



Facile processing of oriented macro-porous ceramics with high strength and low thermal conductivity

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ABSTRACT

Unidirectionally oriented architectures demonstrate a notable efficiency in enhancing the properties of macro-porous materials, yet are difficult to construct in a time- and cost-effective fashion. Here a facile approach was exploited for fabricating oriented macro-porous ceramic materials by employing natural graphite flakes as a fugitive material and preferentially aligning the flakes within ceramic matrices using accumulative rolling technique. Flaky to near-ellipsoid shaped pores with a homogeneous distribution were created in macro-porous zirconia ceramics with their porosity and microstructural characteristics adjustable by controlling the additive amounts of graphite flakes. The resulting materials exhibited a good combination of properties with high compressive strength up to over 1.5 GPa, which exceeds those of most other porous zirconia ceramics with similar porosities, along with low thermal conductivity of $0.92\text{--}1.85\text{ Wm}^{-1}\text{K}^{-1}$. This study offers a simple means for developing new oriented macro-porous materials with enhanced properties, and may promote their application by allowing for easy mass production.

1. Introduction

Macro-porous ceramic materials are distinguished by combining the intrinsic property advantages of ceramic materials, such as high strength along with good thermal and corrosion resistance, with the merits endowed by the porous structures, such as low densities and outstanding insulation properties. As such, they have been widely used in a variety of applications ranging from insulation and filtration materials, catalyst supports, to bone substitutes [1,2]. Macro-porous zirconia ceramics are particularly attractive as compared to other material systems owing to their low thermal conductivity, high thermal shock resistance and good biocompatibility [3,4]. Strength and thermal insulation capacities are two of the most important properties for many macro-porous ceramic materials, including zirconia. However, these properties are often mutually exclusive and therefore are difficult to improve

simultaneously. This is caused by the fact that the enhancement in the thermal insulation capacity of macro-porous materials is principally realized by increasing their porosity, which invariably tends to lower their strength [5]. In this context, overcoming such a trade-off is of notable significance to the development of high-performance macro-porous ceramic materials and the promotion of their applications.

As a prototype of macro-porous materials that is optimized by Nature, natural wood has developed highly oriented architectures with long-term evolution to achieve an outstanding combination of both mechanical and functional properties. The majority of pores in wood, which are mainly composed of the inner cavities of wood cells, tracheids, vessels and sieve tubes, are preferentially aligned along the growth direction [6–8]. This endows wood with the highest load-bearing capacity along its axial direction to resist compression and bending, and simultaneously hinders the heat transfer with its

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surroundings along the radial direction, thereby inducing good thermal insulation properties. The implementation of oriented architectures offers an effective approach for overcoming the exclusive relationships between strength and thermal insulation properties in macro-porous materials [7–10]. This has been verified in our recent study where cement and gypsum materials containing unidirectionally lamellar pores demonstrate notable combinations of improved strengths with lowered thermal conductivities as compared to those for randomly porous materials [11,12].

However, it remains a key, nontrivial challenge to construct oriented macro-porous architectures in materials in a scalable, but time- and cost-effective fashion. The traditional fabrication approaches of macro-porous materials, such as partial sintering, direct foaming, or using replica templates and sacrificial fugitives, demonstrate a limited capability for controlling the geometrical and spatial characteristics of pores [13–17]. Multi-pass co-extrusion of ceramic dough with sacrificial fugitives offers a means for fabricating oriented macro-porous materials, yet it is principally limited to the use of one-dimensional fugitives, e.g., carbon fibers. Ice-templating technique, also known as freeze casting, can effectively create directionally aligned pores in materials by using ice or crystals of other solvents as a fugitive material which are driven to grow preferentially along the freezing direction during the directional solidification of slurries [18–21]. Nevertheless, as the freezing advances, the temperature gradient at the solidification front decreases due to

reduced thermal conductivity, thereby impeding further freezing, limiting the dimension of samples (generally several centimeters in height), and leading to non-uniform microstructures. Additionally, the slow freezing and the sublimation of ice, which is most commonly realized by freeze drying, can be a lengthy process and consume a considerable amount of energy. Additive manufacturing offers an optional and viable method for modulating the architectures of macro-porous materials [22–25]. However, it is also downgraded by high cost and low efficiency, and as such is not suitable for applications where the mass production of macro-porous materials is desired.

Here, we propose a facile processing strategy to construct oriented macro-porous architectures in materials. This is achieved by employing natural graphite flakes as a fugitive material and preferentially aligning these flakes *via* accumulative rolling of the mixed dough within ceramic matrices. The as-fabricated macro-porous ceramics, where zirconia is used as the example, exhibit a good combination of high strength and low thermal conductivity.

2. Experimental methods

2.1. Fabrication and architectural construction

Powders of 3 mol.% yttria-stabilized tetragonal zirconia polycrystals with a median diameter of ~50 nm (Lifeng Co., China) were mixed with

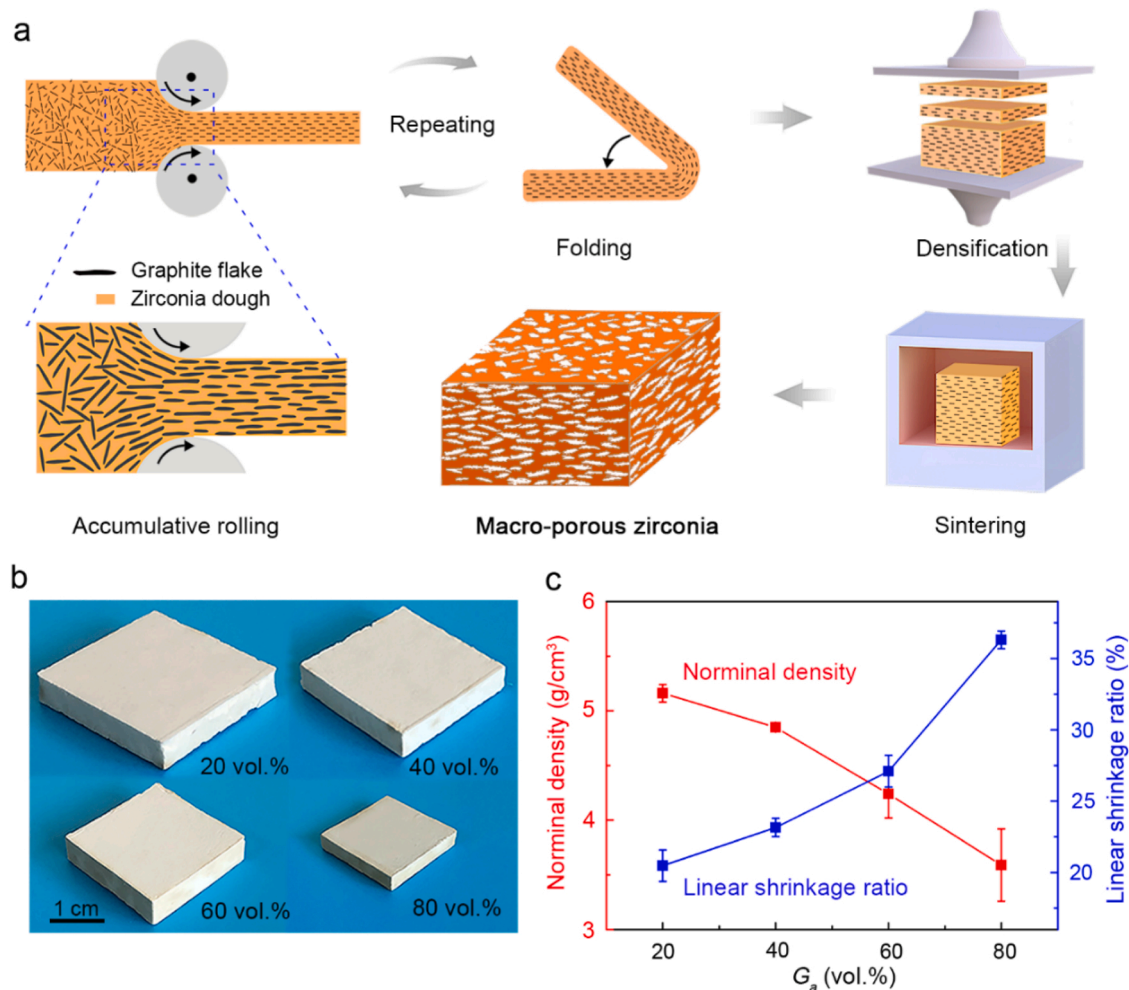


Fig. 1. Formation of macro-porous zirconia ceramics with oriented architectures. (a) Schematic illustration of the fabrication procedure of oriented macro-porous zirconia ceramics and the mechanisms for the formation of preferentially aligned pores. (b) Overall appearance of the macro-porous ceramics fabricated with different additive amounts, G_a , of graphite flakes. (c) Variation in the nominal density and linear shrinkage ratio during sintering for the macro-porous zirconia ceramics as a function of G_a .

natural graphite flakes with a median diameter of $\sim 18 \mu\text{m}$ and thickness of less than $8 \mu\text{m}$ (325 mesh, Jicang Nano., China) in deionized water at a solid-to-water ratio of 0.7 by weight. The additive amounts of graphite flakes in the total of solids, G_a , were respectively 20 vol%, 40 vol%, 60 vol% and 80 vol%. Darvan CN dispersant (R.T. Vanderbilt Co., USA) and hydroxypropyl methylcellulose (Meryer Co., China), accounting for respectively 1 wt% and 0.8 wt% of the mixture, were added to promote the dispersion of the solids and to act as an adhesive. The slurries were ball-milled at a rotation speed of $25 \text{ rot}\cdot\text{min}^{-1}$ for 24 h and then were placed in the oven set at 50°C . During the drying process, the mixture was constantly stirred and kneaded until forming a dough with a moisture content of around 8 wt%.

The dough was then processed by accumulative rolling using a twin-roller to realize the preferential alignment of graphite flakes within zirconia matrices. As illustrated in Fig. 1, the dough was rolled by $\sim 50\%$ reduction in thickness, folded along the rolling direction, and then re-rolled. Such process was repeated by at least 20 cycles to obtain a thin sheet of around 1 mm in thickness which was subsequently cut into several pieces with the same dimension. These pieces were stacked and consolidated to form a green body by pressing along their normal direction at 8 MPa for 1 h. After drying, the bulk was calcined at 600°C for 5 h in air to remove the graphite flakes and then sintered at 1550°C for 2 h to generate the oriented macro-porous ceramics.

2.2. Porosity measurement

The open porosity, *i.e.*, the volume fraction of interconnected open pores, and pore size distribution of sintered macro-porous ceramics were measured by mercury porosimetry using an AutoPore IV 9500 porosimeter (Micromeritics, USA). The total porosity, *i.e.*, the volume fraction of all the pores, was determined using the Archimedes' method [26]. Specifically, a sample with an original weight m_0 was immersed in methanol for 24 h to ensure a complete filling of large open pores with methanol. The weight of the infiltrated sample hanging in methanol was measured to be m_1 . Subsequently, the sample was taken out of methanol and weighed immediately after the extra methanol on the surface volatilized, giving a weight m_2 . The nominal density of macro-porous ceramics, ρ_{nominal} , can be obtained as: $\rho_{\text{nominal}} = m_0 \rho_{\text{methanol}} / (m_2 - m_1)$. The total porosity of the sample, P_{total} , can be calculated from its nominal density as: $P_{\text{total}} = 1 - (\rho_{\text{nominal}} / \rho_{\text{true}})$, where ρ_{true} is the density of fully dense zirconia as $6.08 \text{ g}\cdot\text{cm}^{-3}$. The porosity measurement was repeated for at least 3 times for each group of samples with the results presented in form of mean $\pm$ standard deviation.

2.3. Microstructural characterization

X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance X-ray diffractometer (Bruker AXS, Germany) with $\text{Cu}\cdot\text{K}\alpha$ radiation. The microstructures of the macro-porous ceramics were characterized by scanning electron microscopy (SEM) using an LEO Supra-35 field-emission scanning electron microscope (Zeiss Co., Germany) operating at an accelerating voltage of 20 kV. Prior to observation, all the samples were sputter-coated with a film of gold to reduce the charging effect. The SEM images were analyzed using the image measurement software Nano Measurer System 1.2.5 (Fudan University, China). The 3-D architectures were visualized by X-ray tomography (XRT) imaging using an Xradia Versa XRM-500 3-D X-ray tomography system (Zeiss Co., Germany) operating at an accelerating voltage of 80 kV. For such observations, cuboid samples with dimensions of $0.25 \text{ mm} \times 0.25 \text{ mm} \times 5 \text{ mm}$ were rotated by 360° along the long axes which were aligned normal to the profile for the X-ray source and detector. A total of 1600 2-D projections were taken for each sample by imaging per 0.225° during rotation, and then were inverted into 3-D volume renderings based on the Fourier back-projection algorithm. The results were processed and analyzed using the Avizo Fire 7.1 software (Visualization Sciences Group, France).

2.4. Compression tests

Cube-shaped samples of $3 \text{ mm} \times 3 \text{ mm} \times 3 \text{ mm}$ in dimension were used for compression tests, in line with the ASTM C133–97 standard. These samples were excised from the sintered bulk using an STX-202A precision diamond wire saw (Ke-jing Auto-Instrument Co., China). Uniaxial compression tests were performed at room temperature with a constant strain rate of 10^{-3} s^{-1} using an Instron 5982 testing system (Instron Corp., USA). Considering the anisotropic nature of the architectures, the compressive loads were applied along two orthogonal directions, respectively parallel and perpendicular to the profile of preferentially aligned pores. At least 8 tests were conducted for each group of samples with the results presented in form of mean $\pm$ standard deviation.

2.5. Thermal insulation measurement

Room temperature thermal diffusivity, α , and heat capacity, C_p , of the macro-porous ceramics were measured using a LFA 467 laser flash diffusivity apparatus (Netzsch, Germany). The experiments were conducted with thermal conduction perpendicular to the aligned pores, *i.e.*, normal to the rolling plane, using disk samples with a diameter of 12.7 mm and thickness of 1 mm. The samples were sputter-coated with a film of carbon before measurement to reduce laser transmission. The thermal conductivity, λ , was obtained according to the relationship as $\lambda = \alpha C_p \rho_{\text{nominal}}$, where ρ_{nominal} is the nominal density.

3. Results and discussion

3.1. Formation of oriented macro-porous architectures

Fig. 1a illustrates the fabrication procedure of oriented macro-porous zirconia ceramics, specifically associated with the formation mechanisms of the pores. Graphite flakes, which are fairly abundant in nature, are employed as a sacrificial fugitive material. Their flaky geometries and micrometer-sized dimensions make them ideal templates for creating non-isometric pores in ceramics. The spatial arrangement of graphite flakes within ceramics is regulated by means of accumulative rolling, which has been widely used for the processing of metals, alloys and their composites with ultrafine-grained structures [27,28]. This technique is particularly effective for producing intensive accumulative deformation in materials. For instance, such a treatment with n cycles of rolling, with 50% reduction in thickness for each cycle, as adopted in the current study, leads to a total of roughly $1/2^n$ in reduction in thickness, specifically to an equivalent strain of $0.8n$ [28].

During rolling, the dough is subject to shear stresses exerted by the rollers as it extends along the rolling direction. In such a process with the large flow deformation of the dough, the graphite flakes are activated by the shear stresses to reorient with their basal planes along the rolling direction. Such preferential alignment of the graphite flakes within the rolled dough can be clearly manifested by the strong diffraction peaks of their (002) and (004) crystal planes on the XRD patterns of the dough on its rolling profile, as shown in Fig. S1 in the Supplementary Materials. Subsequently, the pairs of dough can be folded and then bonded together. The ordering of the alignment of the flakes can be additionally enhanced with consolidation by pressing along the normal direction of rolled sheets. The subsequent calcination of the graphite flakes and sintering of the ceramic matrices eventually lead to the formation of macro-porous ceramics containing oriented pores which roughly replicate the flakes.

Fig. 1b shows the overall appearance of the sintered macro-porous ceramics fabricated with different additive amounts of graphite flakes, G_a . These materials demonstrate a uniform shrinkage during sintering without obvious change in shape or the formation of macro-scale cracks; nevertheless, the extent to which they shrink is different depending on the ingredients of the dough. As shown in Fig. 1c, the linear shrinkage

ratio, defined by the relative change in the width of sample after sintering with respect to its original value across the rolling profile, displays an increasing trend as G_a is increased. This is accompanied by a decrease in the nominal density of the bulk, indicating that the total porosity of macro-porous ceramics is increased. The porous ceramics are composed mainly of tetragonal zirconia phase with a small amount of monoclinic phase, as shown in Fig. S2.

3.2. Microstructural characteristics

Fig. 2a shows the 3-D architectures of the macro-porous ceramics fabricated with different G_a . Micrometer-sized pores with flaky to near-ellipsoid shapes are seen to be homogeneously distributed within the ceramic matrices and preferentially aligned along the rolling profile. This qualitatively resembles the structural features of natural wood wherein non-isometric pores are principally oriented along the growth direction of the plant. Fig. 2b shows the microstructures of the through-thickness cross-sections for the macro-porous ceramics. The porosities and microstructural characteristics of the involved pores, including their shape, interconnectivity and dimensions, are all dependent on the initial ingredients of the dough used in the fabrication process. In general, an increase in G_a tends to lead to a larger degree of porosity in the macro-porous ceramics with a gradual morphological transition of their shape from plate-like shaped to ellipsoidal. It can be noted that the pores are principally composed of those templated by graphite flakes, but are nearly absent within the solid walls of ceramics which are densely

sintered, as shown in Fig. 2c.

Fig. 3a shows the variation in the total porosity and open porosity of the macro-porous zirconia ceramics as a function of G_a in the dough during fabrication. The total porosity can be regulated from ~15 vol% to ~44 vol% by increasing G_a from 20 vol% to 80 vol%. The open porosity increases from ~2.3 vol% to ~42.9 vol%, with its ratio with respect to the total porosity varying over a wide range from ~15% to ~98% (inset). This clearly indicates a notable enhancement in the interconnectivity between the templated pores with increasing G_a . Specifically, the volumetric proportion of open pores in the total rises to ~96% as G_a increases to 60 vol%, indicating that the majority of pores become interconnected.

Fig. 3b,c shows the variation in the incremental and cumulative pore volumes measured by mercury porosimetry as a function of the equivalent diameter of the pores, i.e., by assuming a cylindrical pore geometry, in the macro-porous zirconia ceramics fabricated with different G_a . The incremental pore volume curve displays a unimodal shape (Fig. 3b); accordingly, the cumulative pore volume shows a sharp drop as the equivalent pore diameter increases. This clearly indicates that the characteristic dimensions of the pores are relatively uniform in the macro-porous zirconia ceramics. Additionally, the equivalent pore diameter corresponding to the unimodal peak or the sharp drop displays an increasing trend from 0.43 μm to 1.05 μm as G_a increases from 20 vol% to 80 vol%.

The dimensional characteristics of the pores can be quantitatively described using the lengths of their major and minor axes, a and b , along

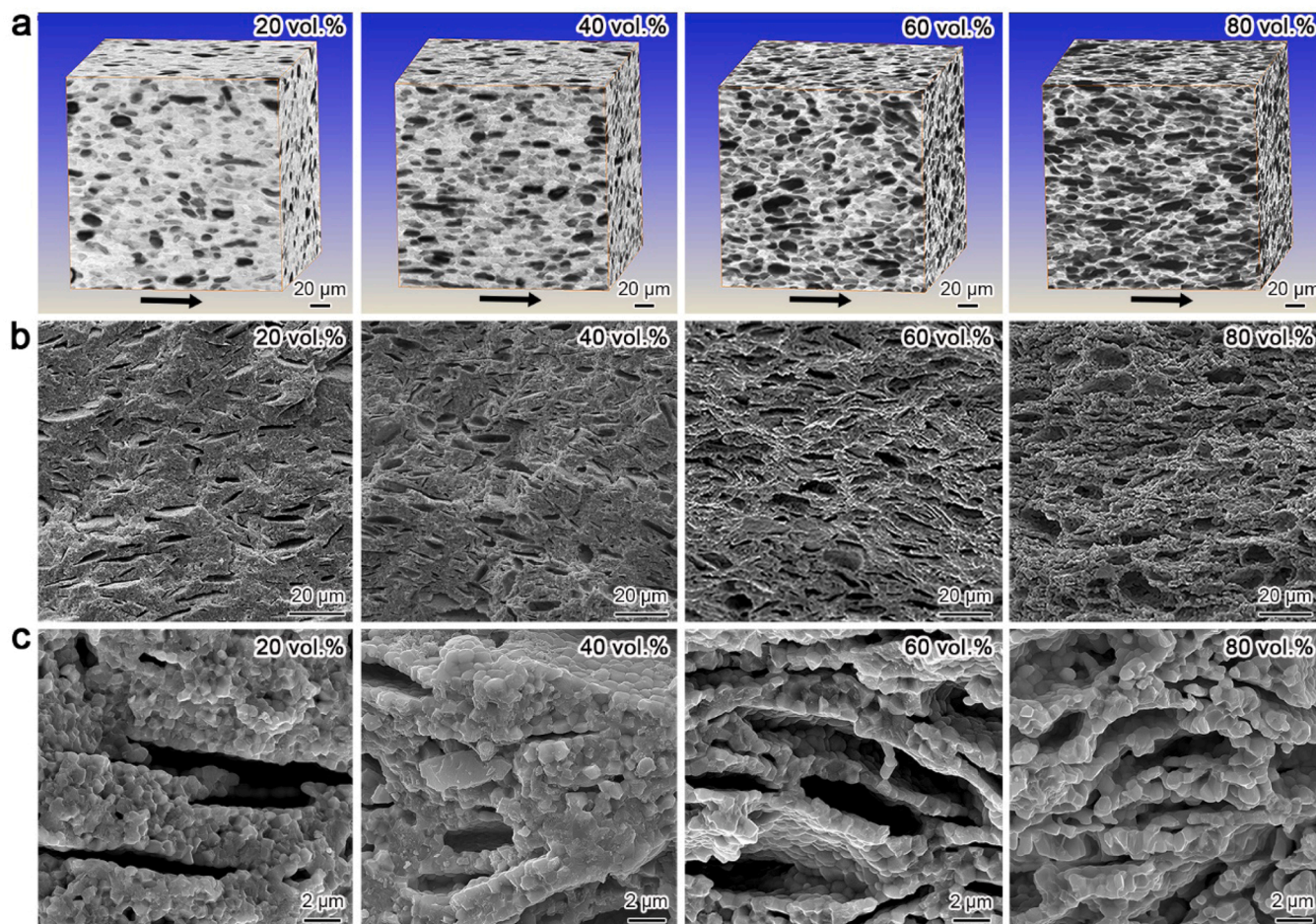


Fig. 2. Microstructures of oriented macro-porous zirconia ceramics. (a) XRT volume renderings of the macro-porous zirconia ceramics fabricated with different additive amounts, G_a , of graphite flakes. The pores in the ceramics are highlighted in the black color. The rolling direction is indicated by the arrows. (b) SEM micrographs of the macro-porous zirconia ceramics on their through-thickness cross-sections. (c) Magnified SEM micrographs of the solid walls between the pores templated by graphite flakes.

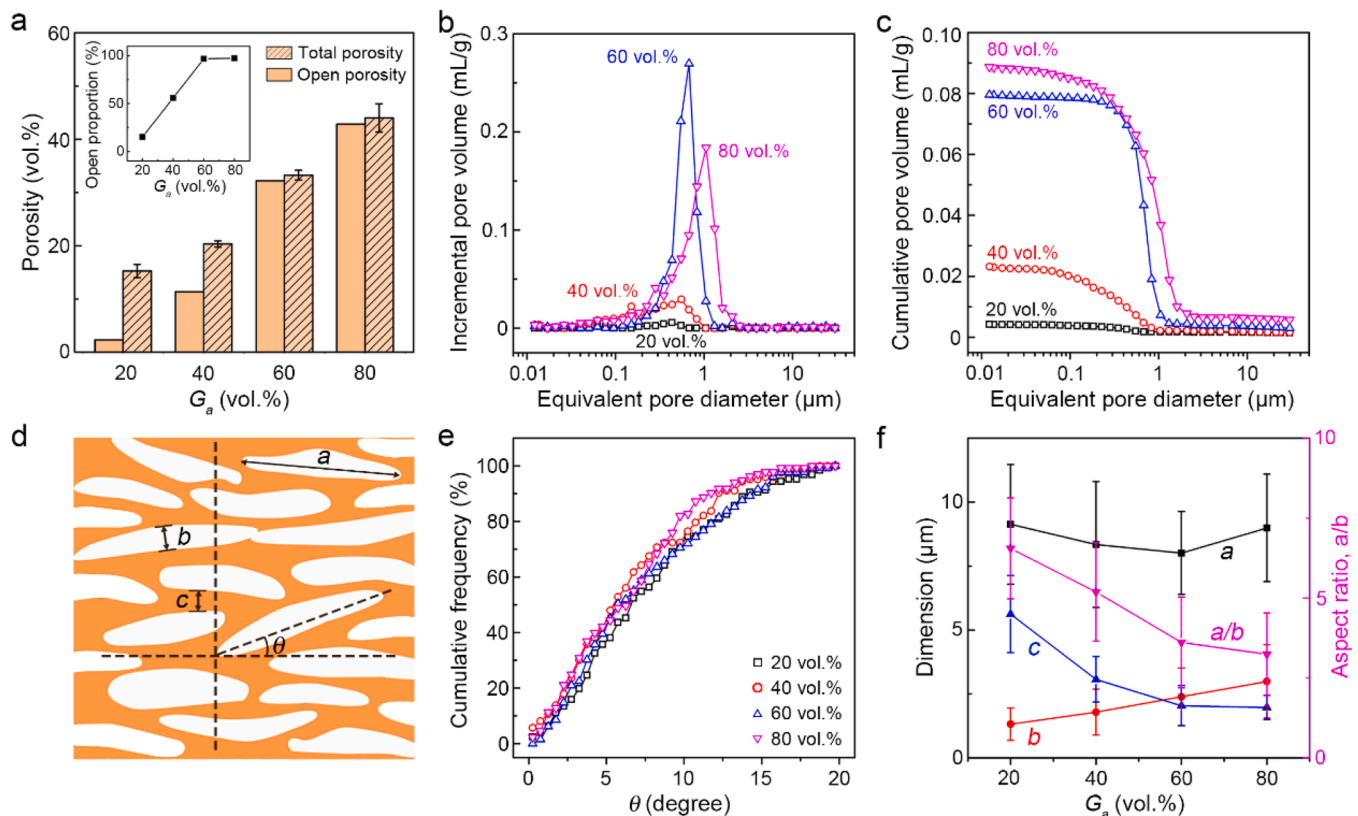


Fig. 3. Microstructural characteristics of oriented macro-porous zirconia ceramics. (a) Variation in the total and open porosities of the macro-porous zirconia ceramics as a function of the additive amounts, G_a , of graphite flakes. The inset displays the volumetric proportion of open pores in the total with G_a . (b, c) Variation in the (b) incremental and (c) cumulative pore volumes as a function of the equivalent diameter of pores. (d) Schematic illustration of the alignment and characteristic dimensions of the pores, including the inclination of their long axes with respect to the rolling profile (indicated by the horizontal line) θ , the length of their major and minor axes a and b , and the wall thickness between pores c . (e) Cumulative frequency of the pores with the inclination angle, θ , in the macro-porous ceramics fabricated with different G_a . (f) Variation in the characteristic dimensions of a , b , c and a/b as a function of G_a . At least 150 pores were analyzed for determining their inclination and dimensions for each group of samples.

with the wall thickness between them, c , as illustrated in Fig. 3d. The orientation of their alignment can be accessed by the inclination angle of the long axis with respect to the rolling profile, θ . As shown in Fig. 3e, the majority of pores exhibit a low θ of smaller than 20° , with those having $\theta \leq 15^\circ$ accounting for over 90% of the total, in all these macro-

porous ceramics, regardless of their different G_a for fabrication. This validates the viability of the accumulative rolling technique in generating a preferential alignment of pores for fabricating oriented macro-porous materials. Additionally, despite a relatively uniform diameter with an average a of 8–9.1 μm , the average thickness of the pores, b ,

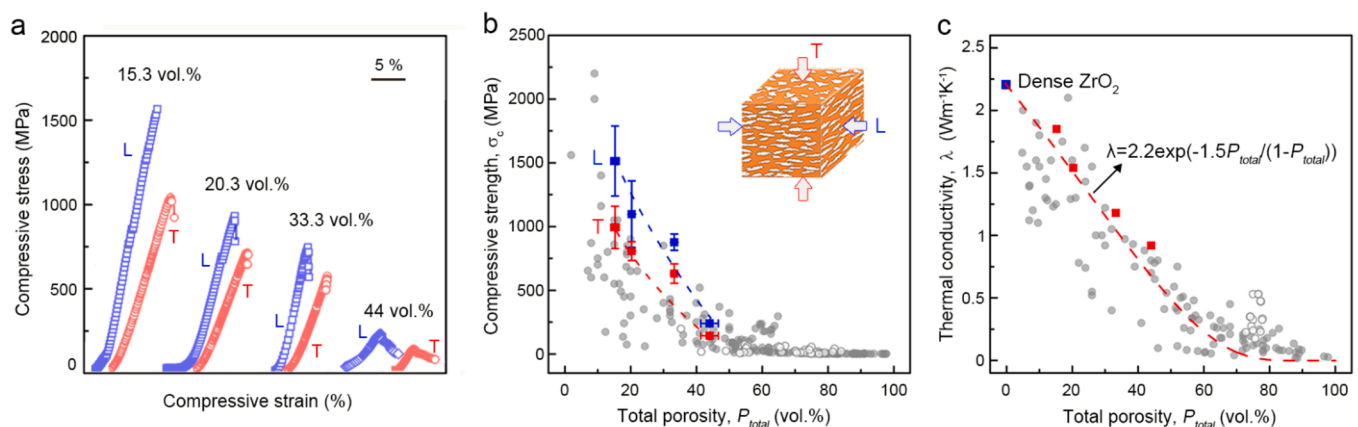


Fig. 4. Mechanical and thermal properties of oriented macro-porous zirconia ceramics. (a) Representative compressive stress-strain curves of macro-porous zirconia ceramics with different total porosities along their longitudinal (L) and transverse (T) directions. (b) Variation in the compressive strength as a function of total porosity for the oriented macro-porous zirconia ceramics along L and T directions. The data for other porous zirconia ceramics having nearly isometric pores (solid dots) or oriented pores made by other techniques (hollow dots) are also shown for comparison [14,16,17,30–42,44,45]. The inset illustrates the loading configurations with respect to the architecture. (c) Variation in the thermal conductivity of the oriented macro-porous zirconia ceramics along their through-thickness direction compared with those of other porous zirconia ceramic materials [14,17,30,32,40,43–49].

displays an increasing trend from $\sim 1.3 \mu\text{m}$ to $\sim 3 \mu\text{m}$ as G_a increases (Fig. 3f). This leads to a monotonic decrease in the aspect ratio of pores, a/b , indicating a lowered slenderness of pore shape; this is accompanied by a concomitant decrease in the wall thickness between pores, c .

3.3. Mechanical and thermal properties

Fig. 4a shows the mechanical properties of these oriented macro-porous zirconia ceramics in terms of representative compressive stress-strain curves for materials with different total porosities along the longitudinal (L) and transverse (T) directions, which are respectively parallel and perpendicular to the preferential alignment of pores (inset). In general, an increase in total porosity tends to decrease the compressive strength – a trend that is essentially universal for porous materials [5, 29]. Nevertheless, the compressive strengths are constantly higher along the longitudinal (L) direction than along the transverse (T) direction at a given level of porosity; this clear anisotropy is associated with the conformity of the alignment of solid walls with the loading direction.

In particular, the macro-porous ceramics exhibit high strengths, e.g., over 600 MPa for porosities up to 30.7 vol% and even over 1.5 GPa along the L direction in case of a low porosity of 15.3 vol%. Their fracture behavior also demonstrates some dependence on porosity. Specifically, in both orientations, the compressive stress shows a sudden drop after reaching its maximum when the porosities are below ~ 30 vol%; this leads to an instantaneous fracture of the materials. However, in materials where the porosity is 44 vol%, the post maximum stress displays a slow, continuously decreasing trend with the increase in strain, implying the gradual collapse of the solid walls.

Fig. 4b presents a direct comparison of the compressive strengths of porous zirconia ceramic materials which have nearly isometric or oriented pores fabricated by current approach and by other techniques such as ice-templating or co-extrusion [14,16,17,30–42,44,45]. The compressive strengths generally show an increasing trend as the porosity is decreased. The strengths of current macro-porous zirconia ceramics exceed those of most of others at equivalent levels of porosity, especially in the lower range where porosities are below ~ 35 vol%. Such high strengths stem principally from the following features. First, their architectures are uniform and fine with all the characteristic dimensions, i.e., a , b , and c , typically smaller than $10 \mu\text{m}$ for the majority of pores. However, the pores generated by other methods, such as replica templating using sacrificial fugitives, or direct forming with pore-forming agent, generally display coarse dimensions of some tens of micrometers to even several millimeters in diameter [14,16,17,30, 38–42,44,45,]. Second, the solid walls between pores are continuous and closely interconnected in 3-D space, and are not prone to buckling because of the limited aspect ratio of the pores (i.e., lower than 6.5). In comparison, the solid lamellae in ice-templated porous materials are fairly thin, typically with several to tens of micrometers in thickness but up to several to tens of millimeters in length; moreover, they often demonstrate poor interconnectivity, which can lead to an apparent ease of fragmentation [31–37]. Moreover, the strengths of our current materials along their L direction are additionally enhanced due to the preferential alignment of the solid walls along with the pores.

Fig. 4c shows the thermal conductivities of current oriented macro-porous zirconia ceramics along their T direction, i.e., perpendicular to the preferential alignment of pores [14,17,30,32,40,43–49]. In general, the thermal conductivity displays a decreasing trend with the increase in total porosity in all the porous zirconia ceramic materials. However, at equivalent levels of porosity, the thermal conductivities are comparable for the porous zirconia ceramics regardless of the shape and arrangement of their pores. Specifically, the current oriented macro-porous zirconia exhibits relatively low thermal conductivities ranging from $1.85 \text{ Wm}^{-1}\text{K}^{-1}$ to $0.92 \text{ Wm}^{-1}\text{K}^{-1}$ as the total porosity increases from ~ 15 –44 vol%, implying good thermal insulation properties. The variation in the thermal conductivity λ with total porosity P_{total} can be well described ($R^2 = 0.97$) according to the modified exponential equation: λ

$= \lambda_0 \exp(-1.5P/(1-P))$ [50], where λ_0 is the thermal conductivity of dense zirconia as $2.2 \text{ Wm}^{-1}\text{K}^{-1}$.

The combination of relatively low thermal conductivities with high strengths makes the oriented macro-porous zirconia ceramics appealing for structural and thermal insulation applications. Additionally, we demonstrate that the current accumulative rolling technique has notable advantages for fabricating macro-porous materials. On the one hand, it offers an effective means for constructing oriented porous architectures in materials by creating preferentially aligned pores with uniform distribution and fine dimensions. This allows for an improvement in strength while ensuring good thermal insulation properties. On the other hand, the technique is simple and efficient, easily scalable for mass production, and demonstrates good feasibility for extension to other material systems. Another primary advantage is that the dimensions of materials that can be processed by this technique are virtually unlimited. Moreover, in addition to graphite flakes the technique is effective for generating the preferential alignment of other micro- or nano-sized powders with non-isometric geometries. By such means, it can provide a facile approach for fabricating new materials with ordered architectures, such as those mimicking natural nacre. Such a concept has been validated in our recent study and will be reported elsewhere.

4. Conclusions

A facile approach has been exploited for processing macro-porous ceramic materials with highly oriented architectures based on the accumulative rolling technique. Natural graphite flakes are used as a fugitive material and are induced to reorient towards the rolling direction by the shear stresses during the rolling process. The pores templated by the graphite flakes have flake-like to near-ellipsoid shapes, exhibit a homogeneous distribution, and are preferentially aligned in the rolling profile. Accordingly, the resulting macro-porous zirconia ceramics exhibit increasing levels of porosity with enhanced interconnectivity between pores with the increase in the additive amounts of graphite flakes during fabrication. The compressive strengths of these macro-porous ceramics show a decreasing trend with increasing porosity from $> 1.5 \text{ GPa}$ to $\sim 150 \text{ MPa}$, but are consistently higher along the longitudinal, as compared to the transverse, direction, demonstrating clear anisotropic features. The current materials are stronger, at equal porosities, than most of other porous zirconia ceramics having nearly isometric or oriented pores. They also exhibit relatively low thermal conductivities of 0.92 – $1.85 \text{ Wm}^{-1}\text{K}^{-1}$, and as such have a promising potential for industrial application as load-bearing thermal insulation materials. The processing approach also demonstrates a good feasibility for mass production and can be easily extended to other material systems.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data that support the findings of this study are available from the corresponding author, Prof. Zengqian Liu, at zengqianliu@imr.ac.cn, upon reasonable request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jeurceramsoc.2022.07.044](https://doi.org/10.1016/j.jeurceramsoc.2022.07.044).

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