INTRODUCTION

In Parts 1 and 2 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 and rigorous bounds and nonlinear relations have been given [2]. In Parts 3 and 4 the effective elastic moduli of polycrystalline alumina and zirconia have been calculated from monocrystal data and compared with published values [3] and measured data for porous alumina and zirconia have been analyzed using several fit models, including newly proposed ones [4]. It is the purpose of the present paper to bring all this knowledge together and to predict, analyze and discuss the effective tensile moduli of alumina-zirconia composite ceramics (AZ composites), dense as well as porous. In the experimental section the materials and their processing (slip casting and starch consolidation casting for dense and porous AZ composites, respectively) are briefly described and the measurement methods applied are mentioned (tensile modulus via the resonant frequency method, porosity determination via the bulk density measured by the Archimedes method). In the first part of the results section the effective theoretical density and the effective elastic moduli of dense AZ composites of arbitrary composition are discussed in some detail and handy formulae are given for general use. In the second part of the results section the effective tensile modulus of two typical AZ composites is investigated in dependence of the porosity: zirconia-toughened alumina with a zirconia content of 15 wt.% (labelled here ZTA) and alumina-containing tetragonal zirconia with a zirconia content of 80 wt.% (labelled here ATZ). The effective tensile modulus is measured by the resonant frequency method and its porosity dependence is analyzed using 11 different fit models.

EXPERIMENTAL

Dense alumina and alumina-zirconia composite ceramics (AZ composites) were prepared by co-milling mixed aqueous suspensions of submicron alumina and zirconia powders in a high-energy planetary mono mill (Fritsch Pulverisette 6, Germany) and subsequent slip casting of these suspensions (containing 75 wt.% solids) into plaster molds. After demolding and drying the AZ composites were fired at 1530°C. Further processing details can be found elsewhere [5-7].
The powder types used are AA04 (Sumitomo, Japan), a very pure (>99.99 wt.% Al₂O₃) powder with highly isometric grain shape and a median particle size of \( D_{50} = 0.4 \mu m \) and TZ-3Y (Tosoh, Japan), a tetragonal zirconia type with a median particle size of \( D_{50} = 0.3 \mu m \), containing 3 mol.% (5 wt.%) \( Y₂O₃ \). Microstructural investigation by image analysis on thermally etched polished sections revealed a maximum alumina grain size of 1.3 \( \mu m \) (± 0.5 \( \mu m \)) and a maximum zirconia grain size of 0.6 \( \mu m \) (± 0.3 \( \mu m \)) in the AZ composites after firing. Note that the alumina grain size in AZ composites is significantly smaller than in (identically processed) pure alumina, which can be 2 \( \mu m \) (± 1 \( \mu m \)), an effect which is attributed to the mechanical constraint exerted by the zirconia grains on the alumina grains, which inhibits alumina grain growth, cf. [5-7].

Depending on the mixture composition we denote the AZ composites by the simple and self-evident notation A90Z10, A80Z20 etc., which denote AZ composites with 90 wt.% alumina and 10 wt.% zirconia, AZ composites with 80 wt.% alumina and 20 wt.% zirconia and so on.

Porous AZ composites were prepared from commercial mixed powders by starch consolidation casting (SCC) from aqueous suspensions containing 70-76 wt.% solids 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/cm³). The suspensions were cast into brass molds and heated up to approx. 80°C in order to initiate swelling of the starch grains and subsequent gelation of the suspension. After demolding and drying the AZ composites were fired at 1530°C and 1550°C, the lower temperature referring the composites with higher zirconia content. Further processing details can be found elsewhere [8], cf. also [9-14].

Two special, though widely used and thus typical, compositions of AZ composites were selected for the SCC process, A85Z15 (labelled ZTA in the following) and A20Z80 (labelled ATZ in the following). Commercial powder mixtures were used: ZTA-85 (Daiichi, Japan), a mixed powder with 15 wt.% zirconia (tetragonal zirconia containing 3 mol.% \( Y₂O₃ \)) and ATZ-80 (Daiichi, Japan), a mixed powder with 80 wt.% zirconia, both submicron with a median particle size of \( D_{50} = 0.3 \mu m \). The starch used is native potato starch (Naturamy, Czech Republic) with a median size of approx. \( D_{50} = 50 \mu m \) (starch globules in the native state, i.e. before swelling) and oval, almost spherical shape. The pore size resulting from the starch remains approx. 50 \( \mu m \) after firing. Interestingly, (linear) firing shrinkage is independent of the starch content and depends only on the alumina-zirconia ratio, i.e. the oxide composition (15-18 % for ZTA and 23-26 % for ATZ), cf. [8]. This is a clear indication of the fact that the starch-pores do not shrink during the sintering process. Thus, it can be expected that after firing the pores are almost 2 orders of magnitude larger than the grain size.

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 \( \rho \) was determined by the Archimedes method and the total porosity \( \phi \) was calculated from the bulk density and the theoretical density \( \rho_0 \), according to the standard formula

\[
\phi = 1 - \frac{\rho}{\rho_0}
\]

where the theoretical density of alumina and (tetragonal) zirconia was assumed to be 4.0 g/cm³ and 6.1 g/cm³, respectively (for AZ composites see below). 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 resonant frequency tester Erudite (CNS Electronics, UK) in the frequency range 0-100 kHz and calculated via the formula for resonant frequencies of longitudinal vibrations

\[
c = \sqrt{\frac{E}{\rho}} \Rightarrow E = \frac{c^2 \rho_0}{2L^2}
\]

where \( c = 2LF \) is the sound velocity, \( E \) is the effective tensile modulus, \( \rho \) the bulk density, \( L \) the specimen length and \( F \) the resonant frequency [15,16]. To apply this formula it is recommended that the length-to-diameter ratio of the specimens should be between 5 and 20 [17,18], which is fulfilled in our case.

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

RESULTS AND DISCUSSION

Dense Alumina-Zirconia Composite Ceramics

Figure 1 shows the effective theoretical density of alumina-zirconia composite ceramics (AZ composites) as a function of the zirconia weight fraction \( X \), calculated under the assumption that all zirconia is tetragonal (solid line) and monoclinic (dashed line), respectively. The constituent phase densities have been assumed to be 4.0 g/cm³ (alumina), 6.1 g/cm³ (t-zirconia) and 5.6 g/cm³ (m-zirconia). To the precision required, these are almost universally accepted values. The extreme case of 100 % m-zirconia should be considered as illustrative. It should serve in order to assess the possible error introduced into the calculations when part of the t-zirconia has transformed to m-zirconia, e.g. due to...
hydrothermal ageing (surface degradation at moderately elevated temperature in aqueous environments) [19-23]. For an as-prepared AZ composite, which has not yet undergone degradation, the t-zirconia content is usually close to 100% (with respect to the total zirconia content).

Third-order polynomials can be used to fit the $\rho_0 - X$ dependences (with correlation coefficients >0.99999). In the extreme case of AZ composites with 100% t-zirconia we obtain

$$\rho_0 (X) = 4.0 + 1.41 X + 0.3 X^2 + 0.4 X^3$$  (3)

while in the case of AZ composites with 100% m-zirconia we have

$$\rho_0 (X) = 4.0 + 1.10 X + 0.3 X^2 + 0.2 X^3$$  (4)

These handy formulae (with all terms in g/cm$^3$) can be used to calculate the theoretical density of a (classical, i.e. non-nano) AZ composite of arbitrary composition when the zirconia weight fraction is given.

Trivially, the corresponding dependences of the theoretical density $\rho_0$ on the zirconia volume fraction $\phi_z$ are given by simple linear mixture rules (cf. the straight lines in figure 2),

$$\rho_0 (\phi_z) = 4.0 + 2.1 \phi_z$$  (5)

$$\rho_0 (\phi_z) = 4.0 + 1.6 \phi_z$$  (6)

for the extreme cases of AZ composites with 100% t-zirconia and 100% m-zirconia, respectively. With the help of these formulae (or, alternatively, figures 1 and 2) it can easily be verified that under the assumption of 100% prevalence of t-zirconia the zirconia volume fraction is 0.105 for the ZTA composite (corresponding to $X = 0.15$) and 0.726 for the ATZ composite (corresponding to $X = 0.80$).

In order to estimate or predict the effective elastic moduli of dense AZ composites we use the $E$, $G$ and $K$ values recommended in [3] for alumina and t-zirconia containing 3 mol.% Y$_2$O$_3$ (the "pure" end members of AZ composites), respectively. These are $E = 400$ GPa, $G = 163$ GPa, $K = 247$ GPa (alumina) and $E = 210$ GPa, $G = 80$ GPa, $K = 184$ GPa (zirconia). Using the $E$ values, the Voigt-Reuss bounds [2] for the effective tensile moduli of dense AZ composites can be readily calculated. These are shown as solid lines in figure 3, in which experimentally determined effective tensile moduli of dense AZ composites (with porosity < 3%) prepared by slip-casting are also shown. It is evident that all measured values (cf. table 1) fall within the Voigt-Reuss bounds. Although the Voigt-Reuss bounds are rather close in the case of dense AZ composites, an even more precise estimate (prediction) can be given via the Hashin-Shtrikman bounds. Under the assumption of statistical isotropy (cf. [2]), which is justified here, the Hashin-Shtrikman bounds for the elastic moduli of dense AZ composites can be calculated via the relations given in [2]. The results are shown as dashed lines in figure 3 and are on the one hand very close to each other and on the other hand in very good agreement with the measured data. This indicates that the precision of the measuring method is excellent and that the scatter observed for porous ceramics (cf. also [4] and below) reflects random variations in microstructure.

Evidently, the arithmetic mean of the Hashin-Shtrikman bounds is an excellent estimate for the effective elastic moduli of AZ composite of arbitrary composition when the zirconia volume fraction $\phi_z$ is given. The resulting dependences can be fitted with second-order polynomials (with correlation coefficients >0.99995) to obtain the following handy formulae (with all terms in GPa).

![Figure 1. Effective theoretical density of AZ composites as a function of the zirconia weight fraction, calculated for a two-phase composite under the assumption that all zirconia is tetragonal (solid line) and that all zirconia is monoclinic (dashed line), respectively; constituent phase densities 4.0 g/cm$^3$ (alumina), 6.1 g/cm$^3$ (t-zirconia) and 5.6 g/cm$^3$ (m-zirconia).](image1)

![Figure 2. Effective theoretical density of AZ composites as a function of the zirconia volume fraction for the case that all zirconia is tetragonal (solid line) and that all zirconia is monoclinic (dashed line), respectively; constituent phase densities 4.0 g/cm$^3$ (alumina), 6.1 g/cm$^3$ (t-zirconia) and 5.6 g/cm$^3$ (m-zirconia).](image2)
Effective tensile modulus of dense AZ composites:

\[ E = 400 - 245.9 \phi_Z + 56.3 \phi_Z^2 \]  
(7)

Effective shear modulus of dense AZ composites:

\[ G = 163 - 110.4 \phi_Z + 28.3 \phi_Z^2 \]  
(8)

Effective bulk modulus of dense AZ composites:

\[ K = 247 - 73.6 \phi_Z + 10.8 \phi_Z^2 \]  
(9)

According to these formulae, the best estimates (predictions) for effective elastic moduli of AZ composites are:

- \( E = 375 \) GPa,
- \( G = 151 \) GPa,
- \( K = 239 \) GPa for the ZTA composite (corresponding to \( X = 0.15 \) and thus \( \phi_Z = 0.105 \)),
- \( E = 251 \) GPa,
- \( G = 97 \) GPa,
- \( K = 199 \) GPa for the ATZ composite (corresponding to \( X = 0.80 \) and thus \( \phi_Z = 0.726 \)).

**Porous Alumina-Zirconia Composite Ceramics**

The effective tensile moduli of two types of AZ composites (ZTA and ATZ), both prepared by starch consolidation casting (SCC) are listed in tables 2 and 3 for five different porosities. Figures 4 and 5 show the measured data, together with the Voigt-Reuss bounds (solid lines), Hashin-Shtrikman bounds (dashed lines) and data measured by the resonant frequency technique for AZ composites prepared by slip-casting (full squares).

**Table 1.** Measured (without asterisk) and calculated (with asterisk *) effective tensile moduli of dense (porosity < 3 %) alumina, zirconia and AZ composites (prepared by slip-casting); the estimated measurement error is between ±2 and ±4 GPa.

<table>
<thead>
<tr>
<th>Zirconia weight fraction X</th>
<th>Zirconia volume fraction ( \phi_Z )</th>
<th>Tensile modulus ( E ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure alumina</td>
<td>0</td>
<td>399 (400)</td>
</tr>
<tr>
<td>A90Z10</td>
<td>0.10</td>
<td>385</td>
</tr>
<tr>
<td>A85Z15 (ZTA)</td>
<td>0.15</td>
<td>376 (375)</td>
</tr>
<tr>
<td>A80Z20</td>
<td>0.20</td>
<td>365</td>
</tr>
<tr>
<td>A75Z25</td>
<td>0.25</td>
<td>353</td>
</tr>
<tr>
<td>A70Z30</td>
<td>0.30</td>
<td>350</td>
</tr>
<tr>
<td>A60Z40</td>
<td>0.40</td>
<td>333</td>
</tr>
<tr>
<td>A20Z80 (ATZ)</td>
<td>0.80</td>
<td>255 (251)</td>
</tr>
<tr>
<td>Pure zirconia</td>
<td>1</td>
<td>210</td>
</tr>
</tbody>
</table>

It has to be noted that the application of the rigorous upper bounds for two-phase materials (porous media) in this case involves the tacit assumption that the solid AZ composite matrix (skeleton) can be replaced...
by a "quasi-one-phase" continuum (effective medium at the microscale) with effective properties "smeared out" with respect to the length scale of the pores (macro-scale). This assumption is justified only because the pore sizes are 1-2 orders of magnitude larger (tens of microns) than the alumina and zirconia grain sizes (approx. 1 µm). Otherwise the material would have to be modeled as a three-phase composite, for which the Hashin-Shtrikman bounds (in case one phase is the pore phase, only the Hashin-Shtrikman upper bound) cannot be written in the simple explicit form given in [2]. Since our model assumes the existence of two quite distinct length scales it could be termed hierarchical "pseudo-binary" composite model.

In analogy to Part 4 of this series of papers [4], the \( E - \phi \) dependence for ZTA and ATZ can be fitted using the 11 relations (fit models) introduced in [2]. For theoretical background and a more detailed discussion of the individual relations cf. [24-29]. For easy reference, we repeat the relations here.

Model 1
\[
\frac{E}{E_0} = \exp(-2\phi) 
\]

Model 2
\[
\frac{E}{E_0} = \exp(-B\phi) 
\]

Model 3
\[
\frac{E}{E_0} = \exp\left(-\frac{2\phi}{1-\phi}\right) 
\]

Model 4
\[
\frac{E}{E_0} = \exp\left(-\frac{B\phi}{1-\phi}\right) 
\]

Model 5
\[
\frac{E}{E_0} = \exp\left(-\frac{2\phi}{1-\phi/\phi_C}\right) 
\]

Model 6
\[
\frac{E}{E_0} = \exp\left(-\frac{B\phi}{1-\phi/\phi_C}\right) 
\]

Model 7
\[
\frac{E}{E_0} = (1 - \phi)^2 
\]

Model 8
\[
\frac{E}{E_0} = (1 - \phi)^N 
\]

Model 9
\[
\frac{E}{E_0} = (1 - \phi/\phi_C)^N 
\]

Model 10
\[
\frac{E}{E_0} = \frac{1 - \phi}{(1 - \phi/\phi_C)} 
\]

Model 11
\[
\frac{E}{E_0} = (1 - \phi) \cdot (1 - \phi/\phi_C) 
\]

In all these relations \( E_0 \) is the tensile modulus of the dense (i.e. pore-free) ceramic and, except for the Hasselman relation (Model 10), the fit parameter \( \phi_c \) can in principle be assigned the physical meaning of a critical porosity, for which the integrity of the structure breaks down, i.e. \( E = 0 \) for \( \phi = \phi_c \). The fit parameters are listed and commented in tables 4 through 7.

As expected, the simple exponential relations (Models 1 and 2) yield unphysical behavior in the high-porosity limit (\( E > 0 \) for \( \phi = 1 \) and violation of the Voigt bound for porosities close to unity). Relatively reasonable behavior is exhibited by the modified exponential relations (Models 3 and 4), while the Mooney-type relations (Models 5 and 6) are either unsuccessful in fitting or need initial guesses and nevertheless lead to artefacts (\( E_0 \) and \( B \) too high, \( \phi_c \) unphysical, partially convex fit curve with inflection point). Models 7 and 8 are rather reasonable, with Model 7 (one parameter) being more robust and Model 8 (two parameters) yielding better fits.

Table 2. Measured effective tensile moduli of porous ZTA composite ceramics prepared by SCC.

<table>
<thead>
<tr>
<th>Porosity ( \phi )</th>
<th>Tensile modulus ( E ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.166</td>
<td>250</td>
</tr>
<tr>
<td>0.215</td>
<td>195</td>
</tr>
<tr>
<td>0.235</td>
<td>175</td>
</tr>
<tr>
<td>0.379</td>
<td>108</td>
</tr>
<tr>
<td>0.578</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 3. Measured effective tensile moduli of porous ATZ composite ceramics prepared by SCC.

<table>
<thead>
<tr>
<th>Porosity ( \phi )</th>
<th>Tensile modulus ( E ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.193</td>
<td>147</td>
</tr>
<tr>
<td>0.230</td>
<td>134</td>
</tr>
<tr>
<td>0.265</td>
<td>127</td>
</tr>
<tr>
<td>0.279</td>
<td>117</td>
</tr>
<tr>
<td>0.406</td>
<td>74</td>
</tr>
</tbody>
</table>

In Figure 6, the tensile modulus porosity dependence fitted by exponential models (ZTA composite ceramics prepared by SCC).
The three-parameter Phani-Niyogi relation (Model 9), although delivering fits with high correlation coefficients, can be said to have failed in both cases, due to unrealistic values of the fit parameters. The same can be said of the Hasselman relation (Model 10). Of all relations tested the newly proposed Model 11 turned out to be the most useful tool for fitting $E - \phi$ data. This finding confirms the comparative results for porous aluminium and zirconia in Part 4 of this series of papers [4] and seems to hold for all porous materials where deviations from the isometric pore shape are negligible.

The intrinsic tensile moduli $[E]$, as determined from Models 4 and 8, are between -1.7 and -2.6 for ZTA and between -1.5 and -2.2 for ATZ. The considerable scatter in these values around the isometric pore value of $[E] = -2$ might be caused by the fact that the data are too rough for deviations from isometric pore shape to be detected. In any case these fitting results yield no indications of anisometric pore shape in our samples.

The values of $E_0$ and $\phi_c$ determined by Model 11 are 351 GPa and 0.796 for porous ZTA and 237 GPa and 0.882 for porous ATZ composite ceramics.

**Table 4.** Fit parameters ($E_0$ in GPa) for the tensile modulus porosity dependence fitted by exponential models (ZTA composite ceramics prepared by SCC).

<table>
<thead>
<tr>
<th>Corr. coeff.</th>
<th>$E_0$</th>
<th>$\phi_C$</th>
<th>$B$</th>
<th>Initial guess</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>0.908</td>
<td>292.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 2</td>
<td>0.996</td>
<td>466.8</td>
<td>3.959</td>
<td>-</td>
<td>$E_0$ too high</td>
</tr>
<tr>
<td>Model 3</td>
<td>0.972</td>
<td>351.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 4</td>
<td>0.976</td>
<td>322.9</td>
<td>1.706</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 6</td>
<td>0.998</td>
<td>645.9</td>
<td>-1.011</td>
<td>6.719</td>
<td>$E_0 = 375$, $E_0$ and $B$ too high, $\phi_c$ unphysical</td>
</tr>
</tbody>
</table>

**Table 5.** Fit parameters ($E_0$ in GPa) for the tensile modulus porosity dependence fitted by power-law and related models (ZTA composite ceramics prepared by SCC).

<table>
<thead>
<tr>
<th>Corr. coeff.</th>
<th>$E_0$</th>
<th>$\phi_C$</th>
<th>$N$</th>
<th>Initial guess</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 7</td>
<td>0.975</td>
<td>322.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 8</td>
<td>0.989</td>
<td>380.0</td>
<td>2.626</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 9</td>
<td>0.996</td>
<td>466.8</td>
<td>47504</td>
<td>188060</td>
<td>$E_0$ and $N$ too high, $\phi_c$ unphysical</td>
</tr>
<tr>
<td>Model 10</td>
<td>0.999</td>
<td>756.9</td>
<td>-0.11</td>
<td>-</td>
<td>$E_0$ too high, $\phi_c$ unphysical</td>
</tr>
<tr>
<td>Model 11</td>
<td>0.985</td>
<td>351.1</td>
<td>0.796</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 6.** Fit parameters ($E_0$ in GPa) for the tensile modulus porosity dependence fitted by exponential models (ATZ composite ceramics prepared by SCC).

<table>
<thead>
<tr>
<th>Corr. coeff.</th>
<th>$E_0$</th>
<th>$\phi_C$</th>
<th>$B$</th>
<th>Initial guess</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>0.933</td>
<td>207.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 2</td>
<td>0.988</td>
<td>273.6</td>
<td>3.089</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 3</td>
<td>0.965</td>
<td>249.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 4</td>
<td>0.997</td>
<td>213.4</td>
<td>1.530</td>
<td>-</td>
<td>inflection point</td>
</tr>
<tr>
<td>Model 5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 6</td>
<td>0.997</td>
<td>198.6</td>
<td>0.792</td>
<td>1.186</td>
<td>$E_0 = 251$, inflection point</td>
</tr>
</tbody>
</table>

**Table 7.** Fit parameters ($E_0$ in GPa) for the tensile modulus porosity dependence fitted by power-law and related models (ATZ composite ceramics prepared by SCC).

<table>
<thead>
<tr>
<th>Corr. coeff.</th>
<th>$E_0$</th>
<th>$\phi_C$</th>
<th>$N$</th>
<th>Initial guess</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 7</td>
<td>0.991</td>
<td>226.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 8</td>
<td>0.994</td>
<td>238.9</td>
<td>2.188</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model 9</td>
<td>0.988</td>
<td>273.6</td>
<td>-24516</td>
<td>-75730</td>
<td>$\phi_c$ and $N$ unphysical</td>
</tr>
<tr>
<td>Model 10</td>
<td>0.987</td>
<td>293.1</td>
<td>-0.34</td>
<td>-</td>
<td>$\phi_c$ unphysical</td>
</tr>
<tr>
<td>Model 11</td>
<td>0.994</td>
<td>237.0</td>
<td>0.882</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
spectively. The $\phi_C$ values are reasonable from a physical viewpoint and correspond well to the visual inspection of the graphs. The $E_0$ values are in good agreement with those determined via the other reasonable models where fitting was successful (Models 3, 4, 7 and 8), viz. $E_0 = 344 \pm 24$ GPa and $E_0 = 232 \pm 13$ GPa for ZTA and ATZ, respectively. There seems, however, to be a general tendency of extrapolated $E_0$ values of being slightly underestimated (the theoretical values for dense ceramics are 375 GPa for ZTA and 251 GPa for ATZ, see above). The same was found for porous zirconia in [4]. With respect to the high precision of the resonant frequency method this phenomenon might be attributed to a tendency of determining the porosity to high. This can happen when a certain amount of zirconia has transformed into the monoclinic phase and thus the theoretical density in equation (1) is assumed higher than it actually is. Nevertheless, the ultimate reason of this finding must remain a subject of further research.

CONCLUSIONS

In this fifth and last paper of a series on the effective elastic properties of alumina-zirconia composite ceramics (AZ composites) the tensile modulus of dense and porous AZ composites has been investigated, both theoretically and experimentally. For dense AZ composites the Hashin-Shtrikman bounds turned out to be sufficiently close to each other and excellent agreement was found between theoretically predicted and measured values, so that the arithmetic average of the Hashin-Shtrikman bounds can be used for predicting effective elastic moduli for arbitrary compositions. Handy formulae have been given for the fast calculation of effective theoretical densities and effective elastic moduli of dense AZ composites, cf. equations (3) through (9). For dense zirconia-toughened alumina (ZTA) with 15 wt.% and dense alumina-containing tetragonal zirconia (ATZ) with 80 wt.% of zirconia the theoretically predicted effective tensile moduli are 375 GPa and 251 GPa, respectively.

Adopting a hierarchical "pseudo-binary" composite model, i.e. based on the assumption that the solid AZ composite matrix (skeleton) can be replaced by a "quasi-one-phase" continuum (at the microscale) with effective properties "smeared out" with respect to the length scale of the pores (macroscale), the porosity dependence of the effective tensile modulus has been analyzed for ATZ and ZTA (prepared by starch consolidation casting). The consistency of the experimentally measured data has been assessed with regard to the Hashin-Shtrikman upper bound. Fitting results confirm the superiority of the new relation $E/E_0 = (1 - \phi)(1 - \phi/\phi_C)$, where $E$ is the effective tensile modulus and $\phi$ the porosity, over most other fit models. Extrapolated $E_0$ values are 351 GPa and 237 GPa and critical porosities $\phi_C$ are 0.796 and 0.882 for porous ZTA and ATZ, respectively.
Footnotes:

1 For a classical two-phase composite, in which the phase boundaries play no role in determining the density and other effective properties. Note that these and the following calculations cannot be assumed to be valid for nanocomposites.

2 When higher precision is required the type and content of lattice-stabilizing agents (yttria, ceria, magnesia, calcia etc.) must necessarily be specified.

3 Other means, e.g. the harmonic or geometric mean, would do just as well. Due to the proximity of the Hashin-Shtrikman boundaries play no role in determining the density and other effective properties. Note that these and the following calculations cannot be assumed to be valid for nanocomposites.

4 Of course, the Reuss bounds and the Hashin-Shtrikman lower bounds are zero in this case, cf. [2].

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References


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