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Corrosion resistance of ultra-high purity porous alumina ceramic support

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ABSTRACT

An ultra-high purity porous alumina ceramic support was prepared by boehmite-coated alumina powders at a relatively low temperature. Its corrosion resistance in 20 wt% H_2SO_4 and 10 wt% NaOH hot solutions for 2 to 8 h was investigated. After corrosion in H_2SO_4 solution for 8 h, the mass loss was only 0.55%, the flexural strength decreased by 9.85% and the open porosity increased from 41.14% to 47.25%. Meanwhile, the average pore diameter increased from 1.22 μm to 1.60 μm. While in NaOH solution for 8 h, the mass of the support and the flexural strength were diminished by 0.48% and 8.08%, the open porosity and the average pore size were increased to 46.48% and 1.49 μm. The permeability increases from 7.18×10^{-10} m^2 to 1.35×10^{-9} m^2 and 1.25×10^{-9} m^2, respectively, after acidic and alkaline corrosion for 8 h. The support shows an excellent corrosion resistance.

1. Introduction

Over the past few decades, ceramic membranes have been making rapid progress in applications such as bio-pharmaceuticals, food and beverage processing, environmental protection and water treatment. An increasing number of applications in very harsh environments need such a type of porous ceramic membrane with durable strength and high corrosion resistance [1–3]. High chemical durability enables ceramic membranes to have advantages over organic membranes in these domains. While the applications of ceramic membranes depend greatly on porous ceramic supports which provide the well-established asymmetric ceramic membranes with durable mechanical strength and chemical stability [4,5]. Thus, corrosion resistance of ceramic support plays an important role in the security and lifetime of the complete set of ceramic separation membrane system.

Previous attempts to prepare porous ceramic support with good corrosion resistance have already shown some promising results and there also exist some insufficiencies for subsequent promotion. Cordierite as a common choice material for ceramic support is alkali resistant but it has encountered the drawback of poor resistance to strong acid [6]. It was also reported that porous alumina support was successfully prepared at low temperatures with Kaolin clay and other certain additives as sintering subsidiary components [7,8]. These products are resistant only to strong acid rather than alkali due to the dissolution of silica-rich glassy phase and alkaline oxides. It can be seen that the impurities brought in by these sintering aids impact the corrosion resistance of the alumina ceramic supports greatly because the impurities are inclined to turn into glassy phases after calcination and the glassy phases generally have poor resistance to acid or alkali. Thus, utilizing high-purity raw materials is probably an effective way to prepare ceramic supports with excellent corrosion resistance. In order to improve the sintering character and chemical stability of ceramic support, rutile was usually utilized as a sintering aid [9]. The optimum resistance to corrosion was probably due to the improved microstructure and the increasing crystallinity in support materials and the resistance to alkali was better than that to acid because of the different chemical stabilities. [10]. On one hand, the corrosion resistance of alumina supports is affected enormously by impurities like sintering aids that would form glassy phases. On the other hand, the firing temperature will get too high if not any sintering aids are put to use. Therefore, optimization of the processing route and materials composition has become necessary.

In this work, boehmite-coated alumina powders have been used for preparation of ultra-high purity alumina support at 1580 °C with an open porosity of 41.14% and a flexural strength of 61.9 ± 0.9 MPa. The corrosion resistance of the supports in 20 wt% H_2SO_4 and 10 wt % NaOH hot aqueous solutions has been investigated. The mass loss, flexural strength, open porosity and pore size distribution after corrosion at 80 °C for 2 to 8 h were measured. The specific outcomes of this study can also be used for optimization investigation of high-quality ceramic support for membrane separation.

2. Experimental section

Ultra-high purity alumina supports were prepared from boehmite-coated alumina powders [11]. The porous alumina supports were

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ultrasonically cleaned in absolute ethanol for 10 min. After vacuum drying, the specimens were cut into rectangular bars with the sizes 3 mm × 4 mm × 36 mm and weighed, and then placed into 20 wt% H_2SO_4 and 10 wt% NaOH hot aqueous solutions (80 °C) for 2, 4, 6 and 8 h. After every corrosion experiment, the specimens were ultrasonically washed in deionized water for 10 min for 3 times and then vacuum dried at 105 °C until the mass was constant.

Chemical purity was ascertained by an X-Ray Fluorescence Spectrometer (WD-XRF, PANalytical Axios, Almelo, Netherlands). The permeability was tested on a Fully Automated Fluid and Gas Handling Systems (Convergence Inspector Poseidon, Netherlands). The open porosities of the samples were measured according to the Archimedes method (based on ASTM C 373-14) and the theoretical density of α-Al_2O_3 was taken as 4.03 g/cm^3. Mercury porosimetry (Micrometrics AutoPore9510, USA) was used to determine the average pore size and pore size distribution of the alumina supports. Three-point flexural strength measurements were performed with a mechanical testing machine (Instron5567, Instron, USA) at room temperature. The strength was taken from the average of six individual specimens.

3. Results and discussion

Fig. 1 shows the pore size distribution (A) and SEM morphology (B) of the prepared support without corrosion. It can be noted that huge amounts of weeny spots of crystal grains distribute uniformly on the surfaces of coarse alumina particles, and the pore size distribution is quite narrow. The properties of the prepared porous alumina support have been listed in Table 1. The permeability was measured at 27 °C and the viscosity of water was taken as 0.8545 mPa s.

The mass loss increases with corroding time, and the sample in acidic solution exhibits a larger mass loss for the same corroding time, as shown in Fig. 2a. The mass loss increases relatively rapidly in the first 2 h. This may be attributed to the prior dissolution of the possible amorphous alumina phase. However, even after corrosion for 8 h in acid media, the mass loss is only about 0.56%. Consequently, the dissolution of Al^{3+} in the bulk materials is negligible. Fig. 2b shows the flexural strength of the porous samples decreases gradually with corroding time. The average flexural strength degrades with corroding time almost linearly as the following equation:

$$\sigma = \sigma_0 - kt \quad (1)$$

where σ_0 is the original strength (MPa) and σ is the strength (MPa) after corroded for t hours. In alkaline solution, k=0.62; in acidic solution, k=0.74. As the extension of corroding time, no distinct microcracks or other great defects containing exfoliation of crystal grains can be observed in the microstructure of support (Fig. 3). Only some crystal grain boundaries are eroded slightly. Therefore, no obvious loss in flexural strength after corrosion takes place.

After acidic corrosion for 8 h, the average flexural strength of the support still remains 55.8 ± 0.7 MPa and its strength loss ratio is 9.85%. While in alkaline aqueous solution for 8 h, the strength loss ratio is only 8.08%. The strength durability of the supports in corrosive solutions is superior to that reported in previous literatures [6,7].

The open porosity increases with corroding time, and its growth rate in acidic solution is a little bit higher than in alkaline media (shown in Fig. 4a). When the samples had been corroded for 8 h in H_2SO_4 or NaOH aqueous solutions, their open porosity rates of the samples was increased from 41.14% to 47.25% (in acidic solution) and 46.48% (in alkaline solution) respectively, which leads to the strength reduction directly. Small changes also occur in the pore size. After corrosion for 8 h, the average pore diameter increases from 1.22 μm to 1.60 μm in H_2SO_4 and 1.49 μm in NaOH, and pore size distribution remains as narrow as before (Fig. 4b). The permeability of supports also aggrandizes after acidic and alkaline corrosion and the growth rate accelerates with corroding time (Fig. 4c), which is mainly because of the increase of open porosity and average pore size.

From the above results, it is demonstrated that the high-purity support has good corrosion resistance. The intensity of the grain boundary attack depends on the material purity, since impurities like SiO_2, CaO or MgO, which were prone to react with alkali or acid, have only a small solubility in α-Al_2O_3 and move to the grain boundaries during the sintering process where they segregate or form an amorphous phase. Accordingly, the high purity alumina generally shows the highest resistance against intergranular corrosion.

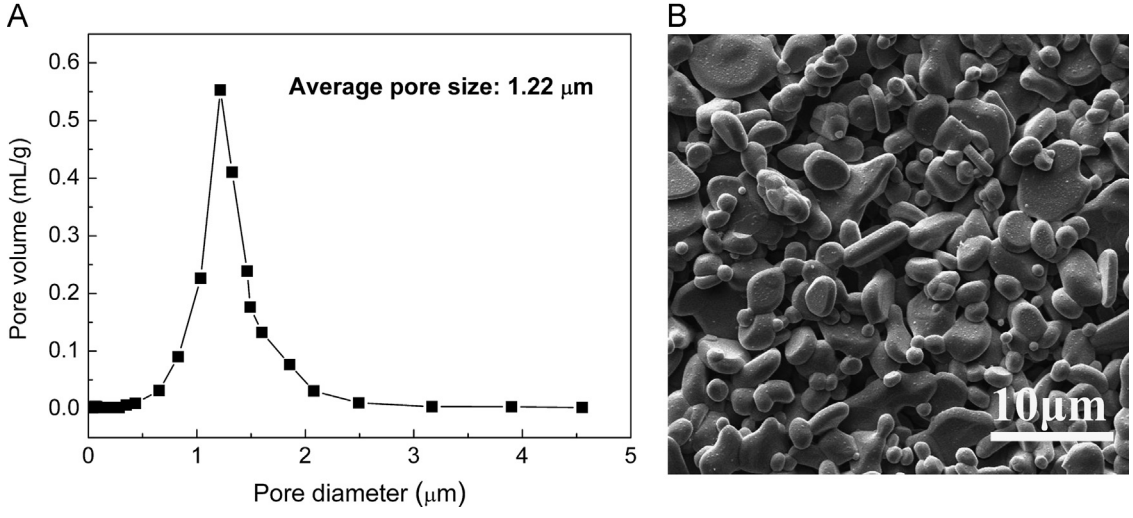

Fig. 1. (A) Pore size distribution and (B) SEM morphology of porous alumina support.

Table 1
Properties of the prepared porous alumina support.

Support type	Open porosity (%)	Bending strength (MPa)	Average pore size (μm)	BET surface area ($m^2 g^{-1}$)	Chemical purity (%)	Permeability ($\times 10^{-10}$ m^2)
Prepared support	41.14	61.9 ± 0.9	1.22	230	99.99	7.18