



Colloidal processing and partial sintering of high-performance porous zirconia nanoceramics with hierarchical heterogeneities

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Received 3 April 2013; received in revised form 27 May 2013; accepted 2 June 2013

Available online 12 July 2013

Abstract

High-performance, porous, Y-TZP nanoceramics with hierarchical heterogeneities originating from uniform, intra- and inter-particle packing were prepared by colloidal processing and partial sintering of a mesoporous powder. The powder consisted of 100–150-nanometer-sized secondary particles initially composed of smaller, loosely aggregated, primary, nanoscale crystallites. Green bodies were prepared by centrifugal slip casting of weakly flocculated suspensions. During the initial stage of sintering, necking between the secondary particles was accompanied by intra-particle pore coalescence, while the pores originating from the secondary particle packing remained intact. Such microstructures with porosity levels between 46 and 18.3% and pore areas between 18 and 4 m²/g led to attractive properties, i.e., much reduced thermal conductivities of 0.63–1.88 W m⁻¹ K⁻¹, high bending strengths of 70–540 MPa and lowered elastic moduli of 32–156 GPa, making them potentially ideal as thermal insulators and/or load-bearing porous biomaterials owing to the possibility of further impregnation with bioactive ingredients.

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Keywords: Mesoporous zirconia; Colloidal processing; Sintering; Thermal conductivity; Mechanical properties

1. Introduction

Porous ceramics have for a long time been the materials of choice in many technological solutions when it comes to applications related to support for catalytic reactions, filtration, sensors, high-temperature thermal insulators, light-weight structural components and, most recently, in the field of biomaterials. A high melting point, tailored electronic properties, high corrosion- and wear-resistant surfaces are the main benefits of these materials in such applications. Moreover, inducing porosity into ceramic materials also results in a lower density, a high surface area, a lower thermal conductivity, an appropriate permeability and a lower dielectric constant.¹

There are many different routes for preparing porous ceramics in addition to the traditional way of partially sintering ceramic powder compacts. These include solid-state reactions, replica

techniques, sacrificial templates and direct foaming methods, resulting predominantly in macroporous or cellular ceramics, which, however, usually possess limited mechanical properties (the exception can be the ones prepared by direct foaming method).¹ It was also shown that porous ceramics with enhanced properties can be prepared by employing advanced sintering techniques, such as pulsed-current sintering (SPS)^{2–4} and hot isostatic pressing (HIP).⁵

In the field of biomaterials, where oxide ceramics tend to predominate, nanoscale mesoporous materials can dramatically enhance their bioactivity,⁶ while the present pores represent an available space for bone ingrowth, when infiltrated with bioactive materials such as hydroxyapatite.⁷ The additional benefits of inducing a tailored porosity into the otherwise dense bioceramics, such as yttria-stabilized tetragonal zirconia (Y-TZP), if done in such a way that would decrease the elastic modulus, while retaining a sufficiently high strength and fracture toughness, would be twofold: (i) it would decrease the elastic mismatch between the ceramics and the bone/dentine,⁸ since this can lead to the development of stresses at the interface between the ceramics and the bone/dentine,⁹ and (ii) it would lower the susceptibility to a low-temperature degradation (LTD)

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process. In addition to bioceramics, Y-TZP porous ceramics with enhanced mechanical properties, especially strength, are being touted as a suitable candidate in the field of insulators, since they possess a low intrinsic thermal conductivity.¹⁰

In particular, when the conflicting demand of a high mechanical strength at a lower elastic modulus is required, methods for the preparation of porous ceramics, where pronounced necking is obtained, are desired. Nanjangud et al. showed that, traditionally, the rapid strength increase is related to the growth of the interparticle contacts by surface diffusion, in the initial stages of sintering,¹¹ where the increase in the elastic modulus is also the highest. The increase in strength with minimum densification is a significant factor for the mechanical behaviour of porous ceramics, in that the strength improvements can be made by control of the sintering mechanism and the geometry of the particles' structure.¹²

Alternatively, there are ways to emphasize the necking formation by using pressureless sintering conditions, as opposed to the neck-enhancement induced by using SPS.^{3,13} Two examples are the core-shell concept¹⁴ and the hydrolysis-assisted solidification (HAS) process.¹⁵ In the former the formation of a shell layer of nanoparticles around the core of basic particles results in a larger area of inter-particle contacts, thereby increasing the strength of the monolith.¹⁴ In the latter, however, the formed boehmite lamellas topotactically transform into transient alumina during the sintering, which, when transformed into nanosized α -alumina particles, dramatically increase the neck surface area and its growth rate between the coarser alumina particles, so improving the mechanical strength of the porous body.¹⁵

In the present work the aim of lowering the elastic modulus for a given particle packing with pronounced necking was achieved by introducing tailored porosity into the Y-TZP ceramics. Colloidal processing was employed to consolidate an initially mesoporous ceramic powder, composed of loosely aggregated primary nanoscale crystallites, which yielded green bodies with hierarchical heterogeneities in terms of intra- and inter-particle pores on account of the spherical mesoporous particle packing. These microstructural features together with a homogeneous particle packing, revealed a unique behaviour during the initial and intermediate stages of sintering, as well as lowering the thermal conductivity of the zirconia nanoceramics for a given porosity, while maintaining good mechanical properties.

2. Materials and methods

2.1. Suspension preparation and characterization

In the present study a custom-made Y-TZP mesoporous powder (Meso-TZ), with 2.94 mol% of yttria and a small content of alumina (0.2–0.4 wt%), was used. The powder is a semi-product with the potential of being commercialized in the near future, and so the producer will not be disclosed here.

The measurements of particle size distribution and zeta-potential were performed with a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK). For the dispersed phase, i.e.,

Meso-TZ, a refractive index of 2.123 and an absorbance of 0.1 were used. Deionized water was used as the continuous phase, for which values of 0.8872 mPa s for the viscosity at 25 °C, 1.33 for the refractive index and 78.5 for the dielectric constant were taken. The ζ -potential was calculated measuring the electrophoretic mobility of a particle and using the Henry's equation:

$$U_E = \frac{2\varepsilon\xi f(Ka)}{3\eta} \quad (1)$$

where U_E is the electrophoretic mobility, ε is the dielectric constant, ξ is the zeta potential, $f(Ka)$ is Henry's function, and η is the viscosity. Henry's function generally has value of either 1.5 or 1.0. For measuring zeta potential in aqueous solutions of moderate electrolyte concentration, a value of 1.5 is used and this is referred to as the Smoluchowski approximation.¹⁶

The measurements were performed in diluted suspensions (0.02 vol.%), with or without citric acid as a dispersant, in which the pH was adjusted prior to the measurement by using either 0.1-M HNO₃ or 0.1-M KOH and measured with a SevenMulti instrument equipped with an InLab Expert NTC30 electrode (Mettler Toledo, International Inc.). A background electrolyte consisting of 0.01-M KNO₃ was added for the electrokinetic measurements to adjust the ionic strength. The suspensions were homogenized using ultrasonication for 10 min with a Vibra cell VCX 130 ultrasound horn (SONICS, Newtown, USA) at 75% power prior to the measurement. The sonication was applied in intermittent pulses of 20 s, with breaks of 15 s in order to reduce the temperature increase.

The viscosities of the suspensions were measured with an Anton Paar Physica MCR 301 rheometer (Anton Paar, GmbH, Graz, Austria), where the temperatures of the suspensions were kept at 25 ± 0.1 °C with a thermostatic bath. To determine the optimum amount of dispersant to be used in the suspensions, 20 vol.% solids-loading suspensions with different amounts of citric acid were prepared and then ultrasonicated before the test, as described above. The homogenization of the suspensions in the experiment, where the influence of the amount of solids loading on the rheological behaviour was studied, was performed by 24-h ball milling in a plastic container using Y-TZP balls ($\varphi = 3$ mm).

Weak flocculation (WF) of the particles in the suspensions was induced by using tribasic ammonium citrate salt. After the ball milling of the suspension containing 35 vol.% of solids loading, the suspension was first diluted to 30 vol.% and then an appropriate amount of 3-M salt was added and mixed with a magnetic stirrer for several hours.

2.2. Casting, sintering and sample characterization

The centrifugation slip casting of the WF Meso-TZ suspensions was performed in a centrifuge (Megafuge 1.0, Heraeus Instruments GmbH, Hanau, Germany) at 4000 rpm for 30 min in a specially designed plastic mould ($\varphi = 20$ mm), which roughly corresponded to a centrifugal force of $2860 \times g$. Before casting the moulds were sprayed with a Teflon-based dry lube so as to increase the hydrophobicity and to prevent sticking of the

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