Toughening macroporous alumina membrane supports with YSZ powders

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Abstract

Macroporous alumina is an important support in membrane fields because of its stabilities to withstand exposure to high temperature, harsh chemical environment and high mechanical strength. However, the essence of brittleness can greatly shorten the life span and restrict the application fields. In this paper, YSZ (ZrO_2 stabilized by 3 mol% Y_2O_3) powders were added into alumina powders to improve the fracture toughness of macroporous Al_2O_3 supports sintered at 1400 °C and 1600 °C. The results show that the fracture toughness and the corresponding bending strength of supports are simultaneously greatly influenced by various YSZ contents. When YSZ content is 6 wt%, the maximum value of the fracture toughness is 3.0 MPa·m$^{1/2}$, and the bending strength is up to 90 MPa. By SEM and XRD analysis, the phase transformation of the uniform distribution t-ZrO_2 into m-ZrO_2 is the main cause which improves the fracture toughness of macroporous Al_2O_3 supports. Lowering of the sintering temperature by adding YSZ additives is also discovered here. The fracture toughness of the supports sintered at 1400 °C by adding YSZ powder is higher than that of the supports sintered at 1600 °C without adding any additives.

1. Introduction

Macroporous ceramic membranes have received much attention in recent years due to their stabilities to withstand exposure to high temperatures, harsh chemical environment and high mechanical strength [1,2], and are widely applied in fields of foodstuff, chemical industry, environmental protection, etc. [3–6]. Such ceramic membrane usually has an asymmetric structure, consisting of a top membrane layer with separation performance and a support which can provide mechanical strength for a top layer to withstand the stress induced by the different pressures applied over the entire membrane, and must simultaneously have a low resistance to filtrate flow [7].

Alumina ceramic with macroporous structure is one of the most important supports because of its advantages of durability, high temperature stability and chemical resistance [8]. However, its fracture toughness shows a low value due to the brittleness essence as well as that of dense ceramic [9],

which limits its applications and/or shortens the life span during such processes as the sealing of ceramic membrane, the assembly processing step and the back flush. Therefore, the fracture toughness of macroporous ceramic supports requires improvement for a greater effectiveness.

At present, there are few literatures reporting on toughening methods and mechanism for porous ceramic. Researchers mainly aim at the novel preparing methods [10,11], the potential advantage properties and more widely application fields [12]. Naturally, high apparent porosity and high mechanical strength are simultaneously required under severe operating condition. When the apparent porosity increased, the corresponding mechanical properties will severely decrease [13]. The improvement of fracture toughness is usually at the expense of high porosity or bending strength. Therefore, it is worthy to study the toughening method and mechanism of macroporous Al_2O_3 support which usually has above 30% porosity to guarantee the fluent flow.

For a dense Al_2O_3 ceramic body, adding ZrO_2 has been considered as one of the most effective approaches [14,15] for giving damage-tolerance ability to brittleness. Some successful approaches were put into practice in many application fields [16,17], such as making ceramic knives, wear-resisting

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materials and other reactor vessels. In porous ceramic fields, it is also expected to improve the fracture toughness by adding suitable content of ZrO$_2$ powders. This paper mainly aimed at the improvement of fracture toughness for Al$_2$O$_3$ macroporous supports by adding YSZ (Zirconia stabilized by 3 mol% Y$_2$O$_3$) powders. The variation of apparent porosity, bending strength and fracture toughness with various feed YSZ powders and sintering temperatures were investigated. The toughening mechanism was also discussed.

2. Experimental procedure

2.1. Preparations of supports

The alumina powders purchased are prepared by hydrothermal method and the average particle size (D$_{50}$) is 24 μm (MasterSizer2000, Malvern Instrument, Co., UK). Fig. 1 shows the particle size distribution of Al$_2$O$_3$ powders (China Great Wall Aluminium Corporation, Zhengzhou, China). The average particle size (D$_{50}$) of YSZ powders (Material self-prepared) as additives is 0.7 μm. Wet-ball-milling was adopted to get the Al$_2$O$_3$/YSZ uniform mixture powders. According to the given composition of supports, mixture powders were put into the nylon jars. De-ionized water as dispersion and high hardness corundum balls were added into the mixture which pH was 6, milling for 24 h. The mixture described above was heated under stirring. After drying in a drying-oven at 110 °C for 48 h and grinding, the uniform Al$_2$O$_3$/YSZ mixture powders that passed through an 80 mesh screen were obtained. PVA (0.15 wt%) and paraffin (3 wt%) were added simultaneously. By dry pressing method, green-body rectangular bars of 6 mm × 6 mm × 50 mm and pellets of Ø30 mm × 2 mm were prepared under a pressure of 8 MPa. After dried at 110 °C for 24 h, the green-body samples were sintered in air for 2 h in an electric-furnace at 1400 °C and 1600 °C, respectively, with a heating rate of 3 °C/min and cooling naturally.

2.2. Characterization

Apparent porosity was measured by the Archimedes method with an immersion medium of water. The calculated formula
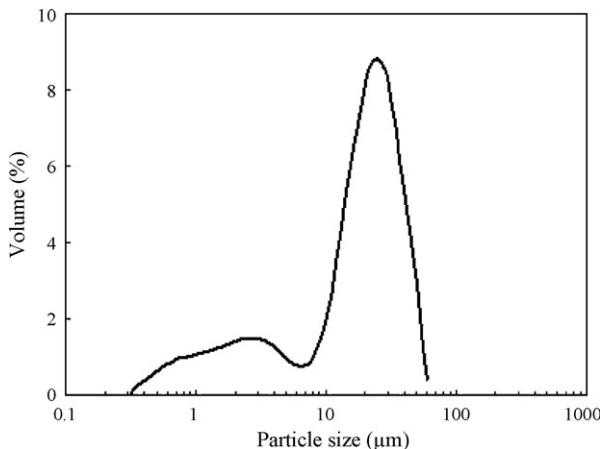

Fig. 1. Particle size distribution (D$_{50}$) of alumina powders.

was given as follows:

$$P = \frac{m_3 - m_1}{m_3 - m_2} \times 100\% \tag{1}$$

where P represents the apparent porosity of the support, m_1 is the weight of the dry support, m_2 is the weight of the support saturated of water suspended in water, m_3 is the weight of the support saturated water. The bending strength was tested by three point bending method. The fracture toughness values (K_{IC}) were determined using the Single Edge Notched Beam (SENB) technique [18]. Each sample was notched precrack of ~2 mm long before testing. The fracture toughness was given by [19]:

$$K_{IC} = Y \frac{3PL}{2bw^2} \sqrt{a} \tag{2}$$

where P is the fracture load, L is the length of the span between two points, b and w are related to the width and thickness, respectively, a is the depth of specimens center crack, and Y is a geometrical constant.

$$Y = 1.93 - 0.37\frac{a}{w} + 14.53\left(\frac{a}{w}\right)^2 - 25.07\left(\frac{a}{w}\right)^3 + 25.08\left(\frac{a}{w}\right)^4 \tag{3}$$

To test the mechanical properties of supports, the rectangular bars were grounded and beveled in advance to eliminate surface stress. The cross section of macroporous Al$_2$O$_3$ support was observed by scanning electron microscopy (SEM, Quanta 200, FEI, The Netherlands). The phase composition of ZrO$_2$ in samples after sintering was analysed by X-ray diffraction (XRD, D8 Advance, Bruker Instrument Co., Ltd. Germany) and the phase content was calculated based on the relative diffraction intensity of t-ZrO$_2$(1 1 1), m-ZrO$_2$(1 1 1) and (1 1 $\bar{1}$) peak, the relative content of t-ZrO$_2$ and m-ZrO$_2$ was obtained from [20]:

$$X_m = \frac{I_m(1\,1\,1) + I_m(1\,1\,\bar{1})}{I_m(1\,1\,1) + I_m(1\,1\,\bar{1}) + I_t(1\,1\,1)} \times 100\% \tag{4}$$

and

$$\phi_m = \frac{1.311 X_m}{1 + 0.311 X_m} \tag{5}$$

where X_m is the integrated intensity ratio of m-ZrO$_2$ volume, the subscripts m and t represent the intensities of the monoclinic and tetragonal phases after the peak separation and fitting procedures, $I_t(1\,1\,1)$, $I_m(1\,1\,1)$ and $I_m(1\,1\,\bar{1})$ represent the intensity of t-ZrO$_2$(1 1 1), m-ZrO$_2$(1 1 1) and m-ZrO$_2$(1 1 $\bar{1}$) peak, respectively, and ϕ_m is the volume fraction of the monoclinic phase.

3. Results and discussion

3.1. Effects of YSZ content

3.1.1. Porosity

According to the phase diagram of Al$_2$O$_3$–ZrO$_2$ [21], there is not any compound obtained in the Al$_2$O$_3$/YSZ system.
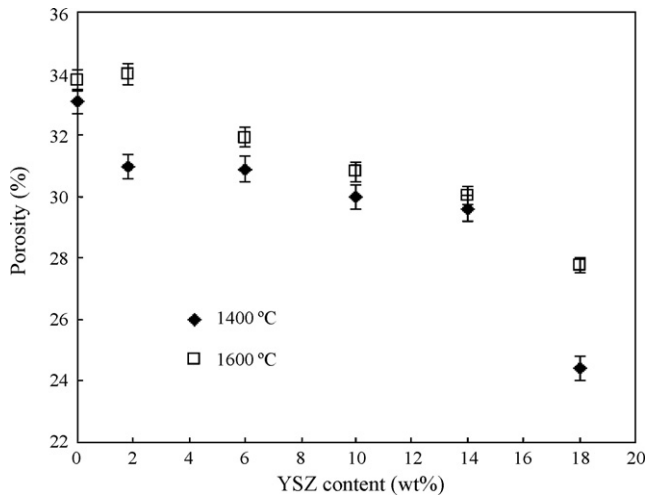
Fig. 2. Relationship between porosity of supports and YSZ content sintered at 1400 °C and 1600 °C.

Fig. 3. Relationship between fracture toughness of supports and YSZ content sintered at 1400 °C and 1600 °C.

Therefore, the phase composition is only Al_2O_3 and ZrO_2 after sintering. In green body, alumina coarse particles form a framework with continuous open pores. Because YSZ particles are fine, they can pad the pores in molding process. With the increasing of YSZ powders added, more pores are padded by plenty of fine particles. Therefore, the apparent porosity of the corresponding supports decreases with the YSZ particles increasing as shown in Fig. 2.

During the sintering process, most of fine particles with high surface area are distributed among the coarse Al_2O_3 particles due to the effective mixing methods. At a certain high temperature, diffusion sintering becomes very strong and the bonding neck is formed by plenty of fine particles. When the sintering temperature increases continuously, the neck growth becomes aggravated. Eventually, these fine particles are transferred to the surface of the coarse particles, and leave a new pore with a new shape [22]. Therefore, the apparent porosity of the support sintered at high sintering temperature is higher than that of the support sintered at low sintering temperature, when the same amount of YSZ fine powders are added.

3.1.2. Fracture toughness

With the increase of YSZ content, the fracture toughness reveals increase, and followed by decrease as shown in Fig. 3. The maximum value of fracture toughness is 3.0 MPa m$^{1/2}$ when YSZ powders is 6 wt%, which is about 10 and 3 times as that of supports sintered at 1400 °C and 1600 °C without adding any additives, respectively. When the YSZ content is above 6 wt%, the decrease trend is observed. The corresponding value
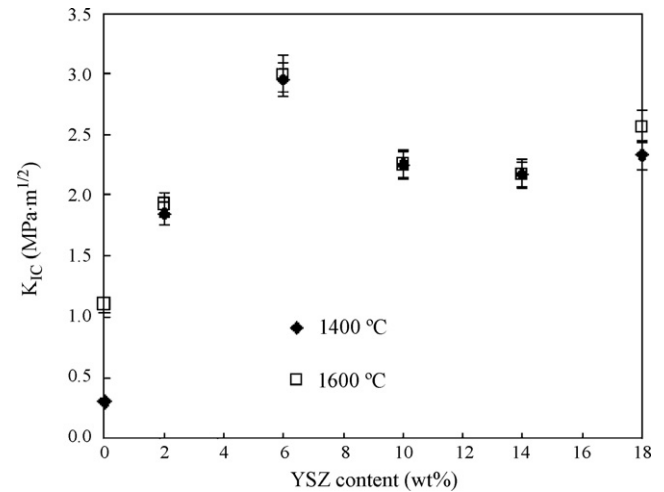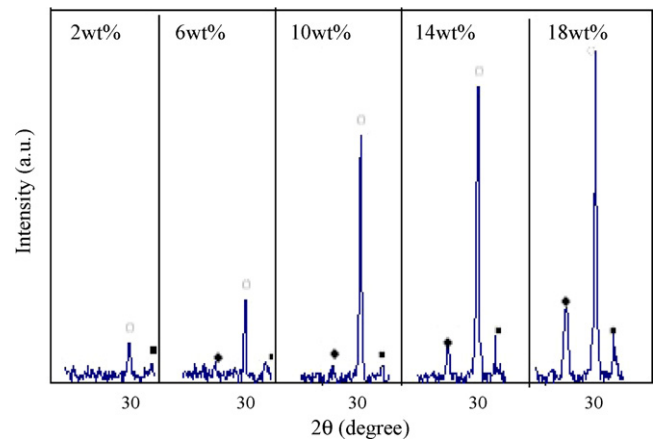

Fig. 4. X-ray diffraction patterns of Al_2O_3–YSZ supports sintered at 1600 °C, ◆: m-ZrO_2 (1 1 $\bar{1}$), □: t-ZrO_2 (1 1 1), ■: m-ZrO_2 (1 1 1).

of fracture toughness is still higher than that of the supports without adding any additives.

After sintered at 1600 °C, the ZrO_2 phase compositions of supports with various YSZ contents are shown in Fig. 4. The transformation ratio of m-ZrO_2 with various YSZ contents at 1600 °C is shown in Table 1. During the cooling stage of sintering process, the alumina particles are subjected to a compressive stress and create some microcracks due to the different thermal expansion coefficients of alumina and YSZ particles [23]. Such microcracks can be closed and the fracture time can be prolonged when there is an external force on the support. Therefore, the fracture toughness of support is

Table 1
m-ZrO_2 ratio transformed from t-ZrO_2 of supports prepared at 1600 °C by adding various YSZ contents.

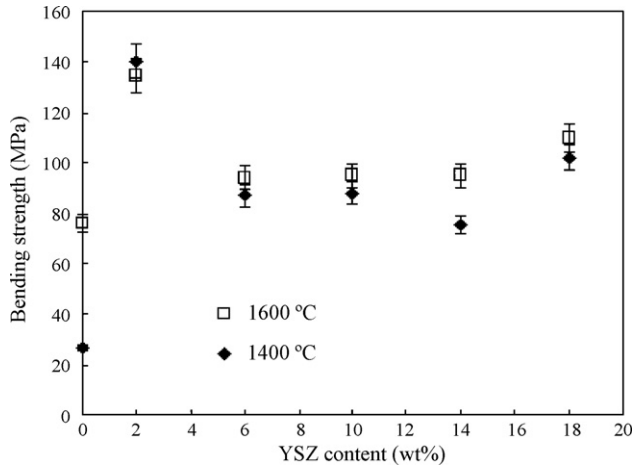| Supports number	A1	A2	A3	A4	A5	A6
YSZ content/wt%	0	2	6	10	14	18
Integrated intensity ration of m-ZrO_2 volume (X_m)	0	32%	36%	13%	22%	28%
Ratio of m-ZrO_2 (φ_m)	0	0.38	0.42	0.16	0.27	0.34

Fig. 5. Relationship between bending strength of supports and YSZ content sintered at 1400 °C and 1600 °C.

improved. The m-ZrO_2 ratio of ZrO_2 composition is different with various YSZ contents. When YSZ content is 6 wt%, the m-ZrO_2 ratio is the highest among samples. The improvement of m-ZrO_2 phase transformed from t-ZrO_2 is benefit to the improvement of fracture toughness for Al_2O_3 materials when the phase transformation is the main cause [24]. Therefore, the maximum value of fracture toughness is obtained when YSZ content is 6 wt%.

3.1.3. Bending strength

Compared with the change of fracture toughness, a small difference may be observed in the curve of bending strength (Fig. 5). The maximum value of bending strength is 140 MPa with adding 2 wt% YSZ powders, which is 5 and 1.4 times as that of the Al_2O_3 supports without adding any additives sintered at 1400 °C and 1600 °C, respectively. When the fracture toughness reaches the maximum value of 3.0 MPa m$^{1/2}$, the bending strength is 90 MPa with adding 6 wt% YSZ powders. Compared with the two curves, the increment of fracture toughness is at the expense of the decrease of bending strength. At the two experimental sintering temperatures, the two curves keep the same trend.

It is conceivable that the neck zone is the crack source when the support is pressed by an external force. With the increasing of YSZ content, the bonding neck increases by the strong surface diffusion of fine particles at a certain high temperature. Simultaneously the stress resulted from the phase transition of t-ZrO_2 will be aggravated. The two behaviors are opposite to the improvement of bending strength. When YSZ content is 2 wt%, the bonding neck area is enough to obtain the high bending strength. And the force resulted from phase transition is active to produce the suitable size microcracks. Such microcracks can absorb the high facture energy by its closing when an external force applied on the supports, but can not result in the formation of cracks. Therefore, the maximum value of bending strength was obtained by adding 2 wt% YSZ powders. When YSZ content is 6 wt%, the transformation ratio of t-ZrO_2 is raised as shown in Table 1. The amount of microcracks which result from phase transformed increases. However, the spread and bridging of microcracks easily occur due to the limit bonding neck. The decrease of bending strength was observed. When an external force acted on the support increase, the microcracks propagation rate into dangerous cracks becomes quick. When YSZ content was 6 wt%, the lower value of bending strength was observed. But the value was still higher than that of Al_2O_3 support without additives.

3.1.4. Microstructure

In fact, special microstructure is helpful to the improvement of fracture toughness and bending strength of supports. Fig. 6 (a and b) show the representative section micrographs of supports sintered at 1600 °C by adding 2 wt% and 6 wt% YSZ powders. According to SEM, YSZ particles uniformly disperse in the framework of Al_2O_3 coarse particles. Some of volume expansion also occurs during the martensite phase transformation process of t-ZrO_2. In the cooling stage, because of the higher expansion coefficient, part of YSZ particles are partly embedded between Al_2O_3 particles and form a "sandwich structure" (see Fig. 6 points A, B, and C), which can improve the compact area between Al_2O_3 particles and create a highly torturous crack path. Consequently, improvements on fracture toughness and bending strength are obtained for the as-prepared
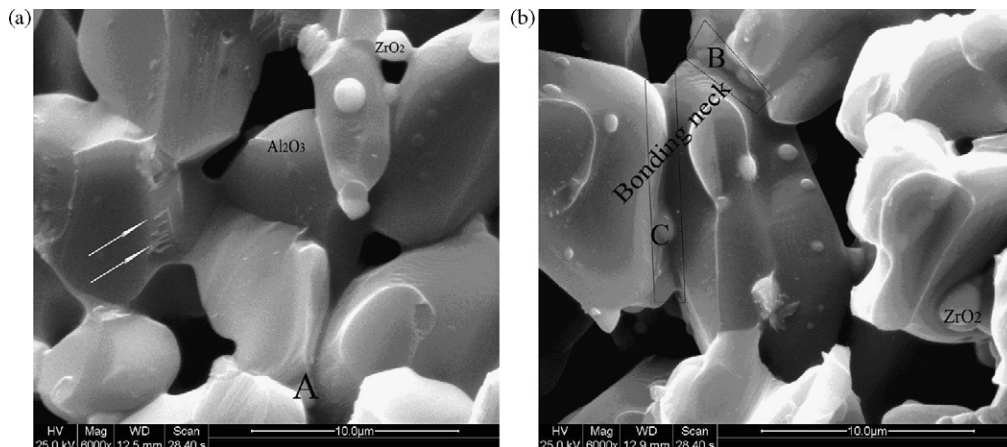

Fig. 6. SEM images of support by adding 2 wt% (a) and 6 wt% (b) YSZ powders sintered at 1600 °C.

Al$_2$O$_3$/YSZ support since the main fracture manner of it is intercrystalline rupture (see Fig. 6 arrow point), which is consistent with other reports [25].

When no additives are added, the framework of microstructure is formed directly by coarse Al$_2$O$_3$ particles. The diffusion sintering effectiveness between the two coarse Al$_2$O$_3$ particles is more difficult than that of fine particles. Therefore, the mechanical properties of supports without additives are not as good as the toughened supports prepared in this paper.

3.2. Effects of sintering temperatures

As far as porous ceramic materials are concerned, the mechanical properties are closely related with sintering temperature. In this study, the properties of supports without any additives are greatly influenced when the heating temperature is raised from 1400 °C to 1600 °C. The value of fracture toughness increased from 0.3 MPa m$^{1/2}$ to 1.2 MPa m$^{1/2}$, and the bending strength raised from 27 MPa to 76 MPa.

One of the interesting effects of microstructure was discovered by Green et al. [26,27], who believed that the neck growth is mainly formed by surface diffusion. In this paper, without any sintering acceleration agent added, these improvements of mechanical properties are only caused by the stronger surface diffusion when the sintering temperature increases, and the diffusion effects becomes very strong at higher sintering temperature. Therefore, the corresponding mechanical properties of supports reveal rising.

Adding YSZ fine particles can also improve the surface diffusion to obtain the better mechanical properties by forming the same bonding neck as well as formed at high temperature without any additives added. When some desired YSZ powders are added, the mechanical properties have no remarkable improvement when the sintering temperature increases from 1400 °C to 1600 °C. The result proves that the improvement of the surface diffusion by adding YSZ fine particles is as efficient as increasing temperature. At 1400 °C, the macroporous supports with high fracture toughness can be obtained by adding YSZ powders, which properties are as well as that of the support sintered at higher temperatures without any additives added. Namely, YSZ powders act as a sintering acceleration agent and can also decrease the sintering temperature of support.

4. Conclusion

The present study reported a method to obtain the macroporous alumina supports with high mechanical properties by adding YSZ powders. The influence of YSZ content on porosity, bending strength and fracture toughness of supports sintered at 1400 °C and 1600 °C were investigated and compared with the supports without adding any additives. The results show that YSZ powders play an important role in the increment of mechanical properties for macroporous Al$_2$O$_3$ supports. When YSZ content is 6 wt%, fracture toughness of the supports reaches the maximum value of 3.0 MPa·m$^{1/2}$, and the corresponding bending strength is 90 MPa. The mechanical

properties of Al$_2$O$_3$-YSZ macroporous supports sintered at 1400 °C and 1600 °C are at the same level. Adding YSZ fine powders can also decrease the sintering temperature of the supports.

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