Preparation and properties of gradient Al₂O₃-ZrO₂ ceramic foam by centrifugal slip casting method

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Abstract: The aim of the present research is to provide a novel technique for preparing gradient Al₂O₃-ZrO₂ ceramic foams. This technique used epispastic polystyrene spheres to array templates and centrifugal slip casting to obtain cell struts with gradient distribution of Al₂O₃ and ZrO₂ particles and high packing density. Aqueous Al₂O₃-20vol.% ZrO₂ slurries with 20vol.% solid contents were prepared and the dispersion and rheological characteristics of the slurries were investigated. The settling velocity and mass segregation of Al₂O₃ and ZrO₂ particles at different centrifugal accelerations were calculated and studied. The drying behavior, macrostructure, microstructure, compressive property and resistance to thermal shock of the sintered products were also investigated. The results show that the difference of settling velocity of Al₂O₃ and ZrO₂ particles increases and mass segregation becomes acute with an increase in centrifugal acceleration. The cell struts prepared at a centrifugal acceleration of 1,690 g have high sintered density (99.0% TD) and continuous gradient distribution of Al₂O₃ and ZrO₂ particles. When sintered at 1,550 °C for 2 h, the cell size of gradient Al₂O₃-ZrO₂ foam is approximately uniform, about 1.1 mm. With the porosity of gradient Al₂O₃-ZrO₂ ceramic foams increasing from 75.3% to 83.0%, the compressive strength decreases from 4.4 to 2.4 MPa, and the ceramic foams can resist 8–11 repeated thermal shock from 1,100 °C to room temperature.

Key words: ceramic foam; centrifugal slip casting; settling velocity; gradient distribution, compressive property


Cellular ceramics are a unique class of lightweight materials consisting of a relatively regular array of hollow cells arranged in a three-dimensional network. Porous ceramics are divided into two subclasses consisting of either open or closed cells. The closed-cell ceramics can be used as a network of soap bubbles. The porous ceramics can be used in catalyst carriers, hot gas collectors, molten metal filters, chemical sensors and separation membranes [1-3]. Al₂O₃ matrix ceramic foam is a kind of representative porous ceramic, which has high resistance to molten aluminum attack and is used in filtering molten aluminum. The three main processes for the fabrication of ceramic foam are the replica technique [4], the sacrificial template method [5], and the direct-foaming technique [6]. The most common preparation method for Al₂O₃ ceramic foam is the polymeric sponge method which involves the impregnation of polyurethane sponges with slurries containing ceramic particles and appropriate binders followed by pyrolysis and sintering at a special temperature [7, 8].

The ceramic foams prepared by this method currently possess low strength and fracture toughness which make them sensitive to structural stress. The reported modification methods included the change of humping slurry content by modifying the polymeric sponge, increasing the thickness of ceramic coating on the polymeric sponge by multicoating method, and ameliorating the uniformity of ceramic coating by two-step centrifuging processing [9, 10]. In the present research, gradient Al₂O₃-ZrO₂ ceramic foams were prepared by centrifugal slip casting to improve the mechanical properties of Al₂O₃ foam ceramics. Centrifugal slip casting can avoid holes and cracks resulting from the pyrolysis of organic sponges and form optimal ceramic particle packing and minimize flaw size in cell struts, so the final products have dense cell struts and good mechanical properties. In addition, the gradient distribution of Al₂O₃ and ZrO₂ particles can generate residual stresses, which can contribute to a further increase in the mechanical properties of the ceramic foams. In this paper, the dispersion and rheological characteristic of Al₂O₃-20vol.%ZrO₂ slurries were studied. The settling velocity of Al₂O₃ and ZrO₂ particles was calculated for different centrifugal accelerations. The effect of centrifugal acceleration on the mass segregation of Al₂O₃ and ZrO₂ in the cell struts of gradient Al₂O₃-ZrO₂ ceramic foams was analyzed. The drying behavior, macrostructure,
microstructure, compressive property and resistance to thermal shock of the sintered products were also investigated.

1 Experimental detail

The α-Al₂O₃ powder of 99.99% purity with an average particle size of 0.2 μm was used. The ZrO₂ powder (TZ-3Y) had 99.5% purity and a median diameter of 0.3 μm. Polycarboxylic ammonium with an average molecular weight of 10,000 was used as dispersant. Epispastic polystyrene spheres (EPS) sieved through a 12-mesh screen were used to array the template. In order to determine the optimal pH value for preparing Al₂O₃-ZrO₂ suspensions, the Zeta potentials of Al₂O₃ and ZrO₂ particles at different pH values were measured by using a Zeta Potentiometer (Zeta PALS BL-ZR3). The Al₂O₃ and ZrO₂ powders were mixed at a fixed proportion (80vol.%Al₂O₃, 20vol.%ZrO₂) and dispersed in de-ionized water containing the special percentage of the dispersant (0.5wt.% of α-Al₂O₃ + ZrO₂ powder content). The suspensions were adjusted to a desired pH value by adding ammonia water, and then ball-milled for 24 h using high purity alumina balls to obtain electrostatically stabilized suspensions with 20vol.% solid content. The viscosity of Al₂O₃-20vol.%ZrO₂ slurries was measured at different shear rates (20, 40, 60, 80, 100, 120, 140, 160 and 180 s⁻¹) and the experimental temperature of 20 °C using a rotational viscometer (NXS-11A), and the curve of shear rate versus viscosity was drawn to present the rheological characteristic of the slurries.

Figure 1 shows a schematic diagram of the process for fabricating the gradient Al₂O₃-20vol.%ZrO₂ ceramic foam. The main steps are as follows: (a) at first form a close-packed template with EPS spheres; (b) immerse slurry in the interstitial spaces of the pre-arrayed EPS template; (c) centrifuge slurries in the template at centrifugal accelerations of 1,118, 1,610, 2,191 and 2,860 g, for 60 min, respectively; (d) dump the supernate, remove the mold and dry the samples under different conditions to find the most successful crack-free drying conditions: (1) in an oven at 50 °C; (2) under special condition (25 °C, 60% Relative Humidity); (3) under ambient condition. The water content of cast compacts at different times was measured to study the dry behavior of cast compacts; (e) the dried samples with a dimension of about Φ40 mm × 40 mm was divided into two groups. One group was all sectioned into 4 segments from the top to the bottom, like cakes, and were numbered 1, 2, 3, 4, respectively. The sliced segments in the group were pyrolyzed at 550 °C for 5 h with a heating rate of 1 °C·min⁻¹ to remove the EPS spheres, and then followed by pre-sintering at 1,000 °C for 30 min with a rate of 5 °C·min⁻¹ to measure the green density of cell struts. The other group were also heated to 550 °C at a low rate of 1 °C·min⁻¹, held for 5 h to remove EPS spheres, and then heated again to 1,550 °C at a rate of 5 °C·min⁻¹, sintered for 2 h to obtain cell struts with gradient distribution of Al₂O₃ and ZrO₂ particles and high packing density, and to measure the sintered density and compressive strength of Al₂O₃-20vol.%ZrO₂ ceramic foams.

In addition, the measured green density was regarded as the green density of each specimen, which was believed to be a tolerable approximation, although these values should be higher (~1%) than the real green densities. The green and sintered densities of cell struts were measured by means of Archimedes’ principle. The porosities of sintered products were calculated using the following equation:

\[
\text{Porosity} = \frac{(\rho_r - \rho_b)}{\rho_r}
\]

where \(\rho_r\) and \(\rho_b\) are the real and bulk densities (kg·m⁻³), respectively.

Since the discs were rather uniform and flat, their bulk densities were simply calculated from their weights and volumes. As for the real densities, the discs were first ground to powder and then measured with a pycnometer. Photographs of the samples were taken using a digital camera. The microstructure and ZrO₂ phase distribution of cell struts were analyzed using a scanning electron microscope (SSX-505) on polished and thermally etched surfaces. The compressive strength of fired product of Φ20 mm × 20 mm was measured using a universal testing machine (CMT5105) at the speed of 0.5 mm·min⁻¹. The resistance to thermal shock of the Al₂O₃-20vol.%ZrO₂ foam was measured using the following method:
the sintered compacts was firstly heated to 1,100 °C and held for 15 min, and then placed in water at 15 °C for 5 min to cool. The above process was repeated until the porous Al2O3-20vol.%ZrO2 ceramic foams were broken. The repetitious time was used to express the resistance to thermal shock of Al2O3-ZrO2 foam.

2 Results and discussion

2.1 Analysis of dispersion and rheological characteristic of Al2O3-20vol.%ZrO2 slurries

Figure 2 shows the relationship between pH value and Zeta potential of Al2O3 and ZrO2 particles. In Fig. 2 the isoelectric points of the Al2O3 and ZrO2 particles lie at about pH 2.6 and pH 3.5, respectively. According to the well-known DLOV theory, the suspension of colloidal particles in polarized liquids is more stable when the pH values are lower or higher than that of isoelectric point. At a pH of 10, Al2O3 and ZrO2 particles have their highest Zeta potential values of 46 mV and 55 mV, respectively. The reason is that the molecule of polycarboxylic ammonium has many carboxylic acid sites or functional groups, and the fraction of functional groups that are dissociated (i.e., COO⁻) varies with the solvent conditions (i.e., pH and ionic strength). At a pH of 10, the surfaces of the Al2O3 and ZrO2 particles can absorb sufficient negative charge to obtain a big repulsive force between the Al2O3 and ZrO2 particles, so the Al2O3 and ZrO2 particles can be well dispersed in the slurries.

2.2 Effect of centrifugal acceleration on green gradient of cell struts

Figure 4 shows the green densities of cell struts in different segments sintered at 1,000 °C for 30 min. As can be seen in Fig. 4, with the increasing of centrifugal acceleration, the difference of green density of the cell struts from segment 1 to segment 4 improves. The difference of green density of the top and the bottom of cell struts is named as gradient in this paper. As the centrifugal acceleration changes from 1,118 g to 2,860 g, the gradient of the cell struts increases from 2.9% to 5.7%, which shows the mass segregation of Al2O3 and ZrO2 particles becomes acute and a gradient distribution of Al2O3/ZrO2 comes into being. When centrifuged at 2,191 g and 2,860 g, the green densities of the cell struts of segments 3 and 4 are very close, but are quite different from those of segments 1 and 2, which shows that the ZrO2 particles accumulate near the bottom of the specimen, and form an obvious gradient distribution of Al2O3/ZrO2. When centrifuged at 1,610 g, the green density of the cell struts of different segments changes evenly, showing that the Al2O3 and ZrO2 particles form a uniform and continuous gradient distribution.

Figure 3 shows the relationship between the viscosity and shear rate for Al2O3-20vol.%ZrO2 slurries with 20vol.% solid content. In the low shear rate region, as the shear rate increases, the viscosity of the Al2O3-ZrO2 slurries decreases rapidly. This is because the three-dimensional network structure among the particles is destroyed, inducing a decrease in the resistance to particles moving. In the high shear rate region, the initial network structure among the particles is completely destroyed and a new stable structure forms, so the viscosity of the slurries only changes slowly. In this study, the Al2O3-ZrO2 slurries have a shear thinning characteristic, which is beneficial to mold filling with slurries and to forming gradient distribution of Al2O3 and ZrO2 particles.
The segregation phenomenon during the centrifugal process essentially derives from a difference in the settling velocities of initial particles with different sizes and densities in a suspension. The basic principle of sedimentation originates from Stokes’ Law, which describes the movement of a sphere in an infinite medium \((v = \frac{2}{9} \frac{\eta^2}{\rho L}}\). As its Reynolds number \((Re = \frac{2 \rho f v^2}{h})\) is below 1 for Al₂O₃-20vol.%ZrO₂ slurries with 20vol.% solid content, the movement of slurries in the mold still follows creeping flow conditions \([13]\). The velocity of a particle moving through a liquid in a centrifugal force field is affected by centrifugal force \((F_c)\), buoyancy force \((F_b)\), and frictional force \((F_f)\), as shown in Fig. 5.

\[
\begin{align*}
F_c &= \frac{4}{3} \pi a^3 \rho_c r \omega^2 \\
F_b &= \frac{4}{3} \pi a^3 \rho_r r \omega^2 \\
F_f &= \frac{4}{3} \pi a^3 \rho_f r \omega^2
\end{align*}
\]

Fig. 5: Schematic diagram of forces on particles in suspensions during centrifugal process

where
- \(\eta\) — Liquid viscosity, Pa·s;
- \(a\) — Particle radius, μm;
- \(\rho_p\) — Particle density, Kg·m\(^{-3}\);
- \(\rho_L\) — Liquid density, Kg·m\(^{-3}\);
- \(\omega\) — Angular velocity, rad·s\(^{-1}\), and
- \(r\) — Radial coordinate in the centrifuge, m.

According to our previous study \([14]\), the settling velocity \((\mu m·s^{-1})\) of \(i\)-type particles in a multiple system is as follows:

\[
v_i = \frac{2}{9} \rho_p \left[ r_p^3 (\rho_p - \rho_L) - \sum_{j} r_p^3 (\rho_{p,j} - \rho_L) \phi_j \right] (1 - \phi_{ni}^{n-1}) r \omega^2
\]

where
- \(\eta\) — Viscosity of slurries, Pa·s;
- \(r_p\) — Radius of \(p\)-type particle, μm;
- \(\rho_{p,i}\) — Density of \(i\)-type particle, Kg·m\(^{-3}\);
- \(\phi_i\) and \(\phi_{ni}\) — Solid content of \(i\) and \(n\)-types particle in the slurry, vol.%;
- \(\phi_{tot}\) — Total solid content of Al₂O₃-ZrO₂ slurries, vol.%;
- \(n_i\) — A function of the Reynolds number and the particle to vessel size ratio;
- \(\rho_{tot}\) — Density of total slurry, Kg·m\(^{-3}\);
- \(r_p,j\) — Radius of \(j\)-type particle, μm;
- \(\rho_{p,j}\) — Density of \(j\)-type particle, Kg·m\(^{-3}\);
- \(\phi_j\) and \(\phi_{nj}\) — Solid content of \(j\) and \(n\)-types particle in the slurry, vol.%;
- \(n_i\) — A function of the Reynolds number and the particle to vessel size ratio;
- \(\rho_{tot}\) — Density of total slurry, Kg·m\(^{-3}\);

Table 1 shows the parameters and data used in this paper. Equation 5 and Table 1 were adopted to calculate the settling velocities of Al₂O₃ and ZrO₂ particles and to analyze the segregation phenomena in Al₂O₃-20vol.%ZrO₂ system. The calculation results are shown in Table 2. The difference of the settling velocity of Al₂O₃ and ZrO₂ particles is less (22.9 μm·s\(^{-1}\)) when centrifuged at the acceleration of 1,118 g in Table 2. But with increasing the centrifugal acceleration, the difference in the settling velocities of two types of particles gets bigger and bigger. The difference in the settling velocities of two types of particles can form severe mass segregation, so the ZrO₂ particles, with the bigger size and higher density, mostly congregate at the bottom and the Al₂O₃ particles, with the smaller size and lower density, mostly accumulate at the top. This means that

\[
\begin{array}{|c|c|c|}
\hline
\text{Centrifugal acceleration} & \text{Al₂O₃} & \text{ZrO₂} \\
\hline
1,118 & 5.7 & 28.6 \\
1,610 & 8.2 & 41.2 \\
2,191 & 11.1 & 56.3 \\
2,860 & 14.5 & 73.2 \\
\hline
\end{array}
\]

### Table 1: Parameters and data used in this paper

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<td>(r)</td>
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<tr>
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<tr>
<td>(d_2)</td>
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<td>(\eta)</td>
<td>1.0×10(^{-3}) Pa·s</td>
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<tr>
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<td>(\rho_2)</td>
<td>6,050 Kg·m(^{-3})</td>
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<tr>
<td>(n_i)</td>
<td>4.65</td>
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</table>

### Table 2: Settling velocity of Al₂O₃ and Al₂O₃ particles at different accelerations of centrifugal slip casting
the cell struts of the compacts centrifuged at high centrifugal acceleration have large gradient of green density, as shown in Fig. 4. However, when centrifuged at the acceleration of 1,610 g, the difference in the settling velocity of Al₂O₃ and ZrO₂ particles is not very big (33 μm·s⁻¹), so the cell struts of ceramic foam can have a more gradual gradient distribution of Al₂O₃ and ZrO₂ particles, leading to the improvement in compressive property of ceramic foam.

2.3 Analysis of drying and sintering behavior

The centrifuged green bodies still contained 9wt.% to 11wt.% water, which evaporated during drying. It is well known that fast evaporation of the liquid can lead to the formation of cracks in the green body and a decrease in the mechanical properties of the sintered body. In order to find the most successful crack-free drying conditions, the drying experiments were performed under three conditions. Drying behavior of cast compacts under various conditions is shown in Fig. 6. The final weight (dry compact) was subtracted from that of the starting weight (wet compacts without supernate) to give the value for the total water content in the cast compact (=100%, Fig. 6). Water content in cast compacts at initial time subtracts that of drying compacts for different times. The difference is divided by drying time and then obtain drying rate. As can be seen in Fig. 6, the drying rates under three conditions from (1) to (3) are 16%, 6%, and 3% per hour during initial 5 h, respectively. According to the experimental experience, if the drying rates are faster than 5% per hour, the possibility of crack formation in the sintered compacts will be increased greatly. Hence, After drying in the oven or under ambient conditions, the sintered compacts could have some cracking. Normally, after a drying period of 3–4 days under special condition (25 ℃, humidity of 60% RH), the sintered compacts have little cracking. The reason is that EPS spheres decompose between 300 and 550 ℃. During this period, the low heating rate (at 1 ℃·min⁻¹) and long holding time (550 ℃ for 5 h) contributes to the EPS spheres slowly decomposing and volatilizing, decreasing the drawbacks and risk of cracks to keep the samples’ integrity. After being sintered at 1,550 ℃ for 2 h, the cell struts in the sintered products had a higher density of about 99.0% theory density.

2.4 Analysis of macrostructure and microstructure of foams

Figure 7 shows the macrostructure of the gradient Al₂O₃–20vol.%ZrO₂ foam. It can be seen that the distribution of cell size is approximately uniform in three dimensions. The average cell size is about 1.1 mm. The difference in cell sizes mainly originates from that of the initial EPS spheres. Figure 8 shows the micrograph of a pore of the sintered specimen. In Fig. 8, in the center of the cell struts there is no triangular hole that normally exists in the foams made from the pyrolysis of organic sponges. This kind of dense structure contributes to the improvement in strength of the cell struts.

Figure 9 shows the microstructures of cell struts in gradient Al₂O₃–ZrO₂ foam prepared at centrifugal acceleration of 1,610 g using the slurry with 20vol.% solid content. In Fig. 9, the dark domain is Al₂O₃ and the white domain is ZrO₂. SEM observation in Fig. 9 shows that the distribution of ZrO₂ particles from the top to middle and bottom of specimens presents a continuous gradient. The top segment has less ZrO₂ particles and more Al₂O₃ particles, but the bottom segment has the inverse distribution. The reason is that ZrO₂ particles have
a higher density, high enough settling velocity and larger size, all these make them tend to accumulate at the bottom of cakes and form a gradient distribution during the centrifugal casting. Figure 10 shows the composition profile for the gradient Al₂O₃-ZrO₂ cell struts prepared at a centrifugal acceleration of 1,690 g with the slurries containing 20vol.% solid content. In Fig. 9, the content of ZrO₂ phase has an obviously continuous gradient distribution, which is consistent with the experimental results from Fig. 4 and Table 2.

### Table 3: Effect of applied load on compressive strength and resistance to thermal shock of gradient Al₂O₃-ZrO₂ foams

<table>
<thead>
<tr>
<th>Applied load (N)</th>
<th>Porosity (%)</th>
<th>Compressive strength (MPa)</th>
<th>Repeated time</th>
</tr>
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<tr>
<td>12.3</td>
<td>75.3</td>
<td>4.4</td>
<td>8</td>
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<td>14.7</td>
<td>77.2</td>
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<td>17.2</td>
<td>79.8</td>
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<tr>
<td>19.6</td>
<td>83.0</td>
<td>2.4</td>
<td>10</td>
</tr>
</tbody>
</table>

EPS spheres at high applied load leads to only small amount of Al₂O₃-ZrO₂ slurry poured into the templates and the contents of solid cell struts of the sintered products reduced.

According to our previous research, the compressive strength of porous Al₂O₃ ceramic with 83% porosity is 1.8 MPa. Compared to this, the gradient ceramic foams referred to in this paper have higher strength. The reason is as follows: first, the gradient ceramic foams prepared in this paper have uniform arrayed cell structure and high strut density, which means that the holes and cracks in the cell struts that normally exist in the foams made from the pyrolysis of organic sponges can be avoided. Secondly, the addition of ZrO₂ particles into the Al₂O₃ matrix contributes to the improvement of mechanical properties of the foam because of the t→m phase transformation of the ZrO₂ particles. Finally, the residual compressive stresses on the surface of the gradient Al₂O₃-ZrO₂ foams can be applied to improve the mechanical properties of the materials. In fact, the residual stresses can be generated by using the material with different thermal mechanical properties. In this paper, Al₂O₃ and ZrO₂ have thermal explosion coefficient of 8.5 × 10⁻⁶ °C⁻¹ and 10.9 × 10⁻⁶ °C⁻¹, respectively. On cooling from sintering temperature, layers with higher ZrO₂ content shrink more than that of with less ZrO₂ content. As a result, compressive stresses are generated on the top and bottom surfaces of the sintered gradient Al₂O₃-ZrO₂ foams. This is the main reason for the improved mechanical properties for the present graded ceramic foams. In Table 3, the prepared gradient ceramic foams can resist 8–11 times repeated thermal shock from 1,100 °C to room temperature. The better properties of resistance to thermal shock can be due to phase transformation and gradient distribution of the ZrO₂ particles in ceramic foam.
3 Conclusions
The gradient Al$_2$O$_3$-ZrO$_2$ ceramic foams can be prepared by the centrifugal slip casting method using EPS spheres as templates. The Al$_2$O$_3$-20vol.%ZrO$_2$ slurry has high dispersion and good rheological characteristic at a pH of 10 and dispersant of 0.5wt.%. Centrifugal acceleration has an important effect on the settling velocity and mass segregation of particles. When the centrifugal acceleration is increased, the difference in the green density from the top to bottom in the cell struts and the settling velocity of Al$_2$O$_3$ and ZrO$_2$ obviously increases, causing a severe mass segregation phenomenon. After being centrifuged at 1,610 g, the specimens sintered at 1,500 °C for 2 h have a high sintered density (99.0% theory density) and a continuous gradient distribution of the ZrO$_2$ particles. The cell size of gradient Al$_2$O$_3$-20vol.%ZrO$_2$ foam is approximately uniform and about 1.1 mm. When the porosity of Al$_2$O$_3$-20vol.%ZrO$_2$ ceramic foams increases from 75.3% to 83.0%, the compressive strength decreases from 4.4 to 2.4 MPa, and the ceramic foams can resist 8-11 times repeated thermal shock from 1,100 °C to room temperature.

References

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