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

Nan Zhang\(^a,b\), Zengqian Liu\(^b,c,d\), Yuanbo Du\(^d\), Qin Yu\(^e\), Shaogang Wang\(^f\), Guoqi Tan\(^b,c\), Bailing Jiang\(^a,\*\), Zhefeng Zhang\(^b,c,d,\*\), Robert O. Ritchie\(^e\)

\(^a\) School of Materials Science and Engineering, Xi’an University of Technology, Xi’an 710048, China
\(^b\) Shi-Changxu Innovation Center for Advanced Materials, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
\(^c\) School of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China
\(^d\) School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin 150090, China
\(^e\) Department of Materials Science and Engineering, University of California Berkeley, CA 94720, USA
\(^f\) Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

\(^\*\) Corresponding authors at: Shi-Changxu Innovation Center for Advanced Materials, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China.

\(\text{E-mail addresses: zengqianliu@imr.ac.cn (Z. Liu), jiangbail@vip.163.com (B. Jiang), zhfzhang@imr.ac.cn (Z. Zhang).}\)

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 environment.
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...
natural graphite flakes with a median diameter of ~18 μm and thickness of less than 8 μm (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, Gₐ, 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 rot 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 ~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 m₀ 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 m₁. Subsequently, the sample was taken out of methanol and weighed immediately after the extra methanol on the surface volatilized, giving a weight m₂. The nominal density of macro-porous ceramics, ρnominal, can be obtained as: ρnominal = m₀/mₙomial/(m₂ − m₁).

The total porosity of the sample, ρtotal, can be calculated from its nominal density as: ρtotal = 1 − ρnominal/ρtrue, where ρtrue is the density of fully dense zirconia as 6.08 g 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 ± standard deviation.

2.3. Microstructural characterisation

X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu-Kα 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 mm × 0.25 mm × 5 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 mm × 3 mm × 3 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 5962 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 ± standard deviation.

2.5. Thermal insulation measurement

Room temperature thermal diffusivity, α, and heat capacity, Cₚ, 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 λ = αCₚ/ρnominal, where ρnominal 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 1/2ⁿ 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, Gₐ. 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 $\mu$m to 1.05 $\mu$m 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
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, \( \theta \). As shown in Fig. 3e, the majority of pores exhibit a low \( \theta \) of smaller than 20°, with those having \( \theta \leq 15 \)° 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 \( \mu m \), the average thickness of the pores, \( b \),
The authors declare that they have no known competing financial interests.

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.
References

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