.2$ can also be derived by the so-called self-consistent scheme approach, cf. [17]. In this micromechanical context, ϕ_c is often interpreted in terms of a (finite) percolation threshold [17].

Semiempiricial extensions of the dilute approximations for the effective elastic moduli of porous materials

Experience has shown that usually the porosity dependence of the effective elastic moduli is not linear. Thus, since it is clear that the linear relation (43) claims validity and practical significance only in the case of very small porosities (dilute approximation), there have been numerous attempts to extend it to higher porosities by allowing for a nonlinear dependence. One of the simplest ways to do so is the Coble-Kingery approach [29, 30] which is as follows: Take the linear relation (43), for the matrix Poisson ratio in question, say $v_0 = 0.2$ or $v_0 = 0.3$, and add a quadratric term in ϕ (second-order polynomial),

$$\frac{M}{M_0} = 1 + [M]\phi + A\phi^2 \tag{48}$$

Then determine the value of the coefficient A via the condition that $M/M_0 = 0$ at least for $\phi = 1$ (this is intuitively plausible but also necessary in order not to violate the Voigt bound). One obtains

$$\frac{M}{M_0} = 1 + [M]\phi - ([M]+1)\phi^2 \tag{49}$$

in general, i.e.

$$\frac{G}{G_0} = \frac{K}{K_0} = \frac{E}{E_0} = (1-\phi)^2 \tag{50}$$

for $v_0 = 0.2$ materials and

$$\frac{G}{G_0} = 1 - 1.909\phi + 0.909\phi^2 \tag{51}$$

$$\frac{K}{K_0} = 1 - 2.625\phi + 1.625\phi^2 \tag{52}$$

$$\frac{E}{E_0} = 1 - 2.005\phi + 1.005\phi^2 \tag{53}$$

for $v_0 = 0.3$ materials. Irrespective of the matrix Poisson ratio, the binomial relation (49) is always a good approximation for E, but not necessarily for G and K. Relation (49) is identical to the result obtained by the differential scheme approach (for for $v_0 = 0.2$ materials materials), cf. [17]. Note that, in contrast to the dilute approximation and the self-consistent scheme approximation, this relation does not allow for a critical porosity (finite percolation threshold) ϕ_c.

The elegant and clear Coble-Kingery approach [29,30] was followed by several less rational attempts in the years to come. Spriggs [31] suggested the use of a simple exponential relation of the form

$$\frac{E}{E_0} = \exp(-B\phi) \tag{54}$$

where B is a parameter to be determined by fitting experimentally measured data. Setting $B = -[E]$ ensures accordance with relation (43) for small porosities ($\phi \to 0$), because of the truncated series expansion

$$\exp([E]\phi) \approx 1 + [E]\phi \tag{55}$$

Of course, the Spriggs relation suffers from the serious drawback that E is not zero for $\phi = 1$, i.e. the Spriggs relation necessarily violates the Voigt bound. For this reason Hasselman [32], based on previous work by Hashin [33], suggested a relation which can be written as

$$\frac{E}{E_0} = \frac{(1-\phi)}{(1-C\phi)} \tag{56}$$

where C has to be determined by fitting experimentally measured data. This relation is clearly nonlinear and monotonically decreasing, and $E = 0$ is guaranteed for $\phi = 1$. Unfortunately, however, the inverse of C cannot be interpreted as a critical porosity since in the limit $\phi \to 1/C$ relation (56) diverges ($E \to \infty$), i.e. $1/C$ must always lie outside of the interval $0 < \phi < 1$. Thus the interpretation $1/C = \phi_c$ is principally inadmissible and there is no physical meaning left in relation (56).

Recently, it has been recognized by the authors [34] that the modified exponential relation

$$\frac{E}{E_0} = \exp\left(\frac{-B\phi}{1-\phi}\right) \tag{57}$$

also circumvents the aforementioned compatibility problem at $\phi = 1$. In order to allow for $E = 1$ already in the case $\phi < 1$, an additional parameter ϕ_c can be intro-

duced, which results in a Mooney-type exponential relation [34]

$$\frac{E}{E_0} = \exp\left(\frac{-B\phi}{1 - \phi/\phi_C}\right) \qquad (58)$$

Again, setting B = -[E] ensures accordance with relation (43) for small porosities ($\phi \to 0$), cf. equation (55). Deviations of the intrinsic tensile modulus (determined by fitting) from the value for isolated (i.e. closed and non-interacting) spherical pores [E] ≈ -2 may then be interpreted as a deviation of the pore shape from spherical, when relations (57) or (58) are used.[10] In contrast to the Hasselman relation (56), the physical interpretation of ϕ_C in relation (58) as a critical porosity is in principle admissible.

Of course, also the Coble-Kingery relation

$$\frac{E}{E_0} = (1 - \phi)^2 \qquad (59)$$

and its generalizations, the Archie-type power-law relation [35]

$$\frac{E}{E_0} = (1 - \phi)^N \qquad (60)$$

do not exhibit any compatibility problem at $\phi = 1$. Setting $N = -[E]$ in relation (60) ensures accordance with relation (43) for small porosities ($\phi \to 0$), because of the truncated series expansion

$$(1 - \phi)^N \approx 1 - N\phi = 1 + [E]\phi \qquad (61)$$

And again, in order to allow for $E = 0$ already in the case $\phi < 1$, an additional parameter ϕ_C can be introduced, which results here in a Krieger-type power-law relation, the so-called Phani-Niyogi relation [36,37]:

$$\frac{E}{E_0} = (1 - \phi/\phi_C)^N \qquad (62)$$

with $N = -[E]\phi_C$. Evidently the physical interpretation of ϕ_C in relation (62) as a critical porosity is admissible and, as before, deviations of the intrinsic tensile modulus (determined by fitting) from the value for isolated (i.e. closed and non-interacting) spherical pores [E] ≈ -2 may be interpreted as a deviation of the pore shape from spherical, when relations (58) or (62) are used. We would like to emphasize that, although sometimes considered to be purely empirical, all the exponential and power law relations mentioned above can be derived via functional equations, cf. [35]. It seems that, from a fundamental point of view, the power-law relations have certain advantages over exponential relations, cf. [28].

Recently, a new relation has been proposed by the authors [38]:

$$\frac{E}{E_0} = \left(1 + [E]\phi - ([E] + 1) \cdot \phi^2\right) \cdot \frac{(1 - \phi/\phi_C)}{(1 - \phi)} \qquad (63)$$

In the case of spherical (or, in practice, isometric) pores ([E] ≈ -2) this relation adopts the extremely simple form

$$\frac{E}{E_0} = (1 - \phi) \cdot (1 - \phi/\phi_C) \qquad (64)$$

This seems to be the simplest relation allowing for a critical porosity ϕ_C. In the absence of ϕ_C (i.e. $\phi_C = 1$) this relation reduces to the Coble-Kingery relation, equation (59), as required. Note that formally the Hasselman relation, equation (56), can be rewritten as

$$\frac{E}{E_0} = \frac{(1 - \phi)}{(1 - \phi/\phi_C)} \qquad (65)$$

Although this relation yields $E = 0$ in the case $\phi = 1$, ϕ_C cannot be interpreted in terms of a critical volume fraction here, since for $\phi = \phi_C$ relation (65) diverges (E $\to \infty$). This is a clear disadvantage of the Hasselman relation.

CONCLUSIONS

In this second paper of a series on the effective elastic properties of alumina-zirconia composite ceramics, principles of micromechnical modeling are reviewed and the most important relations are recalled. Rigorous bounds (Voigt-Reuss bounds) are given for the (scalar) effective elastic moduli (tensile modulus E, shear modulus G and bulk modulus K) of polycrystalline ceramics as calculated from monocrystal data (i.e. components of the elasticity tensor). Voigt-Reuss bounds and Hashin-Shtrikman bounds of the elastic moduli are given for two-phase composites. For porous materials, which can be considered as a degenerate case of two-phase composites where one phase is the void phase (with zero elastic moduli), micromechanical approximations (so-called dilute approximations, Dewey-Mackenzie formulae) are given for E, G and K. In analogy to suspension rheology intrinsic elastic moduli are introduced and the their dependence on the matrix Poisson ratio is emphasized. Apart from a heuristic extension of the dilute approximations in the form of so-called Coble-Kingery relations, semi-empirical extensions of the micromechanical approximations are recalled for the tensile modulus (Spriggs relation, modified exponential and Mooney-type relations, generalized/Archie-type power law relation, Phani-Niyogi/Krieger-type power law relation, Hasselman relation), including the new relation $E/E_0 = (1 - \phi) \cdot (1 - \phi/\phi_C)$, recently proposed by the authors. Several reasons are adduced in favor of the latter. This paper should provide a solid basis for the discussion of the effective elastic properties of dense alumina and zirconia in Part 3, porous alumina and zirconia in Part 4 as well as of alumina-zirconia composite ceramics in Part 5 of this series of papers.

Notation:

[1] In this sense it is true that the difference between "material" and "structure" can be considered as only a question of scale [6].

[2] We assume a function at this early point to simplify discussion. It might be thinkable to assume a functional at this point, but we think that this is a point of merely academic interest at the moment.

[3] For model materials, computer simulations may be an additional tool.

[4] This is the only case in which the complete analogy between stiffnesses and compliances is disturbed.

[5] It should be noted that, according to Voigt and Reuss, even for polycrystals composed of crystallites (monocrystals) with a symmetry lower than orthorhombic/orthotropic only nine elastic constants or elastic coefficients completely determine the elastic response of the polycrystalline aggregate.

[6] When the Voigt and Reuss bounds are not too far apart, the difference between arithmetic average and other types of averages, e.g. the geometric or the harmonic average, is negligibly small.

[7] It is important, however, to recall that by "properties" we mean material properties in the strict sense, i.e. proportionality coefficients in *linear* constitutive equations describing material bodies.

[8] Of course, this is true only when the bulk phases (and not the phase boundaries) are carriers of the property. Properties which depend significantly on the phase boundaries may violate this rule.

[9] What we call *uniform* here for reasons of simplicity can be formally introduced as the so-called *ergodicity assumption*, i.e. the assumption of *statistical homogeneity* that allows one to replace ensemble averages by volume averages.

[10] Significant deviations, however, would certainly require a considerable degree of anisometry (elongation or flattening). Non-spherical pores which are more or less isometric (e.g. of polyhedral shape) cannot be expected to be responsible for deviations in the intrinsic elastic moduli.

Acknowledgement

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MAKROSKOPICKÉ ELASTICKÉ VLASTNOSTI KOMPOZITNÍ KERAMIKY NA BÁZI AL$_2$O$_3$ A ZRO$_2$ ČÁST 2. MIKROMECHANICKÉ MODELOVÁNÍ

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V tomto druhém článku z řady prací zabývajících se makroskopickými elastickými vlastnostmi kompozitní keramiky na bázi Al$_2$O$_3$ a ZrO$_2$ jsou shrnuty principy mikromechanického modelování a nejdůležitější vztahy používané v této oblasti. Pro předpověď elastických modulů (tahový resp. Youngův modul E, smykový modul G a objemový modul resp. modul stlačitelnosti K) polykrystalické keramiky na základě znalosti dat (tj. složek tenzoru elasticity) monokrystalů jsou využity Voigtovy a Reussovy meze. Voigt-Reussovy a Hashin-Shtrikmanovy meze elastických modulů jsou uvedeny pro dvoufázové kompozity. Pro porézní materiály, které jsou speciálním případem dvoufázových kompozitů, u nichž jedna fáze (póry) vykazuje nulové elastické moduly, jsou mikromechanické aproximace (vztahy Deweyho-Mackenzieho) uvedeny pro E, G a K. V analogii k reologii suspenzí jsou zavedeny tzv. „vnitřní elastické moduly" a je zdůrazněna jejich závislost na Poissonově čísle pevné kontinuální fáze. Vedle elegantního rozšíření těchto lineárních aproximací ve formě polynomů druhého řádu (vztahy Cobla-Kingeryho) existuje celá řada semi-empirických rozšíření pro Youngův modul (Spriggsův vztah, modifikované exponenciální vztahy, zobecněné mocninové vztahy, Hasselmanův vztah), včetně nově navrženého vztahu $E/E_0 = (1 - \phi) \cdot (1 - \phi/\phi_C)$, který vykazuje určité výhody oproti jiným vztahům. Tato část by měla poskytnout dostatečný základ pro diskusi makroskopických elastických vlastností hutného polykrystalického Al$_2$O$_3$ a ZrO$_2$ v třetí části, porézní korundové resp. zirkoničité keramiky ve čtvrté části a kompozitů Al$_2$O$_3$-ZrO$_2$ v páté části této řady článků.