Porous alumina and zirconia ceramics with tailored thermal conductivity

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Abstract. The thermal conductivity of porous ceramics can be tailored by slip casting and uniaxial dry pressing, using either fugitive pore formers (saccharides) or partial sintering. Porous alumina and zirconia ceramics have been prepared using appropriate powder types (ungranulated for casting, granulated for pressing) and identical firing regimes (but different maximum temperatures in the case of partial sintering). Thermal diffusivities have been measured by the laser- and xenon-flash method and transformed into relative thermal conductivities, which enable a temperature-independent comparison between different materials. While the porosity can be controlled in a similar way for both materials when using pore formers, partial sintering exhibits characteristic differences between alumina and zirconia (for alumina porosities below 45 %, full density above 1600 °C, for zirconia porosities below 60 %, full density above 1300 °C). The different compaction behavior of alumina and zirconia (porosity after pressing 0.465 and 0.597, respectively) is reflected in the fact that for alumina the relative conductivity data of partially sintered materials are below the exponential prediction, while for zirconia they coincide with the latter. Notwithstanding these characteristic differences, for both alumina and zirconia it is possible to tailor the thermal conductivity from 100 % down to approx. 15 % of the solid phase value.

1. Introduction

Thermal conductivity is a key property of ceramics in many fields of application, ranging from insulating refractories and thermal barrier coatings to electronic substrates and functional ceramic components [1-3]. Depending on the application, either a high or a low thermal conductivity is more desirable [4]. Although grain size effects are non-negligible especially in the case of nanocrystalline ceramics [5] and pore size effects can also be important either at the nanoscale (when the pores are smaller than the mean free path length of the gas filling the pores) or when radiation or convection come into play [4], the dominant factor determining the effective thermal conductivity of ceramics usually is porosity, i.e. the volume fraction of pores. That means, the thermal conductivity of ceramics can be very efficiently tailored by controlling the pore volume fraction of ceramics, e.g. by using

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fugitive pore formers [6-8]. It is known that the porosity dependence of ceramics prepared using fugitive pore-formers (i.e. with essentially convex pores) is well described by an exponential relation [9]. Actually, except for very highly porous (> 80 %) cellular ceramics, the vast majority of experimental data published in the literature are below the power-law prediction [10]. However, even the exponential relation is of course not a universally applicable prediction. Many data published in the literature are well below the exponential prediction (and thus far below all other common predictions). In particular, partially sintered ceramics can be expected to exhibit lower effective conductivity values than ceramics prepared with fugitive pore formers (at comparable porosity levels), because unsintered powder compacts with point contacts are percolative in the sense that for higher porosities the point contacts are disrupted and the conductivity decreases very rapidly to zero (more precisely to that of the surrounding medium, i.e. usually air). Despite the plausibility of this idea, a comparison between the thermal conductivity of partially sintered ceramics and of ceramics prepared with fugitive pore formers is not available in the literature. In this contribution we perform this comparison for alumina and zirconia. Samples are prepared from identical powders by uniaxial pressing and slip casting and fired according identical regimes. It will be shown that there are characteristic differences in the behavior of different materials which are intimately connected to their compaction behaviour during the shaping step. The thermal conductivity is determined from thermal diffusivity values measured using the laser flash method (and for selected samples using the xenon-flash method for comparison). It will be shown that partial sintering is in fact a powerful tool for tailoring thermal conductivity. Although the porosities achievable by partial sintering alone, are usually lower than by using fugitive pore formers (such as starch and other saccharides), the thermal conductivity can be tailored in an equally wide range.

2. Theoretical
The thermal conductivity of solid phases is always higher than that of gases at atmospheric pressure [4]. Even for yttria-doped zirconia, which is one of the best insulating oxide phases, the thermal conductivity is still higher than that of air (at room temperature and normal pressure) by two orders of magnitude. For this reason dense solids are usually not very efficient thermal insulators. The prediction of the thermal conductivity of porous materials, on the other hand, is complicated by the fact that the lower micromechanical bounds approach zero, when the conductivity of the pore phase can be neglected [4]. Therefore any prediction for porous materials must principally be model-based. Fortunately, the upper bounds remain intact, and this helps at least to eliminate inadmissible predictive and fit relations and incorrect experimental results. Generally, the thermal conductivity of a porous material is bounded from above by the upper Wiener bound,

\[ k_r = 1 - \phi, \]  

where \( \phi \) is the porosity (volume fraction of pores) and \( k_r = k/k_0 \) is a dimensionless relative conductivity with \( k_0 \) being the conductivity of the solid phase and \( k \) the thermal conductivity of the porous material as a whole. For isotropic materials (and this is what we can assume in the following) the thermal conductivity of a porous material is bounded from above by the upper Hashin-Shtrikman bound,

\[ k_r = \frac{1-\phi}{1+2\phi}, \]  

Apart from these two rigorous upper bounds there are three nonlinear relations that can be recommended for predicting the effective conductivity of porous materials. These are the Coble-Kingery-type relation [11]
\[ k_r = 1 - \frac{3}{2} \phi + \frac{1}{2} \phi^2, \quad (3) \]

the power-law relation [12]

\[ k_r = (1 - \phi)^{3/2}, \quad (4) \]

and the exponential relation [10]

\[ k_r = \exp\left( -\frac{3}{1 - \phi} \right). \quad (5) \]

While the first of these, proposed in [11], has been used in the recent literature for porous zirconia [10], it is rather close to the Hashin-Shtrikman upper bound and therefore certainly less appropriate than the latter two expressions for predicting the thermal conductivity of real materials. Therefore we will use exclusively the latter two for comparison with our measured values. The exponential relation, which seems to be the most successful estimator not only for the thermal conductivity [8-10] but also for elastic properties (Young’s modulus) of porous materials [14,15], will be used in the sequel also to extrapolate low-porosity results to zero porosity, which is necessary to obtain \( k_0 \) values for calculating the relative conductivity for the temperature in question. It should be emphasized that equations (4) and (5) are not empirical but can be derived by the differential approach [16] or the functional equation approach [9].

3. Experimental

3.1. Materials and their preparation

Samples for thermal conductivity measurement were prepared from commercial submicron alumina and zirconia powders in granulated (for uniaxial pressing) and ungranulated form (for slip casting). The alumina powders are CT-3000-SG and CT-3000-SDP (Almatis, Germany) with a primary particle (crystallite) size of 0.6–0.8 µm, the zirconia powders are TZ-3YE (Tosoh, Japan) with particle size of 0.2–0.6 µm but a crystallite size of 25 nm (i.e. nanocrystalline before firing / sintering). Granule sizes of the powders for pressing (with a very small binder content) are in the range 50–100 µm. Pore formers used in this work were monosaccharides (glucose) and polysaccharides (inulin, corn and wheat starch).

Samples required for the thermal conductivity measurements are disks with a diameter of approx. 12.7 mm or squares with edge length of 10 mm, both typically with 2 mm thickness. Samples for partial sintering were prepared from granulated powders by uniaxial pressing with 50 MPa using a hydraulic press. After demolding, the as-pressed samples were fired according to a standard schedule (heating rate 2 °C/min, dwell at maximum temperature 2 h) at temperatures in the range 1250–1550 °C for alumina and 1050–1450 °C for zirconia. Samples with different percentages of corn or wheat starch as pore forming agents were prepared using two variants of slip casting: traditional slip casting into plaster molds and so-called starch consolidation casting into metals molds. The principles of these methods as well as the resulting types of microstructures have been described in great detail in several previous papers [7,17]. Both methods require careful preparation of the suspensions used for casting. Suspension preparation includes mixing of the (ungranulated) ceramic powders with distilled water and deflocculant, ultrasonication and homogenization by shaking. Further details can be found elsewhere [18]. After casting the molds (and heating in the mold in the case of starch consolidation casting) the molds were opened and the as-cast bodies slowly dried with a stepwise increase of temperature, until constant mass was achieved during drying at 105 °C. The as-dried alumina and zirconia bodies were then fired according to the aforementioned schedule to temperatures of 1570 °C
and 1490 °C, respectively (to ensure that the matrix between the large pores due to starch is fully densified during sintering). Wherever necessary, disks or squares were cut using a diamond saw from the as-fired bodies. The bulk density of all samples was determined via the Archimedes method (weighing the dry samples in air and the water-saturated samples in air and in water). The total porosity $\phi$ was calculated from the bulk density $\rho$ and the true (theoretical) density $\rho_0$ of alumina and (3 mol.% yttria-stabilized) tetragonal zirconia (4.0 and 6.1 g/cm$^3$, respectively), according to the formula

$$\phi = 1 - \frac{\rho}{\rho_0}. \quad (6)$$

For thermal conductivity measurement via the laser-flash technique the samples were coated by a graphite layer (in the case of the xenon-flash measurements also with a gold layer) to avoid direct penetration of the laser beam or xenon flash (measurement errors due to radiation).

3.2. Thermal conductivity measurement
Thermal conductivity measurement was performed using the laser-flash technique (LFA1000, Linseis, Germany) and – for a few selected samples – also using the xenon-flash technique (FlashLine 3000, Anter, USA). In these transient methods a small, thin sample is subjected to a high intensity short duration radiant (laser or flash-lamp) energy pulse. The energy of the pulse is absorbed on the front surface of the specimen, and the resulting rear face temperature rise is recorded and evaluated by the instrument producer’s proprietary software. The thermal diffusivity $a$ is calculated from the specimen thickness and the time required for the rear face temperature to reach certain percentages of its maximum value. The thermal conductivity can be calculated from this measured thermal diffusivity value, when the bulk density $\rho$ and the specific heat value $c_p$ is known for the temperature in question, according to the formula

$$k(T) = a(T) \cdot \rho(T) \cdot c_p(T). \quad (7)$$

For alumina and zirconia the temperature dependence of the bulk density is negligible [19]. The specific heat of alumina and zirconia is well known from the literature. Here we use the handy interpolation formulae

$$c_p = 512.6 \cdot T^{0.131}, \quad (8)$$

and

$$c_p = 309.5 \cdot (T + 24)^{0.105}, \quad (9)$$

for alumina and zirconia, respectively, where $T$ is to be inserted in units [°C] and $c_p$ is obtained in units [J/kgK]. These formulae have been recommended in [19] for the temperature range between room temperature and approx. 1500 °C, being based on an extensive literature search and comparison of many different sources. Note that near to room temperature the dependence of the specific heat on temperature is relatively strong, so that the accuracy of the thermal conductivity value depends to some degree on precision of the temperature measurement.

4. Results and discussion

4.1. Porosities achievable using pore formers and by partial sintering
Using fugitive pore formers such as polymers or bioorganic compounds and polymers (e.g. starch and other saccharides), the porosity can be tailored by choosing the appropriate amount of pore former [7]. The porosity and its controllability differ from method to method (e.g. the porosity range is broader for traditional slip casting than for starch consolidation casting, but porosities are usually higher for the latter), but typically range from close to zero to approx. 60 % [17]. Higher porosities (70 %) can be achieved when the use of pore formers is combined with partial sintering [15] or when foaming is involved in the shaping technique (sometimes 90 % and more) [20]. The porosities achievable by partial sintering without pore formers or foaming are generally lower. In fact, the bulk density after pressing sets an upper limit to the porosity achievable by partial sintering. This bulk density of the as-pressed bodies is a consequence of the complex interplay between powder characteristics (particle and granule size, size distribution, shape, surface roughness and state of agglomeration), filling and pressing conditions (mainly pressure, but also pressurization rate and time) and cannot be easily predicted. For the granulated powders used in this work for pressing, the porosity of as-pressed alumina bodies is 0.45 and 0.465 after pressing for 30 s at 100 MPa and 50 MPa, respectively. However, for zirconia the corresponding porosities are significantly higher, viz. 0.564 and 0.597, respectively. The reasons for this different behavior are too complex to be analyzed in this paper, but this empirical finding remains as a fact. As a consequence, the porosity achievable by partial sintering of samples pressed at 50 MPa is restricted to values below 0.465 for alumina and below 0.597 for zirconia. Above these values the powder compact will lose integrity and the thermal conductivity will drop very rapidly to that of the surrounding medium (air).

Figure 1 shows the porosity of partially sintered alumina and zirconia ceramics, respectively. It is evident that the porosity of alumina decreases more slowly with increasing firing temperature compared to that of zirconia and that for alumina the range of achievable is smaller but easier to control (zirconia has a steeper slope).

![Figure 1. Total porosity achievable in alumina (left) and zirconia (right) ceramics via partial sintering; the dashed part of the line indicates the maximum porosity that can be theoretically achieved (porosity of the bodies after pressing at 50 MPa: 0.465 and 0.597 for alumina and zirconia, respectively).](image)

4.2. Measured thermal conductivities of porous alumina and zirconia ceramics

Absolute thermal conductivities are much higher for alumina than for zirconia. At and around room temperature the difference is about one order of magnitude, viz. approx. 33 W/mK for pure alumina (corundum, $\alpha$-$\text{Al}_2\text{O}_3$) and 2.9 W/mK for the zirconia type used here (tetragonal $\text{ZrO}_2$ containing 3 mol% $\text{Y}_2\text{O}_3$) [4,19]. Moreover, the temperature dependence of the two materials is quite different: alumina exhibits a hyperbolic decrease typical for well-ordered crystalline solids, while zirconia (a defective structure because of the yttria doping) exhibits a glass-like behavior, i.e. more or less constant conductivity with increasing temperature [4,19]. Especially in the case of alumina it is very inconvenient to compare conductivity values determined for different temperatures, even if the
difference is relatively small (in this work 15–20 °C). Therefore, figures 2 and 3 compare relative conductivities both for alumina and zirconia.

**Figure 2.** Relative thermal conductivity of porous alumina in dependence of the porosity; from top to bottom rigorous upper bounds (Wiener, Hashin-Shtrikman), model relations (power-law, exponential) and straight line (dashed) connecting the fully dense material (relative conductivity 1) with the as-pressed material (relative conductivity approaching 0).

**Figure 3.** Relative thermal conductivity of porous zirconia in dependence of the porosity; from top to bottom rigorous upper bounds (Wiener, Hashin-Shtrikman), model relations (power-law, exponential) and straight line (dashed) connecting the fully dense material (relative conductivity 1) with the as-pressed material (relative conductivity approaching 0).
It is evident that all measured values are not only below the Hashin-Shtrikman bound (Maxwell-Eucken relation) but even below the power-law relation (and thus \textit{a fortiori} also below the Coble-Kingery type relation). Our exponential relation, equation (5), seems to provide the best prediction for most values. It seems that in the case of zirconia (figure 3) all values are satisfactorily (within experimental scatter, which involves both sample preparation and measurement scatter) predicted via this relation. However, although our exponential relation has proven to be the most successful relation for predicting not only the thermal conductivity but also elastic properties (Young’s modulus) of porous ceramics prepared using pore forming agents [14,15] (irrespective of the material [21]) it is completely clear that this relation (and also any other predictive relations of this type) cannot be universal. Pore shape is expected to play a significant role here, because fugitive pore formers lead to essentially convex pores, whereas partial sintering leads to essentially concave pores between ceramic particles, and in the latter case the pathways for conduction are obviously more restricted for comparable degrees of compaction (levels of porosity). Of course, when full density is approached, the concave interstitial voids “spheroidize” and the difference between the two types of microstructure is reduced to differences in pore size, which are of minor importance compared to pore shape.

Indeed, closer inspection of figure 2 indicates that the values determined for partially sintered alumina are below the exponential prediction. The dashed straight line is a guide to the eye, connecting the fully dense material (for which the relative conductivity is unity) with the porosity of the as-pressed body (above which the conductivity drops rapidly to zero). The relative conductivity values for partially sintered alumina (figure 2) seem to follow this line more closely than the exponential curve. However, in the case of zirconia (figure 3) the corresponding line is rather close to the exponential, and this explains why the thermal conductivity values determined for partially sintered zirconia are very similar (in practice indistinguishable because of inevitable data scatter) to those of zirconia prepared using pore-forming agents. The findings indicate that partial sintering is an efficient method for thermal conductivity control in both cases (alumina and zirconia). The range of porosities achievable via partial sintering is dependent not so much on the material but on the powder type used and depends primarily on the raw bulk density of as-pressed powder compacts: in the case of the zirconia powder used here it can be from almost zero to almost 60 %, whereas with the alumina powder used here porosities of 45 % can hardly be achieved. Nevertheless, it has to be emphasized that the relative thermal conductivity can be tailored in a comparable way with both materials: for alumina the lowest relative conductivity value achieved in our set of samples is 0.14 (for a porosity of only 42 %), while for zirconia the lowest value is 0.16 (for a porosity of 54 %).

5. Summary and conclusion
This contribution treats the possibility of tailoring the thermal conductivity of porous ceramics prepared by slip casting methods and by uniaxial dry pressing, using either fugitive pore formers (corn and wheat starch in connection with casting, glucose and inulin in connection with pressing) or partial sintering for achieving different volume fractions of porosity and principally different pore shapes (essentially convex in the case of pore formers, essentially concave in the case of partial sintering). Porous alumina and zirconia ceramics have been prepared using appropriate powder types (ungranulated for slip casting, granulated for pressing) and identical firing regimes (heating rate, dwell time) but different maximum temperatures in the case of partial sintering. Thermal diffusivities have been measured by the laser-flash method at room temperature (18 ± 2 °C) (and for selected cases checked by the xenon-flash method at 100 °C). Using reliable specific heat values and bulk density values measured via the Archimedes method, the measured diffusivity values have been transformed into thermal conductivities and these transformed into relative conductivity values to enable a temperature-independent comparison between different materials. (For the latter transformation, the thermal conductivity values of the densest samples have been extrapolated to zero porosity using the exponential relation).

While the porosity can be controlled in a similar way for both materials when using pore formers (by adding appropriate amounts of pore formers, porosities of up to 60 % are possible), partial sintering exhibits characteristic differences between alumina and zirconia (for alumina porosities
below 45 % with a slow porosity decrease with increasing firing temperature up to 1600 °C, for zirconia porosities below 60 % with a rapid porosity decrease with increasing firing temperature up to 1300 °C). The different compaction behavior of alumina and zirconia (porosity after pressing 0.465 and 0.597, respectively) is reflected in the fact that for alumina the relative conductivity data of partially sintered materials are below the exponential prediction, while for zirconia they coincide with the latter. However, notwithstanding these characteristic differences in porosity control, for both alumina and zirconia it was possible to tailor the thermal conductivity from 100 % down to approx. 15 % of the solid phase conductivity.

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