Novel nanoporous silica aerogel impregnated highly porous ceramics with low thermal conductivity and enhanced mechanical properties

Chang-Qing Hong,* Jie-Cai Han, Xing-Hong Zhang and Jian-Cong Du

Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150080, People’s Republic of China

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Novel nanoporous silica aerogel impregnated highly porous zirconia ceramics were successfully synthesized from silica gel and camphene-based freeze-cast porous zirconia ceramics. The resultant porous ceramic–aerogel composites exhibited high compressive strength of 36.8 MPa, and ultra-low thermal conductivity ranging from 0.041 to 0.098 W m$^{-1}$ K$^{-1}$, as the porosity increased from 46.5% to 69.8%. The present work provides an efficient way to fabricate high-strength thermal insulation materials with ultra-low thermal conductivity.

Porous materials with controllable properties have attracted widespread interest: rising energy costs have emphasized the importance of efficient thermal protection [1,2]. Owing to their unique combination of properties, such as low density, controlled porosity, high thermal shock resistance, high specific strength and chemical stability at high temperatures, porous ceramics (especially highly porous ceramic with porosities exceeding 60 vol.%) are considered as candidate materials for use in a wide range of applications including high-temperature insulation, active cooling, hot gas burner media, lightweight structural materials, and preforms for metal–matrix composites [3–6].

Although porous ceramics can achieve a degree of thermal insulation, their thermal conductivity is relatively high and must be reduced through careful processing. However, the high porosity and the nanoporous nature of the framework decrease the solid and gaseous thermal conductivity, respectively [7,8]. Nanoporous silica aerogels are unique materials often having a high specific surface area, a high porosity (75–99%), low index of refraction and ultra-low thermal conductivity (0.01–0.03 W m$^{-1}$ K$^{-1}$) [9–11]. These properties make aerogels advantageous for a wide variety of actual applications, such as superthermal insulators, catalysis, sensors, and electrochemical device components [12]. Aerogel-based composite materials with enhanced mechanical reliability reinforced by carbon fiber, ceramic fiber, carbon nanotubes or nanofibers have been studied [13–15].

Recently, our research group has developed a novel strategy for the synthesis of 3-D ceramic framework-reinforced aerogel composites with controllable and adjustable microstructures/properties. We demonstrate that ceramic aerogels can be made by camphene-based freeze-casting followed by infiltration with SiO$_2$ sol to form SiO$_2$ aerogel with porous ceramic framework through a special drying route. These 3-D ceramic framework-reinforced aerogel composites with submicron and nanosized pores have been confirmed to possess higher compressive strength and lower thermal conductivity, making them potentially suitable for thermal applications.

The highly porous ZrO$_2$ ceramic is manufactured by a camphene-based freeze-casting method; its porosity ranged from 60 to 80 vol.%, depending on the processing employed (i.e. initial solid content, sintering temperature and cooling conditions). Here, the ice-water was used to freeze the ceramic slurry and initial ceramic solid contents of 8, 10, 12 and 15 vol.% were used. More
extensive details of the processing of these highly porous ceramics are given in our previous work [16–18]. The freeze-cast green body was removed from the moulds and left to sublime at room temperature to remove the camphene entirely and achieve a highly porous structure. Following sublimation, sintering of the green body at 1550 °C/50 min enabled densification of the samples and a concomitant improvement in mechanical strength.

The prepared porous ceramics are impregnated with SiO$_2$ gels. In this experiment, SiO$_2$ gels were prepared by the acid (HCl)-catalyzed sol–gel method using tetraethoxysilane (TEOS), EtOH and H$_2$O in the molar ratio 1:7:4 as precursors for the silica. The pH value of the above mixture was adjusted to 2 by addition of HCl (0.2 mol l$^{-1}$). The TEOS/EtOH/HCl/H$_2$O mixture was refluxed at 80 °C for 40 min. Finally, 0.25 ml of 0.05 mol NH$_3$·H$_2$O was added to the solution and mixed for about 10 min until solution became transparent. After 24 h of aging in TEOS/EtOH solution to strengthen the gel network structure, the pore fluids in the wet gel were exchanged with ethanol to facilitate subsequent surface modification. Finally, supercritical drying was performed (i.e. the critical point is T$_c$ = 243 °C, P$_c$ = 6.3 MPa for ethanol) to acquire non-cracked porous ceramic–aerogel composites.

The fabricated porous ZrO$_2$ ceramics impregnated with aerogels were investigated by evaluating their pore structures, including pore size and porosity, using scanning electron microscopy (SEM, Hitachi S-4700, Japan). Pore size distribution was analyzed by mercury intrusion porosimetry on certain parts of the sample with different freezing environments. The bulk density of the sintered samples was measured from the sample mass and dimension, and the relative density, and thus the porosity, was determined from the ratio of the measured bulk density to the theoretical density of ZrO$_2$ material. Three samples were used to determine the average porosity.

Our goal is to obtain micro-/nanoporous ceramic–aerogel composites with low thermal conductivity and good mechanical properties. These materials are expected to exhibit higher thermal stability and render both porous ceramics and nanoporous aerogels suitable for practical applications. Figure 1a schematically illustrates the synthesis strategy for microporous ZrO$_2$ ceramics impregnated with aerogels. TEOS is selected as raw material in this work because it can form a nanoporous aerogel structure via the sol–gel process. Homogeneous mixed sol (Fig. 1b, left) was obtained from TEOS/EtOH/HCl/H$_2$O solution by stirring. The porous ceramic (Fig. 1b, middle) was immersed in SiO$_2$ sol, and SiO$_2$ gel forms in the porous ceramic via the addition of NH$_3$·H$_2$O. Finally, the micro-/nanoporous ceramic–aerogel composite (Fig. 1b, right) nanostructure was formed via the subsequent supercritical drying process.

Figure 2 shows the microstructure of the porous ZrO$_2$ ceramics with 3-D interconnected pore channels before impregnation (a), after impregnation (b), silica aerogels (c) and porous ceramic impregnated with silica aerogels (d).
The thermal conductivity of porous ZrO$_2$ and aerogel-impregnated porous ZrO$_2$ ceramics is shown in Table 1. It can be seen that, for a given porosity, the thermal conductivity of porous ZrO$_2$ ceramic after impregnation was lower than that before impregnation. The thermal conductivity for both non-aerogel- and aerogel-impregnated porous ZrO$_2$ ceramics revealed a similar decreasing trend as the porosity increased. The total porosity varied from 68.5–81.5\% (before impregnation) to 46.1–69.3\% (after impregnation), while the thermal conductivity decreased from 0.22–0.085 to 0.098–0.041 W m$^{-1}$ K$^{-1}$, respectively. These thermal conductivities are almost the same as the molecular conductivity of air and silica aerogel.

The mean free path of aerogels (~50 nm) is smaller than that of air (~69 nm). Air molecules can hardly pass through the aerogels, and the aerogels replaced air in the pore regions of porous ZrO$_2$, resulting in a decrease in thermal conductivity and making the material a better thermal insulator than air. The gas molecules within the aerogels experienced the Knudsen effect [19,20], which virtually eliminated exchange of energy in the gas, effectively eliminating convection and lowering the overall thermal conductivity. These results indicate that the obtained ceramic–aerogel composites exhibit a nanoscale porous structure within the highly porous ceramics. The remarkable result is that a very low thermal conductivity is achieved for specimens possessing a rigid porous ceramic framework.

It was found that the mechanical properties of freeze-cast porous ceramics were improved upon impregnation with silica aerogel. Table 1 shows the compressive strength of porous ZrO$_2$ ceramics before and after impregnation with silica aerogels. Due to the high porosity which led to an exponential decrease in strength, the compressive strength of the porous ZrO$_2$ ceramics in the present work, 9.2–25.5 MPa, was much lower than the corresponding value of dense zirconia ceramics. The compressive strength of porous ZrO$_2$ ceramics after impregnation with silica aerogels was much higher than that before impregnation. In particular, after impregnating porous ZrO$_2$ ceramics with silica aerogels, the compressive strength increased from 9.2–25.5 to 15.4–36.8 MPa. Decreased porosity and pore size, as well as a stiffened network due to impregnation with silica aerogels, contributed to the increased compressive strength of the final ceramic–aerogel systems. This demonstrates that impregnating porous ceramics with silica aerogel can improve the materials’ mechanical properties.

In summary, this paper describes the synthesis of novel high-strength thermal insulation materials with low thermal conductivity and good mechanical properties based on camphene-based freeze-cast 3-D porous ceramic frameworks and silica gel. The introduction of nanoscale porous aerogel can reduce the effective thermal conductivity and enhance the mechanical stability of the highly porous ZrO$_2$ ceramics.

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### Table 1. Porosity, thermal conductivity and compressive strength of highly porous ZrO$_2$ ceramics before and after impregnation with silica aerogel.

<table>
<thead>
<tr>
<th>Initial solid loading (vol.%)</th>
<th>Porosity$^b$ (%)</th>
<th>Thermal conductivity$^b$ (W m$^{-1}$ K$^{-1}$)</th>
<th>Compressive strength$^b$ (MPa)</th>
<th>Porosity$^a$ (%)</th>
<th>Thermal conductivity$^a$ (W m$^{-1}$ K$^{-1}$)</th>
<th>Compressive strength$^a$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>81.5 ± 1.1</td>
<td>0.085 ± 0.01</td>
<td>9.20 ± 1.25</td>
<td>69.3</td>
<td>0.041 ± 0.01</td>
<td>15.4 ± 1.20</td>
</tr>
<tr>
<td>10</td>
<td>77.8 ± 1.4</td>
<td>0.094 ± 0.02</td>
<td>11.9 ± 0.98</td>
<td>60.2</td>
<td>0.062 ± 0.01</td>
<td>24.9 ± 2.45</td>
</tr>
<tr>
<td>12</td>
<td>73.2 ± 0.8</td>
<td>0.15 ± 0.03</td>
<td>16.4 ± 1.12</td>
<td>54.8</td>
<td>0.081 ± 0.01</td>
<td>30.2 ± 2.20</td>
</tr>
<tr>
<td>15</td>
<td>68.5 ± 2.2</td>
<td>0.22 ± 0.02</td>
<td>25.5 ± 2.46</td>
<td>46.1</td>
<td>0.098 ± 0.02</td>
<td>36.8 ± 1.48</td>
</tr>
</tbody>
</table>

$^a$The superscripts a and b denote values after and before impregnation with aerogels, respectively.

(Fig. 2c). TEM micrographs of the obtained porous ceramic–aerogels are also presented in Figure 3a. It can be observed that the interface between ZrO$_2$ and aerogel was clean and tightly bonded, which helps to enhance the mechanical property of the composites. Spherical SiO$_2$ particles a few tens of nanometers in size form a 3-D network containing homogeneous pores (size in the range of 10–30 nm—see Fig. 3b).

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### References


