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EFFECT OF PORE COMPOSITION ON THERMAL SHOCK RESISTANCE OF POROUS CERAMICS

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Porous alumina ceramics with different pore composition (intrinsic pores and extrinsic pores) were prepared by gel injection molding process combined with pore forming technology and effects of intergranular pores and extrinsic pores on thermal shock fracture resistance and thermal shock damage resistance were studied. The results show that, when the solid phase content or total porosity is the same, the porous ceramic material with extrinsic pores has higher damage tolerance, thermal shock critical temperature difference (ΔT_c) and residual strength retention rate. A ratio parameter (K_{IC}/E) for evaluating the thermal shock stability of materials is deduction. The larger the ratio is, the better the thermal shock resistance of materials.

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1. Introduction

In various high temperatures and harsh environments, the application of structural ceramics will inevitably be affected by instantaneous thermal stress. Excessive thermal shock often causes fracture and damage of the ceramic components, which is not conducive to the engineering safety. Although the commonly used strengthening and toughening methods improve the thermal shock fracture resistance of the materials to a certain extent, they often overlook the thermal impact resistance of the material. Recent studies[1-3] have shown that the introduction of pores into the ceramic matrix is beneficial to the improvement of thermal shock resistance. By adjusting the micro pore structures, and the mechanical/thermal properties of the material can be adjusted to improve the thermal shock fracture resistance. This provides the possibility of optimizing both the thermal shock fracture resistance and thermal shock resistance of the ceramic material simultaneously.

According to the critical stress fracture theory, the strength of ceramic material remains unchanged when subjected to thermal shock. When the thermal shock temperature difference (ΔT) increases to the critical value (ΔT_c), the fracture occurs and the crack initiates. The parameter r is used to determine the minimum thermal shock required for thermal shock crack initiation and the maximum thermal stress that cause the fracture.

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$$R = \frac{(1-\mu)\sigma_f}{E\alpha} \tag{1}$$

Where σ_f is the breaking strength, E is young's modulus, λ is the thermal conductivity, α average coefficient of thermal expansion, μ is Poisson's ratio. Obviously, the material with high strength and thermal conductivity and low thermal expansion and Young's modulus, which can avoid the generation of thermal shock cracks.

Hasselman[4] evaluates the material thermal shock resistance by using the “damage degree” on the basis of crack growth, and deduces the evaluation parameter R'''' for the ability of material to resist crack growth and thermal shock damage.

$$R'''' = \frac{E\gamma_f}{(1-\mu)\sigma_f^2} \tag{2}$$

Where γ_f is the fracture surface energy of the new crack. For brittle materials, the relationship between γ_f and fracture toughness is as follow,

$$K_{IC} = \sqrt{2E\gamma_f} \tag{3}$$

then,

$$R'''' = \frac{1}{(1-\mu)} \cdot \left(\frac{K_{IC}}{\sigma_f}\right)^2 \tag{4}$$

Therefore, in order to improve the thermal stress damage resistance of the material, it is necessary to increase the young's modulus and fracture surface energy and reduce the strength of the material.

The reports of porosity improving the thermal shock performance of ceramics are mostly concerntrated on the total porosity of the pore composition are all related to intergranular pores. Research on the effect of extrinsic pores on the thermal shock resistance of the material is still relatively rare.

The effect of pores on thermal shock fracture resistance of porous ceramics depends on the material system and pore composition. Based on pore origin and size, pores in ceramics can be categorized into intrinsic and extrinsic[5]. Intergranular pores are inter-particle pores due to the packing of particles and their size is typically of the order of the grain size the particle size. Extrinsic pores are typically introduced from the burn out of pore forming agent and their size is similar to that of the pore forming agent size. At present, it is rare to study the effect of extrinsic pores on the thermal shock resistance of materials.

In this paper, the basic ceramic material of α-Al_2O_3 is selected as the research object. The porous alumina ceramics with different porosity and pore composition were prepared by combining the gel injection molding process with the addition of pore forming agent. The effects of foreign pores on thermal shock parameters (R and R'''') were predicted. The predicted thermal shock parameters were compared with the actual thermal shock behavior. On one hand, the purpose of this work is to comprehensively evaluate how the extrinsic pores affect the initiation and propagation of cracks under thermal shock, and on the other hand, to provide an experimental basis for the theoretical study on the effect of micro pore structure on the thermal shock resistance of the materials.

2. Experimental procedure

Using 99.5% α-Al_2O_3 powder (particle size 1.2 μm, Jiyuan brothers Materials Co., Ltd., Henan, China) as raw material, commercially available starch(Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd., China) as pore-forming agent, the average particle size of starch granules is 11.32 μm. Using 1 wt.% agarose(analytical grade, Shanghai Blue Season Biotechnology Development Co., China) as binder, 1 wt.% MgO(99.9%, Tianjin Guangfu Fine Chemical Research Institute, China) was used as sintering aid, 0.6 wt.% sodium hexametaphosphate $(NaPO_3)_6$(analytical grade, Tianjin Guangfu Fine Chemical Research Institute, China) as dispersant. Based on agarose gel casting process, porous Al_2O_3 ceramics were prepared. 5 vol.% and 15 vol.% starch (relative to the total volume of Al_2O_3 and starch) were added to the alumina suspension with pH = 9 (volume fraction of Al_2O_3 was 30 vol.% and 45 vol.%) and milled for 5 h. After vacuum defoaming, the milled slurry was heated in 85 ℃ water bath for 3 min to completely dissolve agarose, and then poured into the mold to dry naturally for 3 days. After demolding, a gelatinization dried body is obtained. The dry body was sintered at 1600 ℃ for 2 h, and then cooled in the furnace. All compositions are expressed with a general formula Al_xPf_y, Al and Pf represents alumina and pore-forming agent, respectively. And the subscript “x” and “y” in the above formula indicates solid loading (vol.%) relative to the total volume of Al_2O_3 and solvent water as well as the pore-forming agent content (vol.%) relative to the total volume of Al_2O_3 and pore-forming agent, respectively.

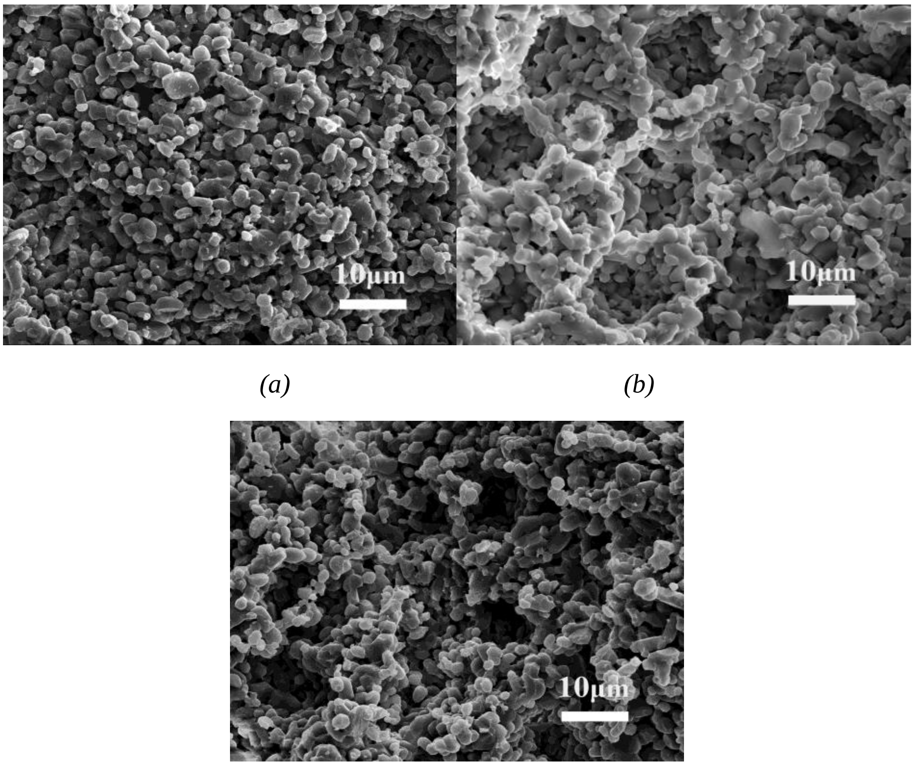
The microstructure of the porous ceramics was inspected by scanning electron microscope (SEM, Hitachi SU8020, Japan). The density and total porosity were determined by the Archimedes method. Flexural strength(σ_f) and residual σ_f were tested in three-point bending tests on 3×4×36 mm bars, using a 30 mm span and a crosshead speed of 0.5 mm/min. For the fracture toughness(K_{IC}) measurements, samples with 2×4×30 mm were loaded by a single-edge notched beam (SENB) method with a cross head speed of 0.05 mm/min. Young's modulus(E) was measured using cubic test bar of 4×4×4 mm by the pulse echo method (Model 5077PR, Olympus, Japan). The experimental results of these characteristics are given in Table 1. Thermal shock test was performed by water-quenching, the temperature difference was set as 100 ~ 600 ° C.

Table 1. Porosity and mechanical properties of porous Al30Pf0 , Al30Pf15 and Al45Pf5 ceramics

Materials	Overall porosity P_t (%)	Intergranular porosity P_i (%)	Extrinsic porosity P_o (%)	Flexural strength σ_f (MPa)	Young's modulus E (GPa)	Fracture toughness K_{IC} (MPa·m$^{1/2}$)
Al30Pf0	38.7	38.7	0	56.32	53.61	0.80
Al30Pf15	46.5	32	14.5	38.75	13.98	0.57
Al45Pf5	39.2	34.6	4.4	54.9	44.6	0.73

3. Results and discussion

Fig.1a shows the SEM morphology of Al30Pf0 sample. Without the addition of pore forming agent, alumina particles are naturally stacked together and evenly distributed, there are small irregular pores between the particles. Since the content of organic monomer in the green body is very small (1 wt.%) of Al_2O_3, the space volume occupied by it is negligible. Therefore, the pores generated during the sintering densification process are completely intergranular pores formed by the accumulation of Al_2O_3 particles. Therefore, the material properties mainly depend on the porosity of intergranular pores. Fig.1b and c are the SEM morphologies of Al30Pf15 and Al45Pf5 sample respectively. It is obvious that there is no obvious difference in the morphology of Al_2O_3 grains. In addition to the intergranular pores, there are also larger spherical pores, which are formed due to the introduce of starch, are called extrinsic pores. Therefore, the extrinsic pores and the intergranular pores together affect the properties of the material.



(a) *(b)*

(c)

Fig.1. SEM micrographs:（a）Al30Pf0（b）Al30Pf15（c）Al45Pf5.

In order to determine the effect of intergranular pores and extrinsic pores on the maeiral properties, it is necessary to estimate the porosity of the intergranular pores and extrinsic pores. According to the experimental[6,7], it is assumed that: (ⅰ) the shrinkage of intergranular pores is not affected by the extrinsic pores, and the intergranular porosity depends on the effective solid content; (ⅱ) when the effective solid content is the same, the sintering shrinkage of powder particles remains unchanged under the same sintering conditions. The porosity of the intergranular and foreign pores can be calculated using the following formula:

$$P_{\mathrm{o}} = P_{\mathrm{t}} - P_i \tag{5}$$

Where P_{t} is the total porosity, P_{o} is the porosity of the extrinsic pores, and P_{i} is the porosity of the intergranular pores. The porosity matching relationship of porous Al_2O_3 ceramics prepared by experiments is shown in Table 1. It can be seen that 14.5% extrinsic pores can be introduced by adding

15vol.% pore forming agent to 30 vol.% solid content, and porous ceramics with the same porosity (~ 39%) and different proportions of intergranular and extrinsic pores can be obtained by adjusting the solid content and pore forming agent volume fraction.

It can be seen from table 1 that compared with Al30Pf0 sample, the strength, Young's modulus and fracture toughness of Al30Pf15 and Al45Pf5 sample decrease in varying degrees due to the influence of extrinsic pores. Essentially, a hole is essentially a kind of crack or defect. Under the action of external force, stress concentration will occur at the crack tip. The larger the pore is, the larger the equivalent defect size is. Therefore, when subjected to external forces, the damage occurs at the end of the extrinsic pores, which makes the strength, modulus and fracture toughness of the ceramic materials decrease.

Damage tolerance (σ/E)[8] describes the maximum failure strain that a material can withstand, and is an important parameter in proportional to the thermal stress fracture resistance factor R, the larger of the σ/E, It means that the material has better resistance to thermal shock fracture. In order to discuss the effect of pore composition on thermal shock resistance, the coefficient of thermal expansion takes a constant value of 7.8×10^{-6} k^{-1}[9,10] and Poisson's ratio is assumed to be constant at 0.25[11]. Table 2 shows the values of the parameters σ/E, R and R'''' calculated from the experimental data in Table 1.

Table 2. Calculated values of σ/E , R and R'''' for porous Al30Pf0, Al30Pf15 and Al45Pf5 ceramics

Materials	P(%)	σ/E ($\times10^{-6}$)	R(℃)	R''''(μm)	ΔT_c^* (℃)
Al30Pf0	38.7	1.05	107.8	251	184.6
Al30Pf15	46.5	2.77	284.3	269	204.5
Al45Pf5	39.2	1.23	126.3	221	201.4

It can be seen from table 2 that: compared with Al30Pf0 sample, although the strength and Young's modulus of Al30Pf15 are reduced due to the introduction of extrinsic pores, but the value of σ/E and R are higher than those of Al30Pf0 sample, which means that the extrinsic pores can increase the total porosity and improve the theoretical thermal shock resistance temperature difference of the matrix at the same time, which makes the ceramic materials have higher crack initiation resistance and crack propagation resistance. Fig.2 compares the thermal shock behavior of Al30Pf0 and Al30Pf15 ceramic samples. It can be seen that they all have intensity attenuation at 200 ℃, and the critical temperature difference (ΔT_C^*) corresponding to 70% of the initial strength of Al30Pf15 is greater than that of Al30Pf0. This trend is consistent with the change trend of the parameter R in Table 2. Both the experimental results and the theoretical calculations verify the interesting phenomenon that the introduction of extrinsic pores helps to improve the thermal shock fracture resistance. Regarding the question of how porosity affects thermal shock fracture resistance, some recent experimental results of scholars have diverged. Although the fact that the increase of porosity will reduce the critical temperature difference has been confirmed by theoretical derivation and experiment[12,13], it has been found that the critical temperature difference increases with the increase of porosity in some systems[14,15].

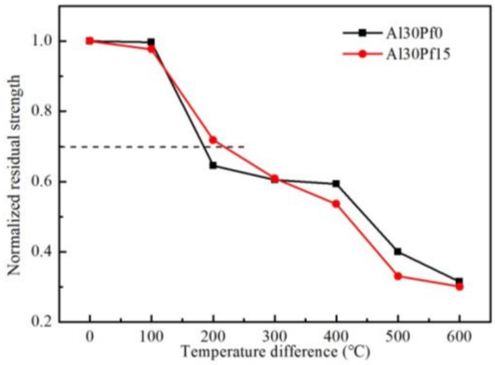


Fig. 2.Normalized residual strength as a function of quenching temperature difference for Al30Pf0 and Al30Pf15 porous Al_2O_3 *ceramics.*

In addition, it can also be seen from Fig.2 that the residual strength retention rate of Al30Pf15 ceramic is higher than that of Al30Pf0 in the range of 0~300 ℃, which is consistent with the change of R'''' calculated in Table 2. According to formula (4), R'''' is directly proportional to K_{IC}/σ_f ratio, which means that the thermal shock damage resistance of a ceramics can be improved by increasing its K_{IC}/σ_f ratio. Due to a relatively high value of K_{IC}/σ_f, Al30Pf15 ceramics were observed to exhibit less strength degradation rate after thermal shock in the range of 0 ~ 300 ℃, as shown in Fig.2.

Fig.3 compares the thermal shock behavior of Al30Pf0 and Al45Pf5 porous ceramics. Because the total porosity is the same, the difference of their properties mainly depends on whether there are extrinsic pores. Obviously, the critical temperature difference corresponding to 70% room temperature strength of Al45Pf5 sample is 201.4 ℃, which is higher than 184.6 ℃ of Al30Pf0 sample. Moreover, the residual strength retention rate of Al30Pf0 specimen is slightly higher than that of the Al30Pf0 specimen, which is consistent with the change of R and R'''' calculated in Table 2. The results show that with the same porosity, the introduction of extrinsic pores increases the critical temperature difference of the material and delays the strength degradation rate.

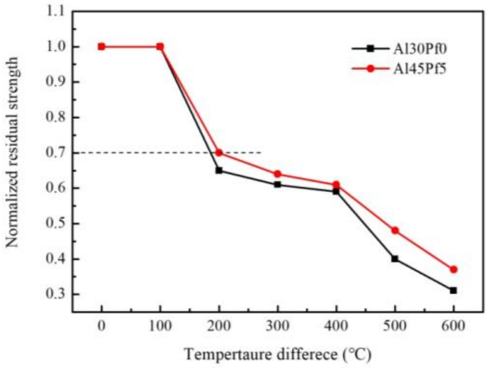


Fig.3.Normalized residual strength as a function of quenching temperature difference for Al30Pf0 and Al45Pf5 porous Al_2O_3 *ceramics.*

Hasselman unified the thermal shock fracture initiation and crack propagation theory of ceramic materials, solved the conflict between thermal shock fracture resistance and thermal shock damage resistance on the material performance, and proposed the stability parameter R_{st}[4] for quasi-static growth of thermal stress crack,

$$\Delta T_c \propto R_{st} = \left(\frac{\gamma_f}{E_0\alpha^2}\right)^{1/2} \tag{6}$$

When the R_{st} is large, the crack propagation is not easy and the material has good thermal stability. By substituting formula (3) into formula (6), we can get

$$R_{st} = \frac{K_{IC}}{E_0\alpha} \tag{7}$$

The stability factor R_{st} is directly proportional to K_{IC} and inversely proportional to E. Therefore, the K_{IC}/E ratio can be used to determine the ability of a material to resist crack propagation. The larger the K_{IC}/E value, the less the cracks will expand and the better the thermal stability. Fig.4 compares the K_{IC}/E ratios of Al30Pf0, Al30Pf15 and Al45Pf5 ceramic samples. It can be seen that the K_{IC}/E ratio increases with the increase of the extrinsic porosity, which means that the extrinsic pores effectively improve the critical temperature difference of the porous ceramic materials, and the crack growth rate is delayed.

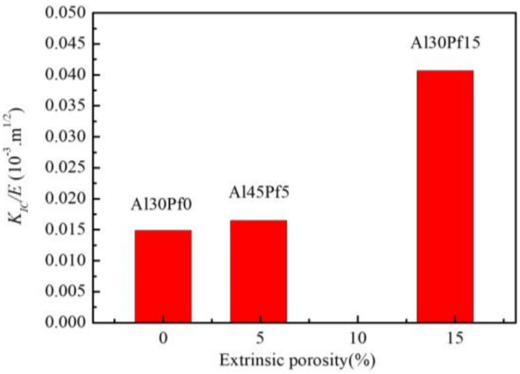
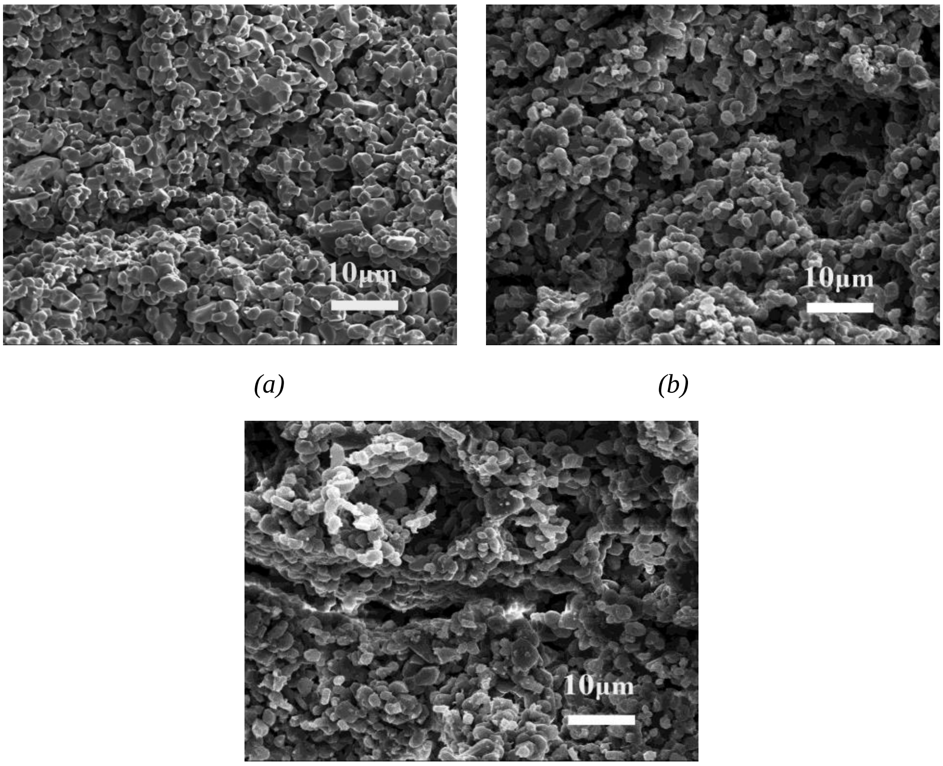


Fig.4.K_{IC}/E ratio of porous alumina ceramics with different content of external pores.

Some research have confirmed that pores can play a role in preventing crack propagation[2]. In the process of thermal shock, larger pores can deflect or even stop long cracks by pinning the cracks, resulting in a reduction in crack depth. When there are more extrinsic pores, short cracks can be prevented from expanding in the long-distance direction. Therefore, the crack growth occurs in a quasi-static manner, delaying the rate of strength attenuation. From the crack morphology of the three groups of materials after thermal shock in Fig.5, it can be seen that the thermal shock cracks of al30pf0 sample propagate along the grain boundary, and the cracks in al30pf15 and al45pf5 samples terminate and deflect at the position of extrinsic pores.



(a) *(b)*

(c)

Fig.5. SEM micrographs of thermal shock crack: *(a) Al30Pf0, (b) Al30Pf15 (c) Al45Pf5*

4. Conclusions

The gel injection molding process combined with the pore former technology was used to prepare porous alumina ceramics with different pore compositions (intergranular pores and extrinsic pores), and the thermal shock behavior of the material was tested. The influence of extrinsic pores on thermal shock fracture resistance and thermal shock damage resistance were studied under the condition of the same solid content or the same total porosity. The results show that the introduction of extrinsic pores into porous ceramics reduces the mechanical properties of the materials, but increases the σ/E, R and R'''', and improves the critical temperature difference.

This interesting phenomenon also exists in porous ceramics with the same total porosity and different pore composition. Experiments have proved that the introduction of extrinsic pores into porous ceramics can increase the resistance to crack initiation and crack propagation, and help improve the thermal shock fracture resistance and thermal shock damage resistance of porous ceramics. According the Hassleman's classic formulas about steady-state crack propagation, a ratio K_{IC}/E is proposed to evaluate the ability of materials to resist crack propagation. The larger the K_{IC}/E value, the less likely the cracks to expand, and the better the thermal stability of the material. The value of K_{IC}/E was larger for samples with higher extrinsic pores ratio. The experimental results are in good agreement with the calculated results.

Acknowledgments

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