EFFECTIVE ELASTIC PROPERTIES OF ALUMINA-ZIRCONIA COMPOSITE CERAMICS PART 4. TENSILE MODULUS OF POROUS ALUMINA AND ZIRCONIA

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In this fourth paper of a series on the effective elastic properties of alumina-zirconia composite ceramics the influence of porosity on the effective tensile modulus of alumina and zirconia ceramics is discussed. The examples investigated are alumina and zirconia ceramics prepared from submicron powders by starch consolidation casting using two different types of starch, potato starch (median size D_{50} =47.2 μm) and corn starch (median size D_{50} =13.7 μm). The dependence of effective tensile moduli E, on the porosity ϕ, measured for porosities in the ranges of approx. 19-55 vol.% and 10-42 vol.% for alumina and zirconia, respectively, using a resonant frequency technique, was evaluated by fitting with various model relations, including newly developed ones. A detailed comparison of the fitting results suggests the superiority of the new relation $E/E_0 = (1 - \phi)\cdot(1 - \phi/\phi_C)$, developed by the authors (with the tensile modulus of the dense ceramic material E_0 and the critical porosity ϕ_C), over most other existing fit models. Only for special purposes and well-behaved data sets the recently proposed exponential relation $E/E_0 = \exp[-B\phi/(1 - \phi)]$ and the well-known Phani-Niyogi relation $E/E_0 = (1 - \phi/\phi_C)^N$ might be preferable.

INTRODUCTION

In Parts 1, 2 and 3 of this series of papers, the linear theory of elasticity has been summarized for anisotropic and isotropic materials [1], the fundamentals of micromechanical modeling have been reviewed [2], and the calculation of effective elastic moduli of polycrystalline alumina and zirconia from monocrystal data, using the Voigt-Reuss-Hill average, has been recalled and critically reviewed [3] by comparing with values reported in the literature and internet data bases, so that we are now in a position to estimate reliable values for the effective tensile modulus of the fully dense ceramics (i.e. values referring to materials with zero porosity) with sufficient accuracy. With a trivial calculation it has been shown that the traditional textbook version of the so-called Coble-Kingery relation for the tensile modulus of porous ceramics (which has been originally derived for the shear modulus [4]) is in error and its correct version has been proposed [5]. Using micromechanical considerations and the so-called functional equation approach, several new exponential and power-law relations have been proposed, largely in analogy with the effective viscosity relations of suspension rheology (Mooney relation, Krieger relation) [6,7]. Finally, using heuristic arguments, a completely new relation has been derived [8], which reveals an interesting feature by being in formal contrast to the so-called Hasselman relation [9] (cf. Part 2 of this series of papers [2]) and seems to be one of the most elegant relations for fitting purposes. Its advantages are utmost simplicity while allowing for a critical porosity ϕ_C and reducing to the (correct version of the) Coble-Kingery relation in the case $\phi_C = 1$ and to the Dewey-Mackenzie relation (with the porosity $E/E_0 = 1 - 2\phi$, the effective tensile modulus of the porous ceramics E and the tensile modulus of the dense ceramics E_0) in the dilute limit ($\phi \to 0$) when $\phi_C = 1$. It is the principal aim of this paper to provide a detailed comparison of the fitting performance of the relations mentioned when applied to porous alumina and porous zirconia ceramics. This comparison is performed with relatively good and with extremely bad data sets, respectively, of adiabatic tensile moduli measured by a dynamical method (the resonant frequency technique). The data reported in this paper concern porous alumina and zirconia prepared by starch-consolidation casting, a new shaping method the principles and experimental details of which are given elsewhere [10-16]. Starch consolidation casting exploits the ability of starch to swell in hot water for the body-formation step. Two starch types, potato starch and corn starch, differing both in size and in shape (but not very much in aspect ratio), have been used for both alumina and zirconia.

Preliminaries

For easy reference, we briefly mention and label the relations used in this paper for describing the porosity dependence of the tensile moduli. For theoretical background and a more detailed discussion of the individual relations cf. [2, 4-8] and the references cited therein.

Model 1 (simple exponential relation for spherical pores), cf. [2, 6]:

$$\frac{E}{E_0} = \exp(-2\phi) \tag{1}$$

Model 2 (Spriggs relation for pores with arbitrary shape), cf. [2, 6]:

$$\frac{E}{E_0} = \exp(-B\phi) \tag{2}$$

Model 3 (exponential relation for spherical pores, yielding $E = 0$ as $\phi = 1$), cf. [2, 7]:

$$\frac{E}{E_0} = \exp\left(\frac{-2\phi}{1-\phi}\right) \tag{3}$$

Model 4 (exponential relation for pores with arbitrary shape, yielding $E = 0$ as $\phi = 1$), cf. [2, 7]:

$$\frac{E}{E_0} = \exp\left(\frac{-B\phi}{1-\phi}\right) \tag{4}$$

Model 5 (exponential relation for spherical pores, allowing for a critical porosity ϕ_C, for which $E = 0$), cf. [2, 7]:

$$\frac{E}{E_0} = \exp\left(\frac{-2\phi}{1-\phi/\phi_C}\right) \tag{5}$$

Model 6 (Mooney-type exponential relation for pores of arbitrary shape, allowing for a critical porosity ϕ_C, for which $E = 0$), cf. [2, 7]:

$$\frac{E}{E_0} = \exp\left(\frac{-B\phi}{1-\phi/\phi_C}\right) \tag{6}$$

Model 7 (Coble-Kingery relation, power-law relation for spherical pores), cf. [2, 4-6]:

$$\frac{E}{E_0} = (1-\phi)^2 \tag{7}$$

Model 8 (Archie-type power-law relation for pores of arbitrary shape) [2, 6]:

$$\frac{E}{E_0} = (1-\phi)^N \tag{8}$$

Model 9 (Phani-Niyogi relation, a Krieger-type power-law relation for pores of arbitrary shape, allowing for a critical porosity ϕ_C, for which $E = 0$) [2]:

$$\frac{E}{E_0} = (1-\phi/\phi_C)^N \tag{9}$$

Model 10 (Hasselman relation [9], formally rewritten with ϕ_C, cf. the discussion in [2]):

$$\frac{E}{E_0} = \frac{(1-\phi)}{(1-\phi/\phi_C)} \tag{10}$$

Model 11 (a new relation, proposed in [8]):

$$\frac{E}{E_0} = (1-\phi)\cdot(1-\phi/\phi_C) \tag{11}$$

In all these relations, except for the Hasselman relation (10), the fit parameter ϕ_C can be assigned the physical meaning of a critical porosity, for which the integrity of the structure breaks down, i.e. $E = 0$. This breakdown phenomenon has can be interpreted as trespassing a percolation threshold, cf. [17,18]. Since ϕ_C is a porosity, evidently the condition $0 < \phi_C < 1$ must be fulfilled. In this sense values >1 and <0 (when obtained as a result of fitting) are unphysical and discredit a fit model.

The fit parameters B and N can be assigned a certain physical meaning by defining an intrinsic tensile modulus $[E]$ in analogy to the so-called intrinsic viscosity $[\eta]$ in suspension rheology [2,19]. It can be shown that $B = -[E]$ and $N = -[E]\phi_C$. For isolated spherical pores the intrinsic tensile modulus is $[E] = -2$, just as the intrinsic viscosity of a dilute suspension with (non-interacting) rigid spherical particles is $[\eta] = 2.5$, i.e. the Einstein value, cf. [20]. Deviations of the intrinsic tensile modulus $[E]$ from $[E] = -2$ might in principle be interpreted as an indication of deviations of the pore shape (aspect ratio) from sphericity (isometry).

The tensile modulus of the dense ceramic E_0 can either be treated as a free fit parameter (for extrapolating measured data to the zero porosity value) or as a constant assumed to be known (from theoretical calculations, cf. [3]). For the purpose of this paper we consider E_0 as a free fit parameter. The standard values of $E_0 = 400$ GPa for dense alumina (α-Al_2O_3) and $E_0 = 210$ GPa for dense zirconia (tetragonal ZrO_2 with 3 mol.% Y_2O_3) can of course serve as a guideline for assessing whether the value of E_0 found by fitting is a physically reasonable from the physical point of view. Needless to say, since E_0 is a tensile modulus it must necessarily be positive. In this sense values <0 (when obtained as a result of fitting) are unphysical and discredit the fit model.

EXPERIMENTAL

Porous alumina and zirconia ceramics were prepared from commercial submicron powder types CT-3000 SG (Alcoa, Germany) and TZ-3YE (Tosoh, Japan) by starch consolidation casting from aqueous suspensions deflocculated with the commercial deflocculant

Dolapix CE 64 (Zschimmer & Schwartz, Germany), containing 75-80 wt.% and 70-72 wt.% alumina and zirconia, respectively (with the maximum attainable solids content depending on the starch content) and nominal starch contents of 5, 10, 15, 30 and 50 vol.% (with respect to the oxide powder content, based on an approximate native starch density of 1.50 g/cm^3).

The alumina powder is a superground, thermally reactive powder with high purity (>99.8 wt.% Al_2O_3) and a median particle size of D_{50} = 0.7 µm, the zirconia powder is tetragonal zirconia with a median particle size of D_{50} = 0.3 µm, containing 3 mol.% (5 wt.%) Y_2O_3 and 0.25 wt.% Al_2O_3. Two types of native starch were used: potato starch (Naturamyl, Czech Republic) with a median size of D_{50} = 47.2 µm (starch globules in the native state, i.e. before swelling) and more or less rounded shape and corn starch (Dr Oetker, Czech Republic) with a median size of D_{50} = 13.7 µm and a more or less polyhedral shape. Note that, in spite of the differences in shape, both starch types are approximately isometric (i.e. with an aspect ratio close to unity).

After mixing, the starch-containing suspensions were cast into brass molds and heated up to allow for starch swelling (and thus body formation). After demolding the green bodies were dried and the as-dried alumina and zirconia samples were fired according to a special schedule at temperatures of 1570 and 1400°C, respectively. Linear shrinkage due to firing is 14-16 % for alumina and 23-25 % for zirconia, largely independent of the nominal starch content (or, equivalently, the porosity after firing). Further experimental details of sample preparation are reported elsewhere [14].

The as-fired specimens were of cylindrical shape with a diameter of approx. 4 mm and a length between 50 and 80 mm. The bulk density ρ was determined by the Archimedes method and the total porosity ϕ was calculated from the bulk density and the theoretical density ρ_0 according to the standard formula

$$\phi = 1 - \frac{\rho}{\rho_0} \tag{12}$$

where the theoretical density of alumina and (tetragonal) zirconia was assumed to be 4.0 g/cm^3 and 6.1 g/cm^3, respectively. The effective tensile modulus of the porous ceramics was measured at the Institute of Rock Structure and Mechanics (Academy of Sciences of the Czech Republic) by the resonant frequency technique, using the Erudic Resonant Frequency Tester (CNS Electronic, UK) in the frequency range 0-100 kHz and calculated via the approximate formula

$$E = \rho \cdot (2LF)^2 \tag{13}$$

where E is the effective tensile modulus, ρ the bulk density, L the specimen length and F the resonant frequency. To apply this approximate formula the length-to-diameter ratio of the specimens must be between 5 and 20 [21-23].

Fitting of the E - ϕ - dependence data sets was performed using the non-linear regression software package CurveExpert 1.3 (Daniel Hyams, USA), without initial guesses for the fit parameters wherever possible (by default, all fit parameters were set equal to unity).

RESULTS AND DISCUSSION

The measured data are listed in tables 1 and 2. Each data pair (E and ϕ) refers to one measured specimen, i.e. information on statistical errors is not available. Therefore, as a first step to roughly assess the quality of the data, we invoke the micromechanical bounds on the effective tensile modulus, cf. [2]. Figures 1 and 2 show the measured data together with the Voigt bound and the Hashin-Shtrikman upper bound. Obviously all data obey the Voigt bound. One data point of the porous alumina (prepared with potato starch), however, is higher than the Hashin-Shtrikman upper bound, which is indicative of a measurement error. Moreover, mere visual inspection reveals that all our alumina data are more ill-behaved than the zirconia data. While the zirconia data (Z-P-data and Z-C-data) exhibit a gentle, almost linear, decrease of the E - ϕ - dependence, the alumina data exhibit unusual features, such as an apparently convex E - ϕ - dependence (A-P-data) or a steeply decreasing (concave) E - ϕ - dependence (A-C-data).

Table 1. Measured effective tensile moduli (E in GPa) of porous alumina prepared by SCC with potato starch (A-P-data) and corn starch (A-C-data), respectively.

Porosity ϕ (A-P)	Tensile modulus E (A-P)	Porosity ϕ (A-C)	Tensile modulus E (A-C)
0.178	215	0.202	305
0.266	193	0.236	223
0.298	186	0.268	217
0.397	159	0.353	119
0.566	38	0.533	42

Table 2. Measured effective tensile moduli (E in GPa) of porous zirconia prepared by SCC with potato starch (Z-P-data) and corn starch (Z-C-data), respectively.

Porosity ϕ (Z-P)	Tensile modulus E (Z-P)	Porosity ϕ (Z-C)	Tensile modulus E (Z-C)
0.132	136	0.073	167
0.191	113	0.158	136
0.249	96	0.200	124
0.315	69	0.298	85
0.424	38	0.415	52

It is not the purpose of this paper, of course, to discuss the possible origins of these measurement errors (which can be at the same time errors in E and in ϕ). On the contrary, it will be examined what can be expected from fitting bad data sets (here alumina) on the one hand and good data sets (here zirconia) on the other and to what extent the information obtained from fitting with an appropriate model can be interpreted in reasonable physical terms.

Figures 3 through 10 show the fit curves and tables 3 through 10 list the correlation coefficients and the values of the relevant fit parameters.

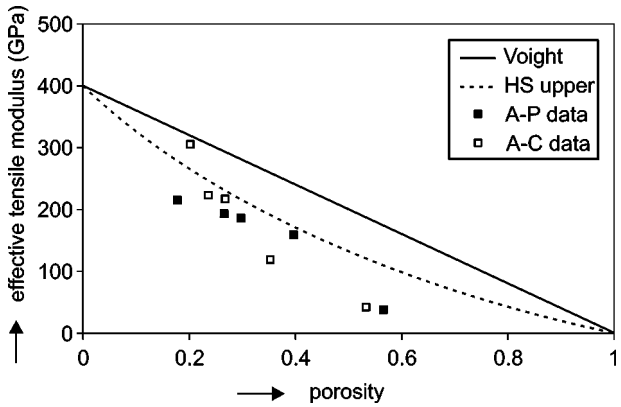

Figure 1. Effective tensile moduli measured for porous alumina prepared by SCC (starch-consolidation casting) with potato starch (A-P-data, full square) and corn starch (A-C-data, open square), respectively, in dependence of the porosity; Voigt bound (full line) and upper Hashin-Shtrikman bound (dashed line) for porous alumina.

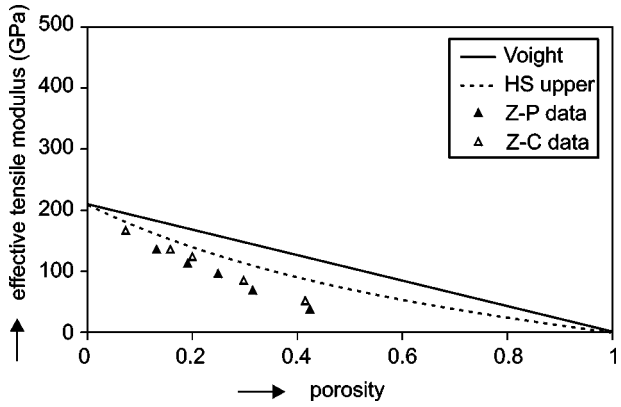

Figure 2. Effective tensile moduli measured for porous zirconia prepared by SCC (starch-consolidation casting) with potato starch (Z-P-data, full square) and corn starch (Z-C-data, open square), respectively, in dependence of the porosity; Voigt bound (full line) and upper Hashin-Shtrikman bound (dashed line) for porous zirconia.

Table 3. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by exponential models; alumina prepared by SCC with potato starch.

model number	corr. coeff.	E_0	ϕ_C	B	initial guess	remark
1	0.877	311.3	-	-	-	
2	0.906	385.4	-	2.764	-	
3	0.867	390.9	-		-	
4	0.963	295.4	-	1.185	-	
5	0.932	354.4	1.713	-	$E_0 = 400$, $\phi_C = 1.25$	ϕ_C unphysical
6	0.999	232.9	0.643	0.382	$E_0 = 400$	convex curve

Table 4. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by power-law and related models; alumina prepared by SCC with potato starch.

model number	corr. coeff.	E_0	ϕ_C	N	initial guess	remark
7	0.936	350.7	-	-	-	
8	0.938	333.8	-	1.843	-	
9	-	-	-	-	-	fit unsuccessful
10	0.917	359.5	-0.63	-	-	ϕ_C unphysical
11	0.936	343.7	1.056	-	-	

Table 5. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by exponential models; alumina prepared by SCC with corn starch.

model number	corr. coeff.	E_0	ϕ_C	B	initial guess	remark
1	0.810	352.7	-	-	-	
2	0.991	990.2	-	5.945	-	E_0 too high
3	0.967	448.9	-	-	-	
4	0.985	594.5	-	2.849	-	
5	0.976	476.7	0.819		-	
6	0.991	1031.9	-12.2	6.242	$E_0 = 400$, $\phi_C = 1.25$	E_0 too high, ϕ_C unphysical

Table 6. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by power-law and related models; alumina prepared by SCC with corn starch.

model number	corr. coeff.	E_0	ϕ_C	N	initial guess	remark
7	0.912	397.8	-	-	-	
8	0.989	740.8	-	4.107	-	
9	-	-	-	-	-	fit unsuccessful
10	0.989	-1081	0.053	-	-	ϕ_C unphysical, ϕ_C too low
11	0.978	530.1	0.596	-	-	

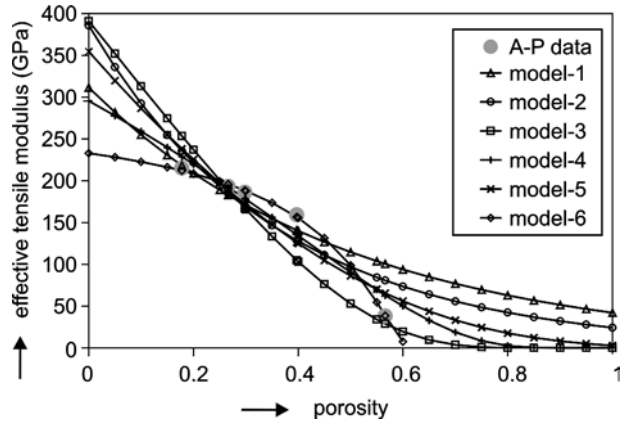

Figure 3. Tensile modulus porosity dependence fitted by exponential models; alumina prepared by SCC (starch-consolidation casting) with potato starch.

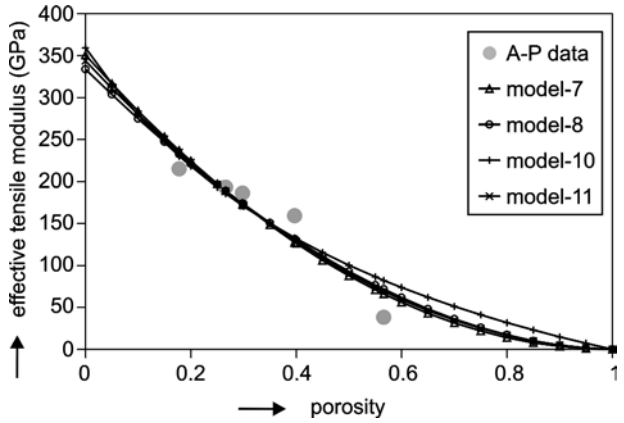

Figure 4. Tensile modulus porosity dependence fitted by power-law and related models; alumina prepared by SCC (starch-consolidation casting) with potato starch.

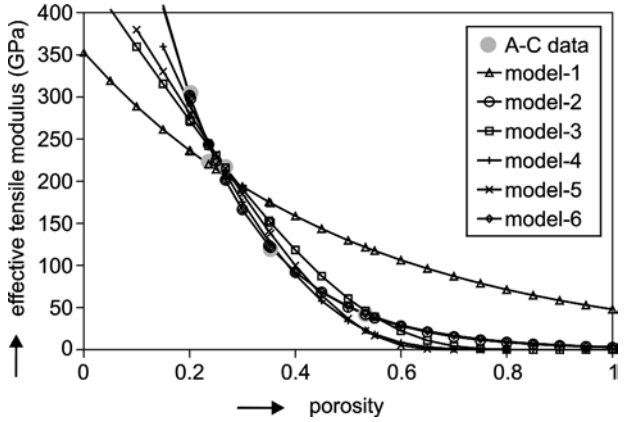

Figure 5. Tensile modulus porosity dependence fitted by exponential models; alumina prepared by SCC (starch-consolidation casting) with corn starch.

Table 7. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by exponential models; zirconia prepared by SCC with potato starch.

model number	corr. coeff.	E_0	ϕ_C	B	initial guess	remark
1	0.878	154.8	-	-	-	E_0 too low
2	0.990	233.9	-	3.890	-	E_0 too high
3	0.997	181.9	-	-	-	
4	0.999	189.6	-	2.157	-	
5	0.999	185.3	0.908	-	$E_0 = 200$, $\phi_C = 0.5$	ϕ_C too high
6	0.999	184.0	0.888	1.957	$E_0 = 200$, $\phi_C = 0.5$	ϕ_C too high

Table 8. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by power-law and related models; zirconia prepared by SCC with potato starch.

model number	corr. coeff.	E_0	ϕ_C	N	initial guess	remark
7	0.955	167.6	-	-	-	E_0 too low
8	0.996	209.1	-	2.917	-	
9	0.999	188.2	0.596	1.297	$E_0 = 200$, $\phi_C = 0.5$	[E] = -2.176
10	0.984	278.7	-0.18	-	-	E_0 too high ϕ_C unphysical
11	0.998	199.2	0.646	-	-	

Table 9. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by exponential models; zirconia prepared by SCC with corn starch.

model number	corr. coeff.	E_0	ϕ_C	B	initial guess	remark
1	0.932	178.3	-	-	-	E_0 too low
2	0.990	216.5	-	3.118	-	
3	0.998	198.9	-	-	-	
4	0.999	194.2	-	1.880	-	
5	0.999	196.9	0.912	-	-	ϕ_C too high
6	0.999	194.2	0.998	1.878	-	ϕ_C too high

Table 10. Fit parameters (E_0 in GPa) for the tensile modulus porosity dependence fitted by power-law and related models; zirconia prepared by SCC with corn starch.

model number	corr. coeff.	E_0	ϕ_C	N	initial guess	remark
7	0.984	188.5	-	-	-	
8	0.997	204.8	-	2.445	-	
9	0.990	195.8	0.638	1.275	$E_0 = 200$, $\phi_C = 0.5$	[E] = -1.998
10	0.987	221.1	-0.38	-	-	E_0 too high ϕ_C unphysical
11	0.998	202.7	0.758	-	-	

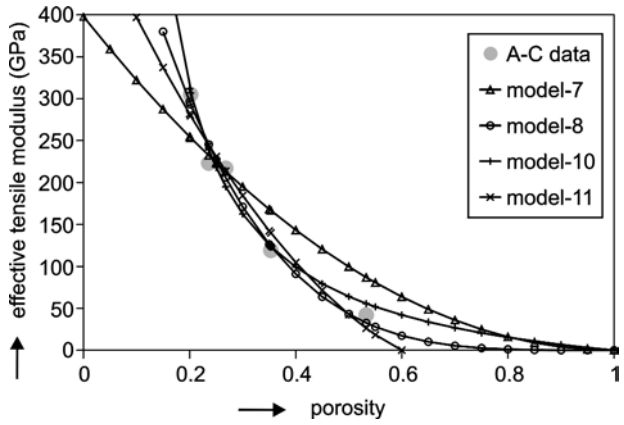

Figure 6. Tensile modulus porosity dependence fitted by power-law and related models; alumina prepared by SCC (starch-consolidation casting) with corn starch.

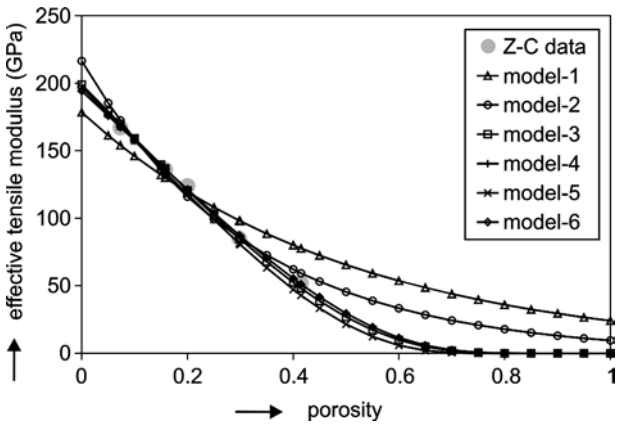

Figure 9. Tensile modulus porosity dependence fitted by exponential models; zirconia prepared by SCC (starch-consolidation casting) with corn starch.

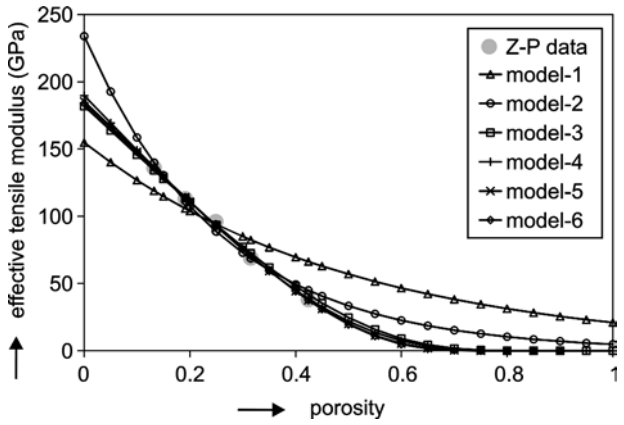

Figure 7. Tensile modulus porosity dependence fitted by exponential models; zirconia prepared by SCC (starch-consolidation casting) with potato starch.

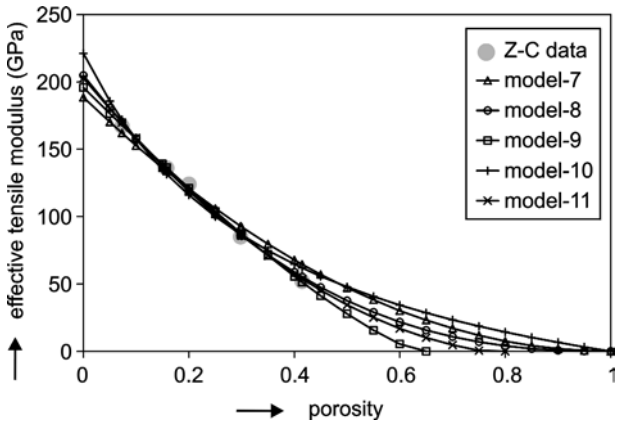

Figure 10. Tensile modulus porosity dependence fitted by power-law and related models; zirconia prepared by SCC (starch-consolidation casting) with corn starch.

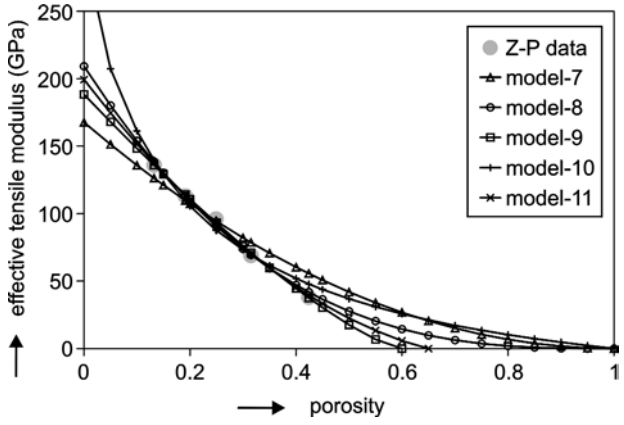

Figure 8. Tensile modulus porosity dependence fitted by power-law and related models; zirconia prepared by SCC (starch-consolidation casting) with potato starch.

It is evident that Models 1 and 2 (simple exponential and Spriggs relation) are generally too rigid for good fitting. Even for good data sets they are not able to represent the course of the E - ϕ - dependence in a satisfactory way, and the extrapolated E_0 values are either too high or too low. Moreover, these model suffer from the principal drawback, that they do not reduce to $E = 0$ for $\phi = 1$. Model 10, the Hasselman relation, which has been proposed very early (1962) [9] in order to avoid this disadvantage of the Spriggs relation (Model 2), often gives poor fits (according to the correlation coefficients), badly estimated or unphysical E_0 values and usually unphysical ϕ_C values. That means, the parameter ϕ_C occurring in the Hasselman relation cannot be interpreted as a critical porosity, an evident disadvantage for a model that should retain some physical significance and intuitive connection to reality.

The modified exponential relations, Models 3 and 4, seem to be rather useful for fitting. Without the necessity of initial guesses they usually give satisfactory fits (with correlation coefficients almost as good as for the more complicated Models 5 and 6) and (in contrast to the latter) do not show any tendency to numerical artefacts (cf. table 3, Model 5 and table 5, Model 6) or to physical artefacts, such as convex curves (cf. table 3, Model 6). Moreover, for the well-behaved zirconia data sets (Z-P-data and Z-C-data) Models 5 and 6 result in ϕ_C close to unity (cf. tables 7 and 9), which indicates that the possible advantage of Models 5 and 6 (i.e. the principal capability of predicting ϕ_C values) is de facto lost and that the possibly additional effort with initial guesses (due to the one additional fit parameter) is not justified. Mere visual inspection of the graphs on figures 7 and 9 shows that Models 5 and 6 exhibit a tendency to crudely overestimate the critical porosity ϕ_C and are thus useless for predicting approximate ϕ_C values for practical purposes. Therefore, Models 3 and 4 should generally be preferred to Models 5 and 6.

Model 7, the Coble-Kingery relation with E_0 as a free fit parameter, is a relatively rigid, i.e. unflexible, model. The fitting is often poor, even for well-behaved data (Z-P-data and Z-C-data, figures 8 and 10) the correlation coefficients are usually much worse than for modified exponential models (Models 3 - 6), cf. tables 3 - 10. The extrapolated E_0 values determined by non-linear regression show a tendency of being too low, cf. figures 6, 8, 10. A clear advantage of this model is the fact that, as a consequence of its relative unflexibility, it is not prone to artefacts, in contrast to the modified exponential models, especially the more complicated Models 5 and 6. It can therefore be recommended for ill-behaved data sets (A-P-data and A-C-data, figures 4 and 6).

Model 8, the Archie-type power-law relation, seems to be equally resistant against artefacts and has the advantage of being more flexible for fitting purposes, which often improves the correlation coefficient. In this case, formally $N = -[E]$, since Model 8 can be considered as a special case of Model 9 (see below) where ϕ_C is set to unity. The physical significance of the $[E]$ value (intrinsic tensile modulus) thus determined, is however obscured just by the fact that no allowance is made for the possible occurrence of a critical porosity, since this affects the curvature of the corresponding fit curve in an artificial way. Therefore, for principal reasons no attempts should be made to interpret deviations of the exponent determined by fitting with this model as deviations of the pore shape from sphericity. Although it could be argued that a similar problem occurs with Model 4, it seems that the problem is less severe in this case. The probable reason is that in modified exponential models the actual value of the critical porosity (which is usually overestimated anyway) does not affect the curvature of the fit curve to any sensible degree.

Model 9, the Phani-Niyogi relation, is one of the most flexible relations for fitting (similar to Model 6 it is a relation with three fit parameters) and, being a power-law model, it has certain principal advantages from a theoretical point of view, cf. [20]. However, due to the large number of fit parameters initial guesses are usually required even in the case of well-behaved data (Z-P-data and Z-C-data, figures 8 and 10). Interestingly, for ill-behaved data (A-P-data and A-C-data, figures 4 and 6) fitting with Model 9 was not successful, even with initial guesses.

In the case of Model 9 attempts are justified to interpret the intrinsic tensile modulus $[E]$ calculated from $N = -[E]\phi_C$, using the ϕ_C value determined from fitting, as a measure of pore sphericity (isometry). In our opinion, the only alternative relation for which such an interpretation is possible is Model 4 (with $B = -[E]$) and, with certain reservations (cf. the general objections against Model 6 and arguments in favor of Model 4 discussed above), Model 6.

Comparing the $[E]$ values for the well-behaved zirconia data (tables 7 - 10) we have $[E]$ values from -1.957 to -2.157 for the zirconia prepared by SCC with potato starch (Z-P-data, approximately spherical pore shape) and $[E]$ values from -1.878 to -1.998 for the zirconia prepared by SCC with potato starch (Z-C-data, polyhedral pore shape). The close proximity of these values to the value for spherical pores ($[E] = -2$) is indicative of the approximate isometry of the pores in both cases (potato starch and corn starch). Measurable deviations from this value are to be expected only for strongly anisometric (i.e. elongated/prolate or flattened/oblate) pores. For the ill-behaved alumina data (tables 3 - 6), $[E]$ values from Model 9 are not available and $[E]$ va-lues from Model 6 have to be discarded because of the above discussed fitting artefacts. The remaining $[E]$ va-lues resulting from Model 4 are approx. -1.2 and approx. -2.8 for the A-P-data and the A-C-data, respectively. This large scatter around the value $[E] = -2$ indicates that, as expected, ill-behaved data sets cannot be used to extract information on the intrinsic tensile modulus or deviations of the pore shape from sphericity (isometry).

Further, as expected, it is difficult to extrapolate ill-behaved data sets in a way to estimate E_0 values which are on the one hand consistent with the measured data (as viewed by mere visual inspection) and on the other hand realistic from a physical point of view. Thus, while it is clear that the E_0 value for dense alumina must be approx. 400 GPa (cf. [3]), the E_0 values determined from fitting our alumina data sets (even after excluding the convex curve value of $E_0 = 233$ GPa obtained from the fit via Model 6, cf. table 3, and the evidently inadmissible value of $E_0 = -1081$ GPa obtained from the Hasselman relation, Model 10, cf. table 6) are

295-391 GPa, i.e. too low, for the A-P-data. For the A-C-data the E_0 values are 353 - 1032 GPa, i.e. exhibit an enormous scatter, from too low up to extremely too high values. In the case of well-behaved data sets (zirconia data, cf. tables 7 - 10) the E_0 values determined by fitting are 155 - 234 GPa for the Z-P-data and 178 - 217 GPa for the Z-C-data when Model 10 (the fit using the Hasselman relation) is excluded. When bad fit curves (with low correlation coefficients) based on Models 1, 2 and 7 are excluded, one obtains 182 - 209 GPa for the Z-P-data and 194 - 205 GPa for the Z-C-data. Since the E_0 value for dense zirconia (with 3 mol.% Y_2O_3) must be approx. 210 GPa (cf. [3]), these results are in rather close agreement with reality, possibly with a general tendency of all fit models to slightly underestimate the E_0 values, even in the case of well-behaved data.

Finally, the fitting results obtained via Model 11 deserve special attention. For the well-behaved data (zirconia data) the E_0 values determined by Model 11 exhibit the smallest difference of all (199.2 and 202.7 GPa for the Z-P-data and Z-C-data, respectively, cf. tables 8 and 10). This is reasonable from a physical point of view, since the E_0 values refer to the dense (i.e. pore-free) zirconia and should therefore be dependent only on the zirconia powder used (which is identical in both cases), but not on the starch type used. The critical porosity ϕ_C determined via Model 11 attains values of 0.646 and 0.758 for the Z-P-data and Z-C-data. These values are slightly higher than the ϕ_C values obtained from fitting with Model 9 (Phani-Niyogi relation), which are 0.596 and 0.638, respectively, but still correspond well to the values which can be estimated by visual inspection of the graphs (figures 8 and 10). Moreover, Model 11 has two advantages over and beyond Model 9: First, being a two-parameter model, fitting can be performed without initial guesses (cf. tables 8 and 10) and second, being extremely simple and relatively rigid, it can be applied in the case of ill-behaved data, where Model 9 usually fails altogether, due to convergence problems with the non-linear fitting procedure (cf. tables 4 and 6). In the case of the convex curve data (A-P-data, cf. figure 4 and table 4) the ϕ_C value attains values close to unity (1.056), i.e. it seems that in such pathological cases Model 11 approaches the very rigid (and always concave) Coble-Kingery relation (Model 7).

Thus in all cases in which the pores are not extremely anisotropic (and where, therefore, the intrinsic tensile modulus [E] is without concern) Model 11 is the best fit model. It is true that Model 9 can provide slightly better fits (due to the fact that the curvature in Model 11 is automatically coupled to the value of ϕ_C, while in Model 9 it can be adjusted independently via N) and slightly more potentially extractable information (since, due to the additional fit parameter N, a value for the intrinsic tensile modulus [E] is accessible). Because of its extreme simplicity, however, Model 11 is applicable in situations where Model 9, the Phani-Niyogi relation, fails. In this sense, Model 11 is more rigid (because it contains one parameter less) and more robust (because initial guesses are not needed) than Model 9. Being a two-parameter fit model, however, it is more flexible than Model 7 (Coble-Kingery relation) and includes an additional, practically significant parameter (the critical porosity ϕ_C).

When an attempt is made to quantify pore anisometry by deviations of the intrinsic tensile modulus [E] from the spherical pore value [E] = -2, Model 4 (also a two-parameter model) should be the model of choice. The additional parameter ϕ_C introduced in Model 6 makes this model more complicated (initial guesses needed) and too fragile (for ill-behaved data it may produce physical artefacts such as convex curves, cf. figure 3, and numerical artefacts such as negative ϕ_C values, cf. table 5). Moreover, even for well-behaved data the ϕ_C values (0.888 - 0.998 for zirconia data, cf. tables 7 and 9) are evidently too high, as can be seen by visual inspection of the corresponding graphs (figures 7 and 9), so that the physical significance of the ϕ_C value determined via Model 6 remains highly dubious at best.

CONCLUSIONS

In this fourth paper of a series on the effective elastic properties of alumina-zirconia composite ceramics the influence of porosity on the effective tensile modulus of alumina and zirconia ceramics was discussed. The examples investigated are alumina (CT-3000SG, Alcoa) and zirconia (TZ-3YE, Tosoh) ceramics prepared by starch consolidation casting using two different types of starch, potato starch (median size D_{50} = 47.2 μm) and corn starch (median size D_{50} = 13.7 μm). The dependence of effective tensile moduli E, on the porosity ϕ, measured for porosities in the ranges of approx. 19-55 vol.% and 10-42 vol.% for alumina and zirconia, respectively, using a resonant frequency technique, was evaluated by fitting with various model relations, including newly developed ones. A detailed comparison of the fitting results obtained with 11 different relations (fit models) for ill-behaved (alumina) and well-behaved (zirconia) data sets suggests the superiority of the new relation $E/E_0 = (1 - \phi)\cdot(1 - \phi/\phi_C)$, developed by the authors (with the tensile modulus of the dense ceramic material E_0 and the critical porosity ϕ_C), over most other existing fit models. The fitted curves are evidently in good agreement with the course of the data (as can be confirmed by visual inspection of the graphs) and the E_0 and ϕ_C values determined by fitting with this model seem to be among the most reasonable ones from a physical viewpoint (e.g. E_0 = 199 - 203 GPa and ϕ_C = 0.646 - 0.758 for the well-behaved zirconia data).

Only for special purposes and well-behaved data sets the recently proposed modified exponential relation $E/E_0 = \exp [-B\phi/(1 - \phi)]$ and the well-known Phani-Niyogi relation $E/E_0 = (1 - \phi/\phi_C)^N$ might be preferable.

In the case of good data sets e.g. the latter provides realistic values at the same time for ϕ_C (0.596-0.638 for our zirconia) and for the intrinsic tensile modulus $[E]$ (between -1.998 and -2.176 for our zirconia), which can be calculated from $N = -[E]\phi_C$. However, this three-parameter model usually needs initial guesses for the parameters and often fails altogether (due to convergence problems) when ill-behaved data (here the alumina data) have to be fitted.

In cases where the Phani-Niyogi relation fails, the modified exponential model $E/E_0 = \exp [-B\phi/(1 - \phi)]$ is the only relation that can be recommended for extracting information on the intrinsic tensile modulus $[E] = -B$. Deviations from the spherical pore value $[E] = -2$ can in principle be interpreted in terms of deviations of the pore shape from sphericity (isometry). In practice, however, such an interpretation is possible only when very good and precise data sets are fitted and when the pores are distinctly anisometric.

For porous materials with approximately isometric pores (whether rounded or polyhedral), i.e. where information on the intrinsic tensile modulus $[E]$ is irrelevant, the new two-parameter relation $E/E_0 = (1 - \phi)\cdot(1 - \phi/\phi_C)$, is doubtlessly the best compromise. For well-behaved and very precise data sets it can be replaced by the three-parameter Phani-Niyogi relation (the most complicated and thus most "flexible" model), while for ill-behaved or very unprecise data it might be replaced by (if it does not by itself reduce to) the one-parameter Coble-Kingery relation (the simplest and thus most "rigid" model).

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MAKROSKOPICKÉ ELASTICKÉ VLASTNOSTI KOMPOZITNÍ KERAMIKY NA BÁZI Al_2O_3 A ZrO_2 ČÁST 4. YOUNGOVY MODULY PORÉZNÍ KORUNDOVÉ A ZIRKONIČITÉ KERAMIKY

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V tomto čtvrtém článku z řady prací zabývajících se makroskopickými elastickými vlastnostmi kompozitní keramiky na bázi Al_2O_3 a ZrO_2 je diskutován vliv pórovitosti na Youngův modul korundové a zirkoničité keramiky. Studována je porézní korundová (CT-3000SG, Alcoa) a zirkoničitá (TZ-3YE, Tosoh) keramika připravovaná tzv. škrobovým litím za použití dvou různých typů škrobu: bramborového škrobu s poměrně velkými (D_{50} = 47.2 μm), téměř kulovitými částicemi a kukuřičného škrobu s poměrně malými (D_{50} = 13.7 μm), polyedrickými částicemi. Závislost efektivního Youngova modulu E na pórovitosti ϕ byla naměřena (pro pórovitosti v oblasti cca. 10-50 obj.%) pomocí metody resonančních frekvencí a vyhodnocena proložením naměřených dat různými modelovými vztahy, včetně nově vyvinutých. Detailní srovnání výsledků fitování pomocí 11 různých vztahů (fitovacích modelů) pro korundová resp. zirkoničitá data ukazuje výhodu námi vyvinutého nového vztahu $E/E_0 = (1 - \phi)\cdot(1 - \phi/\phi_C)$, kde E_0 je Youngův modul hutné, tj. neporézní keramiky a ϕ_C je kritická pórovitost, oproti vetšině jiných fitovacích modelů. Fitovací křivky jsou evidentně v dobrém souladu s průběhem dat a hodnoty E_0 a ϕ_C stanovené proložením tímto modelem jsou poměrně plauzibilní z fyzikálního hlediska (např. E_0 = 199-203 GPa a ϕ_C = 0.646-0.758 pro zirkoničitou keramiku). Jiné modely, např. nedávno navržený modifikovaný exponenciální vztah $E/E_0 = \exp[-B\phi/(1 - \phi)]$ a známý vztah Phani-Niyogiho $E/E_0 = (1 - \phi/\phi_C)^N$, lze doporučit pouze pro speciální účely (např. určení tzv. vnitřního Youngova modulu [E] u silně anizometrických pórů) a pro výjimečně dobrá a přesná data (u kterých např. vztah Phani-Niyogiho poskytuje zároveň [E] a ϕ_C).

Book review

ADVANCES IN FUSION AND PROCESSING OF GLASS III. CERAMIC TRANSACTIONS, VOLUME 141

Varner J.R., Seward III T.P., Schaeffer H.A. (editors)

Published by The American Ceramic Society, 735 Ceramic Place, Westerville, Ohio 43081, USA, 2004; ISBN: 1-57498-193-5, price 109,- USD (87,- USD ACerS Members)

The reviewed book, which is the volume No 141 of Ceramic Transactions series, contains the proceedings of the 7th international Conference on Advances in Fusion and Processing of Glass. This conference was held at July 27-31 in Rochester, NY.

The book is a compilation of 47 papers presented at the conference and it is divided into 9 chapters according to the conference sessions. The first chapter contains 10 papers about advances in the glass melting process. Four papers in the second chapter are devoted to the characterization of glass melts and glass melts properties. Materials for glassmaking and their interactions with glass melts are discussed in the third chapter, followed by five contributions about advances in glass forming. The fifth part shows results of research of polyvalent elements and redox behavior. Effects of composition and forming on glass structure and properties are discussed in chapter 6 (5 papers). Surprisingly, only one paper represents the environmental issues, emissions and recycling. Six papers are collected in the chapter about computer modeling and process control. Last chapter about secondary processing contains two papers.

Not very common in conference proceedings but invaluable is the keyword and author index.

Finally, it can be summarised that the reviewed book gives a good review of the recent research activities in the fields connected with glass production. The book can be ordered using on-line catalogue www.ceramics.org

Aleš Helebrant