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Preparation and properties of high toughness RBAO macroporous membrane support

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Abstract

Reaction bonding of aluminum oxide (RBAO) is a novel technique for preparing porous alumina. By adapting this manufacturing route, macroporous Al_2O_3 supports with high fracture toughness are prepared for ceramic membrane. The effects of sintering temperatures and aluminum (Al) content on mechanical properties of macroporous Al_2O_3 supports are investigated, especially for the improvement of fracture toughness. When the sintering temperatures increase from 1200 °C to 1600 °C, increments of fracture toughness and bending strength are observed. Sintered at 1600 °C, when Al content is 16 wt%, the maximum value of fracture toughness and bending strength of macroporous Al_2O_3 supports are 2.0 MPa $m^{1/2}$ and 137 MPa, respectively, which are 2.0 and 2.6 times than that of the supports without adding any additives. By SEM analysis, many fine Al_2O_3 particles form a network which is beneficial to the improvements of fracture toughness and bending strength. After corroded in nitric acid and sodium hydroxide solutions of 1 mol L^{-1} at 80 °C for 168 h, respectively, the mass loss percentage is lower than 1 wt%. And the bending strength keeps at the level of ~40 MPa which is strong enough to apply in industry. Simultaneously, the toughening mechanism of RBAO macroporous support is also discussed.

Keywords: RBAO; Ceramic membrane; Supports; Fracture toughness; Bending strength

1. Introduction

Alumina ceramic with macroporous structure and high bending strength is an important support for ceramic membrane because of its stabilities at high temperatures and in harsh chemical environments, etc. [1]. Ceramic membrane is usually used for the purpose of liquids purification in various separation processes, for example in food stuff, in waste water treatment, in chemical and metallurgical industries, or used to detain mechanical impurities, colloidal and micro-organisms [2]. However, the potential application fields and the life span of ceramic membrane are greatly restricted due to the low fracture toughness of its supports. When Al_2O_3 ceramic has a porosity of 30% as membrane support, its fracture toughness is only about 0.3–0.5 MPa $m^{1/2}$. Usually, the improvement of fracture toughness is at the expense of bending strength or high porosity. Therefore, macroporous alumina supports with high fracture toughness and high bending strength are required to be prepared.

Adding ductile metallic phase is an effective method to overcome these negative aspects of ceramic materials, which can lead to an improvement of fracture toughness. In general, aluminum (Al) powders are always adopted for this purpose. Various preparation methods are adopted to improve the fracture toughness of Al_2O_3 materials by adding suitable content of Al powders [3–6]. By directed metal oxidation method, Al/Al_2O_3 exhibiting a fracture toughness of 9.5 MPa $m^{1/2}$ is reported [7]. By gas pressure metal infiltration method, Al/Al_2O_3 exhibiting a bending strength of 760 MPa and a fracture toughness of 5.8 MPa $m^{1/2}$ are reported [8]. In general, the improvement of fracture toughness is ascribed to the unoxidized ductile phases and always at the expense of high porosity. According to these methods, the chemical resistance also decreases because of the unoxidized metal phase in the

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grain-boundary area. However, when Al_2O_3 with macroporous structure and high bending strength acted as membrane supports, the chemical resistance also always receives much attention and cannot be decreased because of the special application in industry.

Reaction bonding of aluminum oxide (RBAO) is a novel technique for preparing alumina ceramic and can also improve the fracture toughness without decreasing the bending strength and chemical resistance by adding desired Al content. This technique has been proposed by Claussen as an attractive method to produce alumina dense ceramic, and is being developed successfully [9]. The preparing process consists of mixing Al and Al_2O_3 powders, then shaping, an oxidation treatment and a final heat treatment. Subsequently, Luyten et al. [10] adopt the RBAO method to synthesize porous alumina. The obtained porous RBAO-substrates are three times stronger than the Al_2O_3 ones with comparable porosity. Falamaki et al. [11] used alumina powder with an average size of 1.6 μm and aluminum with an average size of 38 μm to synthesis the supports with an average pore size of 0.2 μm. The obtained porous RBAO material is largely superior to the porous Al_2O_3, such as high bending strength, high permeability and other advanced properties [12–14]. The supports with small size pores are usually used as the support for gas separation membranes. When the supports used as macroporous membrane supports, the average pore size of support are expected several micrometers. Therefore, the coarse Al_2O_3 particles as the main materials are used to prepare the corresponding supports with the larger pore sizes. As the key technique parameters for preparing such excellent RBAO supports, the influences of sintering temperatures and Al content on the improvement of fracture toughness and bending strength by RBAO combination are not clear in released literatures, and the mechanism is not being much understood.

In this paper, the different experimental formulas are designed to study the influence of sintering temperatures and Al content on the fracture toughness and bending strength of macroporous RBAO supports. The mechanisms are also expatiated deeply. Simultaneously, the chemical resistance of as-prepared supports is also investigated.

2. Experimental procedure

2.1. Preparations of supports

The alumina powders with an average particles (D50) of 24 μm (MasterSizer2000, Malvern Instrument, Co., UK) are spherical coarse particles, which are prepared by hydrothermal method. Fig. 1 shows the distribution graph of Al_2O_3 particle size. The average particle size (D50) of Al powders as additives is 1.66 μm, which also has a narrow size distribution. The each Al2O3/Al uniform mixture powders are obtained by ball-milling method. According to the given composition for preparing RBAO supports, mixture powders are put in to the nylon jars. High hardness corundum balls are added into the mixture according to twice weight of the mixture powders. After ball-milled for 24 h, the uniform Al_2O_3/Al mixture is obtained. A certain content of PVA and paraffin are added into the mixture powders and grinded for several minutes in earthen bowl. By dry pressing methods, green rectangular bars of 6 mm × 6 mm × 50 mm and green pellets of Ø 30 mm × 2 mm are prepared under a pressure of ~8 MPa, in stainless-steel moulds. The green bodies are dried in a drying-oven at 110 °C for 24 h, and then are sintered in an electric-furnace for 2 h at 800 °C, 1000 °C, 1200 °C, 1400 °C, 1500 °C and 1600 °C, respectively, at a scheduled heating rate of 3 °C/min and cool naturally.

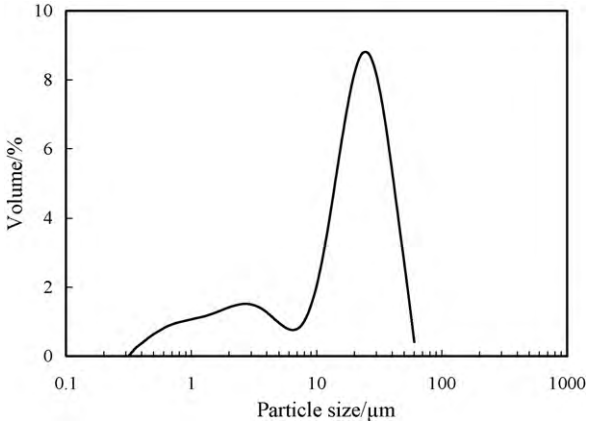

Fig. 1. Particle size distribution of alumina powders.

2.2. Characterization

The linear expansion rate of Al_2O_3/Al green bodies in sintering process is measured by thermal expansion instrument (DIL402C, Netzsch Instrument Co., Ltd. Germany). Apparent porosities of supports are measured by the Archimedes method with an immersion medium of water. The calculated formula is given as follows:

$$P = \frac{m_3 - m_1}{m_3 - m_2} \times 100\% \quad (1)$$

where P represents the apparent porosity of support, m_1 is the weight of dry support, m_2 is the weight of the saturated water support which suspended in water, m_3 is the weight of the saturated water support. Average pore size of the membrane support are measured by the gas bubble pressure method (GBP), which is performed following the American Society for Testing and Materials (ASTM) Publication (F316-80). The bending strength is tested by three point bending method. The fracture toughness values (K_{IC}) is determined using the single-edge-notched beam (SENB) technique [15]. Each support is notched precrack of ~2 mm long before testing fracture toughness. The fracture toughness is given by [16]

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

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

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

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_2O_3 support is observed by scanning electron microscopy (SEM, Quanta 200, FEI, The Netherlands). The phase composition of sintered supports is analysed by X-ray diffraction (XRD, D8 Advance, Bruker Instrument Co., Ltd. Germany).

The corrosion resistance of supports is also investigated according to the mass loss rate and the bending strength after corroded in nitric acid or sodium hydroxide solutions of 1 mol L^{-1} at 80 °C for 168 h. The mass loss percentage ($\%R$) is calculated via the following Eq. (4):

$$\%R = \left(1 - \frac{w}{w_0}\right) \times 100 \quad (4)$$

where w and w_0 are the dry weights of supports before and after corroded in corrosive liquid. The supports must be washed in advance to remove the residual substance before drying to get the corresponding weights.

3. Results and discussion

3.1. Influence of sintering temperature

The relationships between fracture toughness/bending strength of as-prepared supports and sintering temperatures are shown in Figs. 2 and 3, respectively. When the sintering temperatures increase from 800 °C to 1200 °C, the fracture toughness of various supports slowly decrease and the bending strength keep steady. When the sintering temperatures increase from 1200 °C to 1600 °C, the fracture toughness and the bending strength both increase significantly. Fig. 4 shows the linear expansion rate of Al_2O_3/Al green samples by adding 16 wt% Al powders in sintering process, which is measured in advance by thermal expansion instrument. According to the different expansion rates in the different temperature range, the expansion curve can be divided into four regions as shown in Fig. 4. When the sintering temperature is below 800 °C, a dramatic linear expansion of support is observed as shown in the region I. In this course, the Al phase is in molten state and does not begin to oxide [10,11]. The improvement of fracture toughness as-prepared supports sintered in this temperature range results from the Al ductile phase. When the sintering temperature is above 800 °C, the linear expansion becomes slightly. Liquid phase Al begins to oxidize into Al_2O_3. As other literature reported [17], the oxidation phenomenon only results from the surface of liquid phase Al in the initial stage of oxidation process. When the sintering temperature reaches above 1100 °C, the oxidation of the inner Al is found, which is proved by the distinct linear expansion comparison of the II and III regions. When the sintering temperature is up to 1400 °C, the complete oxidation of Al phase has finished, which is proved by XRD analysis as shown in Fig. 5.The various phase composition of support prepared at 800 °C, 1400 °C and

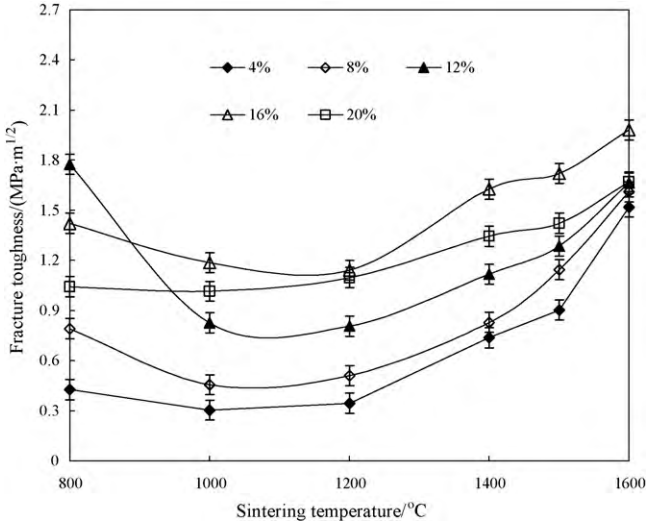

Fig. 2. Relationship between fracture toughness and sintering temperatures with different Al powders.

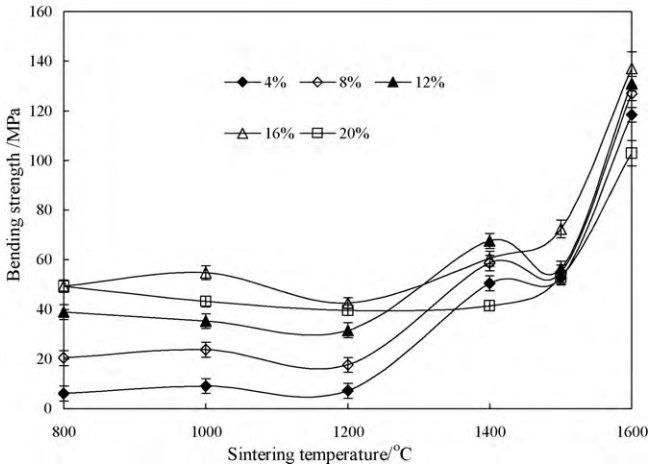

Fig. 3. Relationship between the bending strength and sintering temperatures with different Al powders.

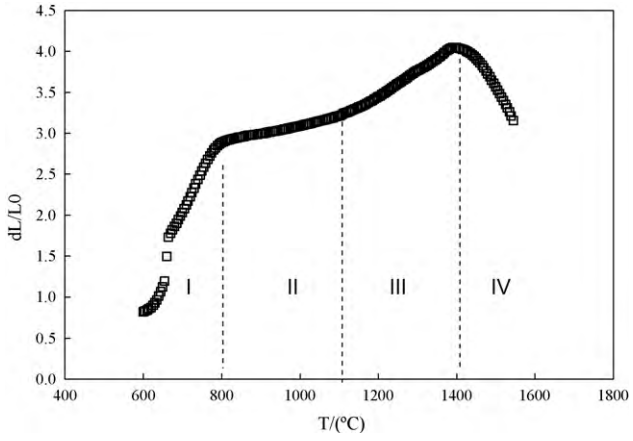

Fig. 4. The linear expansion of Al/Al_2O_3 with the increasing of sintering temperature.

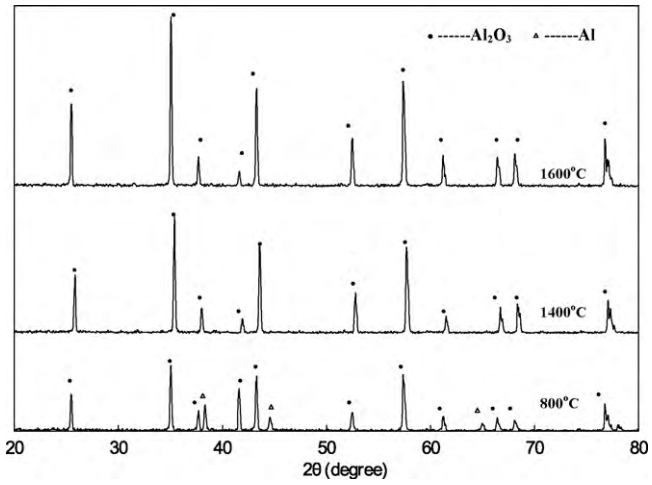

Fig. 5. X-ray diffraction patterns of Al_2O_3 supports at 1600 °C.

1600 °C are provided. When the sintering temperature is above 1400 °C, the continuous expansions of green samples quit. Because the total volume expansion is bigger than the total sintering shrinkage, the curve of linear change still shows some expansion which is shown in the region IV. During the sintering process, Al is oxidized into fine Al_2O_3 particles. The sintering shrinkage results from the accelerating sintering action of fine particles, which is beneficial to the improvement of mechanical properties especially for fracture toughness and bending strength as shown in Figs. 2 and 3.

In order to discuss the reaction mechanism of the processes, the reaction course can be divided into two procedures according to the Al phase reaction mechanism: the molten procedure and the oxidation procedure. When the temperature

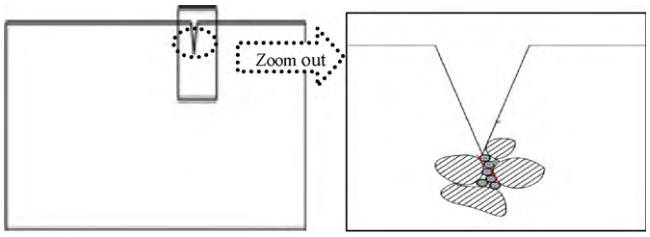

Fig. 6. Schematic representation of a long crack spread route in support.

is below 800 °C, the molten process of Al metal is the main procedure. The improvement of fracture toughness is ascribed to the uniform ductile metal phase [18]. In this procedure, certain of expansion occur when the Al powder turns into the molten Al liquid. However, the framework formed by coarse Al_2O_3 particles has no volume expansion to obtain more pores at such lower temperature. When Al content is 12 wt%, the Al liquid phase is enough to fill the porous body, and the maximum value of fracture toughness is improved to 1.8 MPa $m^{1/2}$. During the fracture process, when the dangerous cracks spread to the metal ligaments zone, the ductility phase of Al metal can absorb the high fracture energy by deformation to delay the fracture time [19,20]. But the bending strength is not improved because of the existence of plenty of Al phase in the support [21].

When the sintering temperature is above 800 °C, Al metal begins to oxide. More expansions occur because of the oxidation of Al powder, which results in more pores existence. The maximum values of fracture toughness and bending strength are observed when Al content is 16 wt%. Due to the uniformity distribution of Al phase, the distribution of fine Al_2O_3 particles oxidized from Al powders is also uniformity by

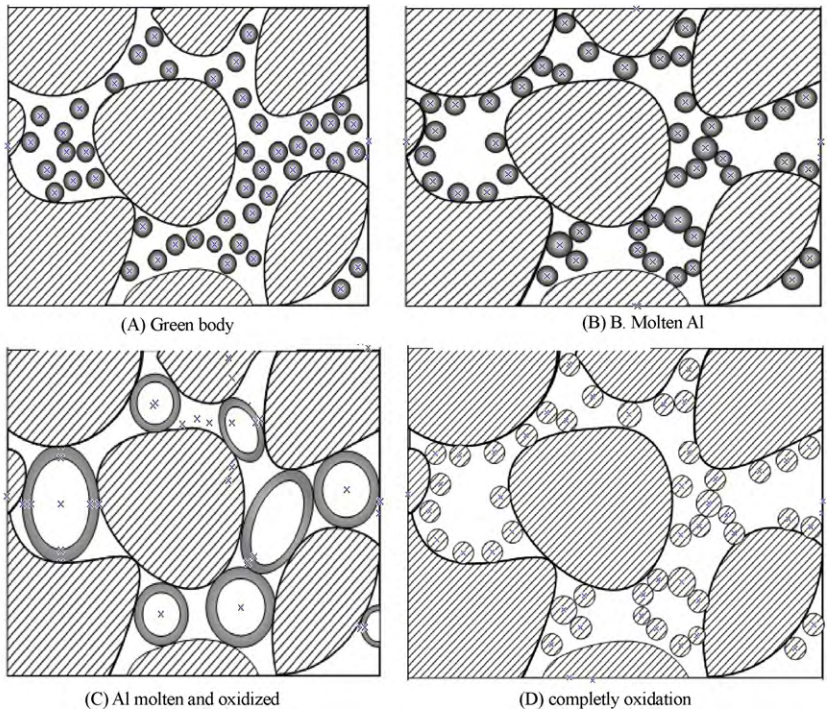

Fig. 7. The sketch of Al phase oxidation process in air.

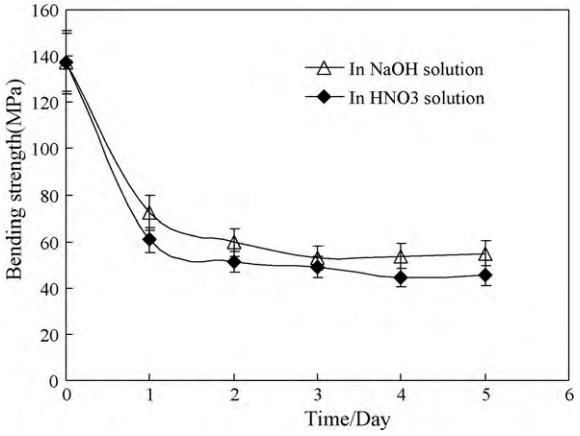

Fig. 8. Relationship between the bending strength and corrosion time.

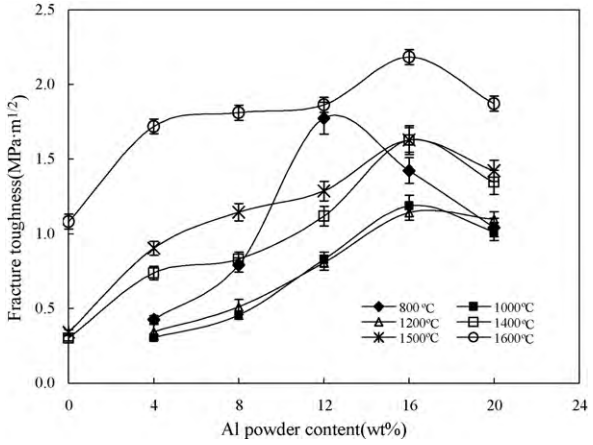

Fig. 10. Relationship between fracture toughness and Al content of supports sintered at different temperature.

in situ oxidization at high temperature. During fracture process, such fine particles can act as pinning action to make the cracks deviate and prolong the crack spread path as shown in Fig. 6, when there is an external force acted on the supports.

In fact, the melting procedure and the oxidation procedure of Al powder take place at the same procedure. When Al powder is molten into Al liquid phase, the surface of the molten Al liquid first begin to oxidize into solid Al_2O_3 thin layer. This layer can prevent the deep oxidation of the inner Al phase. With the increase in sintering temperature, the thin Al_2O_3 layer breaks and many cracks occurred because of the thermal volume expansion. Therefore, the inner Al liquid flows to the surface along the expansion cracks and oxidized again. The oxidation process is then prevented again by the new solid Al_2O_3 layer. Such reaction cycles occur till the complete oxidation of Al phase into Al_2O_3 fine particles with the increasing of sintering temperature [11,22]. Fig. 7 shows the sketch of Al phase oxidation processes in air.

As-prepared supports, the single Al_2O_3 phase composition is beneficial to the improvement of chemical resistance under harsh environment. Fig. 8 shows the relationship between the bending strength of support by adding 16 wt% Al powders at 1600 °C with the corrosion time. After the supports are corroded at 80 °C for 168 h in nitric acid or sodium hydroxide solutions of 1 mol L^{-1}, respectively, the bending strength still keeps at the level of ~40 MPa which is strong enough in industry application. And the mass loss percentage calculated by Eq (4) is lower than 1 wt% as show in Fig. 9. These parameters show that the macroporous support with high fracture toughness and high bending strength also has excellent chemical resistance.

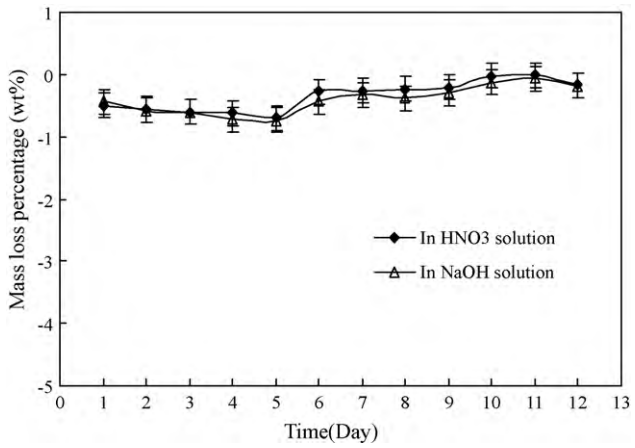

Fig. 9. Relationship between the weight loss percentage and corrosion time.

3.2. Influence of Al content

The relationships between fracture toughness & bending strength of supports and various Al content are shown in Fig. 10 and Fig. 11, respectively. It can be seen that the two mechanical properties both increase with the increasing of Al content. Sintered at 1600 °C, when Al content is 16 wt%, the maximum values of fracture toughness and bending strength of macroporous Al_2O_3 supports are 2.0 MPa $m^{1/2}$ and 137 MPa, respectively, which are 2.0 and 2.6 times than that of the supports without adding any additives prepared at the same sintering temperature of 1600 °C.

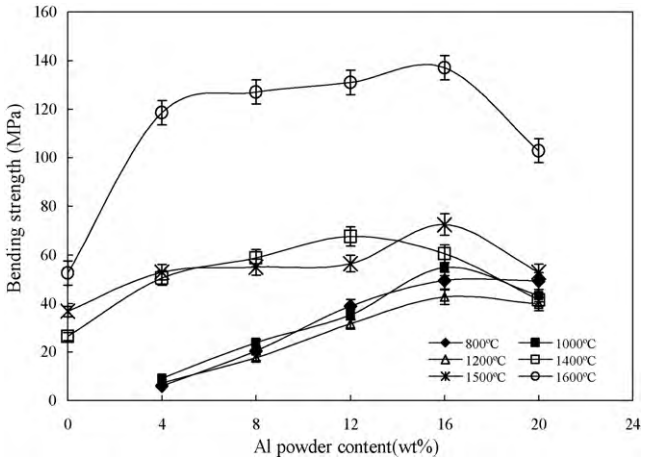

Fig. 11. Relationship between bending strength and Al content of supports sintered at different temperature. (a) Adding 0 wt% Al powder, (b) adding 4 wt% Al powder, (c) adding 8 wt% Al powder, (d) adding 12 wt% Al powder, (e) adding 16 wt% Al powder and (f) adding 20 wt% Al powder.

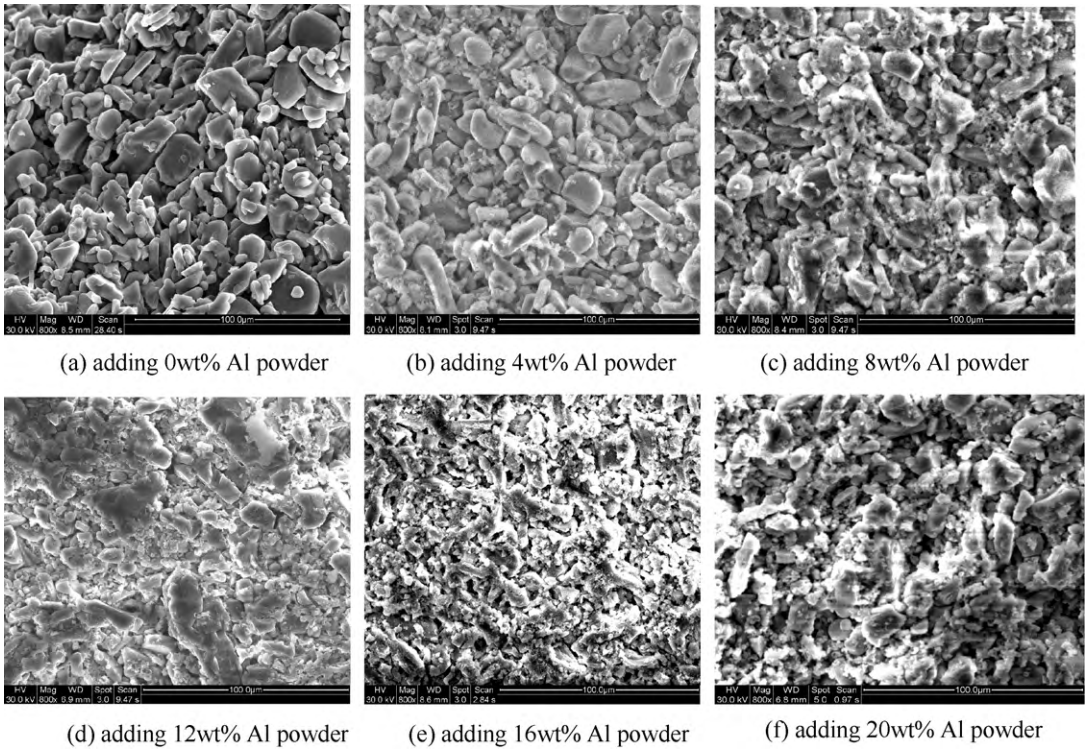

Fig. 12. SEM images of support sintered at 1600 °C with different Al content. (a) Bonding between coarse and fine particles and (b) bonding between coarse particles.

Fig. 12 shows the representative sections micrographs of the supports sintered at 1600 °C when Al content is 0 wt%, 4 wt%, 8 wt%, 12 wt%, 16 wt% and 20 wt%, respectively. With the increasing of Al content, the microstructure of various supports reveals densification, and then becomes porosity relatively. These are caused by the padding function of Al powder and oxidation reaction of Al powders during the whole process. And the particles of each support become fine with the increasing of Al content from 0 wt% to 12 wt%. When Al content increases from 12 wt% to 16 wt%, the grain growth of support is distinct because of the accelerating sintering action of fine Al_2O_3 particles.

When Al content is 16 wt%, fine Al_2O_3 particles oxidized from Al initial powder are relatively obvious. Fig. 13 is the corresponding section graph of supports by adding 16 wt% Al powders magnified by 6000×. Many fine α-Al_2O_3 grains (<1 μm) can act as an accelerating sintering agent to strengthen the bonding neck, which results in the increments of mechanical properties especially for fracture toughness and bending strength [23,24]. By SEM (as Fig. 12), such fine particles are quite enough to form a network between the coarse Al_2O_3 particles, which is also beneficial to the improvements of mechanical properties [10]. When Al content is 20 wt%, the degradations of mechanical properties are observed because of the strong RBAO reaction and excessive Al_2O_3 particles resulted from the excessive Al content [11,25] (Fig. 12(f)).

In the RBAO support sintered at 1600 °C by adding 16 wt% Al powders, the average pore size is (1.88 ± 0.06) μm determined by the gas bubble pressure method (GBP). When the trans-membrane pressure is 1 bar, the pure water flux (PWF)

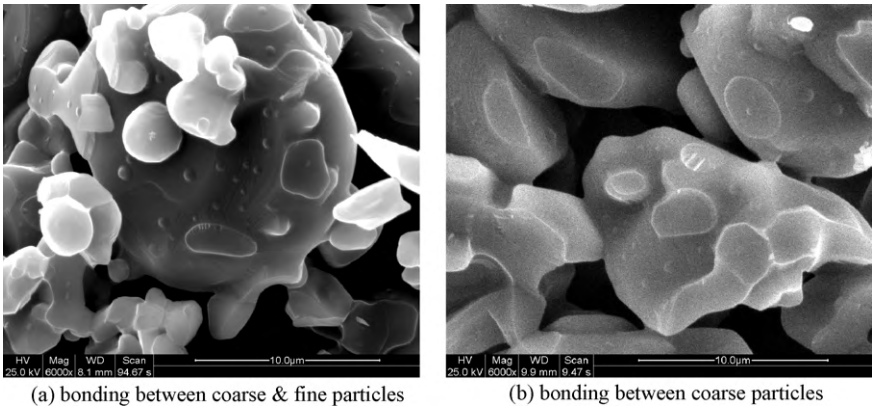

Fig. 13. Cross section of supports with 16 wt% Al content magnified by 6000×.

Table 1
Comparison of support properties before and after toughening.

Comparison items	Before	After
Material	Al_2O_3	Al_2O_3
Porosity (%)	34	30
Average pore size (μm)	1.94	1.82
Bending strength (MPa)	52	137
Fracture toughness (MPa $m^{1/2}$)	1.1	2.0
PWF (L m^{-2} h^{-1} bar^{-1})	6654	4042

is 4042 L m^{-2} h^{-1} at 20 °C. Table 1 lists the performance of supports before and after toughening.

4. Conclusion

In this study, RBAO method is adopted to prepare macroporous alumina supports with high mechanical properties and good chemical resistance. The influence of various sintering temperatures and Al content on mechanical properties of supports is investigated. The results show that Al powder plays an important role in the increments of mechanical properties of supports, especially in the improvement of fracture toughness and bending strength. The optimum values are obtained when Al content is 16 wt% for preparing the macroporous supports sintered at 1600 °C. The fracture toughness and the bending strength are 2.0 MPa $m^{1/2}$ and 137 MPa, respectively, which are 2.0 and 2.6 times than that of the supports without adding any additives prepared at the same temperature. The fine Al_2O_3 particles oxidized from Al phase form a network surrounding the coarse Al_2O_3 particles, which is beneficial to the improvements of mechanical properties for supports. In this investigation, the RBAO support also has a good chemical resistance under harsh environment.

Acknowledgements

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