Research and Development of Ceramic Filtration Membrane

Minglu Deng.Rong Chen,Sirong Liu

Engineering College, Nanchang University of Technology, Jiangxi, China

ABSTRACT
Ceramic filter membrane plays an irreplaceable role in many fields because of its unique advantages. However, the complicated preparation process and high cost still limit the large scale application of ceramic filter membrane. Therefore, to improve the preparation process of ceramic filter membrane, optimize the membrane system structure is the ceramic filter membrane industry is facing major problems. In this paper, the structure, separation principle, preparation technology and application of ceramic filter membrane are introduced.
KEYWORDS: Ceramic filter membrane; Structure; separation principle; Preparation technology

1. Introduction

Ceramic filter membrane is a kind of porous membrane mainly prepared by inorganic materials such as Al_2O_3, ZrO_2, TiO_2 and SiO_2. It has high separation efficiency, acid and alkali resistance, organic solvent, antimicrobial, high temperature resistance, high mechanical strength and high regeneration performance. Good, simple separation process, easy operation and maintenance, long service life and many other advantages [1, 2]. In the environmental protection [3-5], sewage treatment [6,7], gas purification [8], food processing [9,10], membrane catalysis [11-13], bio-medicine [14, 15]], Membrane bioreactor [17], resource recycling [18], fine chemical [19] and other fields have been widely used, can be used in the process of separation, clarification, purification, concentration, sterilization, in addition to Salt and so on. Compared with the same organic film, although the cost of ceramic filter membrane is relatively high, but because of the unique advantages in the treatment of chemical-containing fluids, gases and strong acid, alkali or high temperature for cleaning and regeneration of the occasion, Ceramic filter membrane is difficult to replace.

2. Ceramic filter membrane research status

Ceramic filter membrane research and application began in the 1940s [20]. In the Second World War, Europe and the United States and other countries in order to obtain nuclear fissures needed raw materials uranium 235, must be from the natural uranium ore in the form of UF6 extracted. However, the natural uranium element is usually composed of two common isotopes 235U and 238U, the former can be fission but less than 0.7%, which accounted for 99.3% but not fission. As UF6 is gasifiable, 235U is separated and enriched from natural uranium elements to 3% by using a gas diffusion separation technique using a porous ceramic filter membrane with an average pore size of about 6 to 40 nm. This is the first time in the history of human use of porous ceramic filter membrane to achieve industrial scale gas mixture separation example, known as the Manhattan atomic bomb program (Manhattan Project). As a result of the need for military secrecy at that time, the research and production of ceramic filters were carried out during this period [21].

In the late 1950s and early 1960s, ceramic membrane technology for isotope separation was gradually adopted and reported, and became the basis of the current commercial ceramic filter membrane. In the mid-1960s, the United States Oak Ridge National Laboratory successfully invented the TiO2-C, ZrO2 composite dynamic film, after the technology by France and other countries of the ceramic filter film production company gradually commercialized.

In the 1970s, several European countries, such as France, Italy, Belgium and Spain, decided to build a gas diffusion and separation plant dedicated to the development of nuclear power plants in France, a move that triggered a ceramic filter membrane Separation technology has received new attention. However, it has quickly been discovered that the development of ceramic filter membrane separation technology alone is the development of nuclear power plant applications that are unsustainable and require the development of applications in other areas [22].

United States U.S. Filter is currently the world's largest inorganic ceramic filter membrane and equipment suppliers, the products provided by the 0.01μm dust removal rate of 99.9999%. France's TAMI and Germany's ATECH is high market share of European ceramic filter membrane manufacturers, its ceramic microfiltration membrane and ceramic ultrafiltration membrane treatment of surface water preparation of drinking water has been used in Europe for many years. Japan's NGK, Cemet, TOTO company developed inorganic film equipment in the industrial process to obtain a successful application. Recently, North American Ceramics Technology has successfully completed the assembly of its new dual-disc grinder, which enables the company to produce ultra-flat, ultra-complete ceramic filter membrane technology has reached a leading level [23].

In the 1980s, ceramic filtration membrane separation technology, as a precision filtration and separation technology, began to shift to civilian areas and was used to replace traditional separation techniques such as evaporation, centrifugation, and frame-frame filtration [24]. During the ceramic filter membrane products come out in large numbers, in the water treatment, beverage, dairy and other industrial areas have been partially replaced by organic polymer film. As the ceramic filter membrane has excellent material properties and no phase change process characteristics, its development in the civilian field is very fast, through the cooperation between the government and the company, has successfully developed a variety of commercial ceramic filter membrane, which ceramic micro Membrane and ultrafiltration membrane gradually into the industrial applications, and has been rapid development in the field of membrane separation technology occupies an important position. In the mid-1980s, the ceramic filter membrane preparation technology made a new breakthrough, when Twente University of Burggraf and other researchers using sol-gel (Sol-Gel) technology successfully prepared with multi-layer asymmetric microporous ceramic filter membrane , The diameter of this membrane can reach 3 nm below, reaching the level of gas separation, a strong competitor of organic polymer film. The emergence of sol-gel technology has pushed the preparation of ceramic filter membranes to a new height [25].

In the 1990s, the new ceramic filter membrane material and its application engineering were accelerated. During this period, the research stage of gas separation and ceramic filter membrane separator-reactor composite was carried out. Among them, the successful development of porous carbon molecular sieve, metal and its alloy film and microporous mesoporous composite membrane indicates that the separation technology of ceramic filter membrane has entered the function, compound and miniaturization. In the 21st century, ceramic filter membrane and a variety of application industry integration, and other separation, purification, reaction process, membrane materials and membrane application process of cross-cutting research has become the main trend of the development of ceramic filter membrane.

China's ceramic filter membrane research started late [26]. During the period of the Ninth Five-Year Plan period, under the strong support of the national key scientific and technological projects, the national '863' plan and the National Natural Science Foundation of China, Nanjing University of Technology set up a Membrane Science and Technology Research Institute to complete the low temperature sintering multi-channel porous ceramic filter Film, to achieve a multi-channel ceramic microfiltration membrane of the industrialization of large-scale production, and the completion of the corresponding production base, the initial formation of a new ceramic filter membrane industry. Jiangsu Jiuwu Hi-Tech Co., Ltd. has completed three production lines with an annual output of 10,000 m2 for the production of ceramic filter membrane, the main production of TiO2, Al2O3, ZrO2 ceramic filter membrane products, membrane pore size in the 0.05 ~ 1 μm between. Guangdong King Kong New Materials Co., Ltd. has a leading domestic level of ceramic filter membrane fine filter products pore size of 1 ~ 3 μm, widely used in petrochemical, food engineering, bio-pharmaceutical and cannot use organic film under high temperature gas separation, membrane Catalytic reaction and so on. Nanjing Jiu Si High Technology Co., Ltd.'s main business is the production of ceramic filter membrane and membrane engineering for the complete set of equipment, built with an annual output of 5,000 m2 production line for the production of ceramic ultrafiltration membrane, the main products are: ceramic filter membrane, Pervaporation membrane, ceramic filter membrane experimental equipment, ceramic filter membrane industrial equipment and membrane components. South China University of Science and Technology Huangxiao Rong and other use of molten die centrifugal method of forming a pore size along the radial gradient of the asymmetric alumina film tube, the filter layer and the control layer between the natural transition, the control layer pore size distribution is narrow, Not less than its smallest pore size of the particles [27]. August 2004, by the Beijing MaiSheng Pu Technology Co., Ltd. and Shandong Lu Kang Pharmaceutical Co., Ltd. jointly developed ceramic filter membrane filtration system for the separation and purification of a certain success, which not only optimize the production of such antibiotics, And the recovery rate of antibiotics increased by 15%, which is China's first ceramic filter membrane technology used in antibiotic production.

Although China has made a series of important breakthroughs in the research of ceramic filter membrane, there are still great differences compared with countries such as Europe, America and Japan. Especially in some high-end applications, China still needs to rely on imports. Ultrafiltration membrane can be used for uranium enrichment and other fields. Some high-tech ceramic filter membrane is prohibited to China's exports (such as the length of more than 1 m ceramic ultrafiltration membrane products, etc.).

3. Separation Principles and Structure Classification of Ceramic Filter Membrane

3.1. Separation principle of ceramic filter membrane

The membrane separation process is generally a selective permeation membrane as a separation medium. When there is some kind of driving force on both sides of the membrane (such as concentration difference, pressure difference, potential difference, etc.), the raw material side components selectively through the membrane layer, so as to achieve the purpose of separation, concentration and purification [28].

According to the material through the separation of the driving force when the film separation process can be divided into two categories: one is through the use of external energy, material from low to high flow, such as common microfiltration, ultrafiltration and nanofiltration is through Sieving principle, in the external driving force (such as pressure) under the action of retained liquid - liquid, gas - liquid and solid - liquid mixture in the particle size is greater than a certain critical value of the particles, thus achieving separation, concentration and purification purposes; The water is easily introduced into the membrane, and the inorganic salts (such as Na +, K +, K +, K +, K +, K +, K +, K +, K +, K +, K +, K + Cl-, and others) are difficult to enter, and the salt in the salt solution is removed by the reverse osmosis membrane separation. Table 1 lists some of the common driving forces for membrane process separation [29].

Table 1. The main membrane separation process under different driving forces

Driving Force	Membrane Separation Process
Pressure difference	Microfiltration MF, Ultrafiltration UF, Nanofiltration NF
Electrochemical Potential	Electrodialysis ED
Concentration Difference	Dialysis DD, Control Release CR
Partial Pressure Difference / Concentration Difference	Gas separation GS, Pervaporation PVAP
Concentration Difference / pH Difference	Emulsion Liquid Film (Facilitates Delivery) ELM (ET)
Concentration Difference Plus Chemical Reaction	Membrane Sensor MS

The separation performance of the ceramic filter membrane for the mixture is generally characterized by two parameters: permeability and selectivity. Permeability is the molar flow rate or volume flow through the membrane, taking into account factors such as the thickness and the driving force of the film. In general, the thickness of the film is unknown, typically by the permeation flux instead of the permeation rate of the ceramic filter membrane. The permeation flux, i.e., the unit pressure, and the unit time through the molar amount or volume of the membrane per unit area in m3m-2Pa-1 s-1 or L m-2 bar-1 h-1 or mol m-2 Pa-1 S-1; the selectivity is used to characterize the ability of the ceramic filter membrane to separate the two specified components, generally expressed as the ratio of the independent permeation rates of the two components [30].

3.2. Structure and classification of ceramic filter membrane

In general, ceramic filters can be described as a barrier or fine sieve with selective permeation. Permeability coefficient and separation coefficient is the most important performance index of ceramic filter membrane [31]. For porous ceramic filters, they are generally subject to thickness, pore size and surface porosity control and control; and for dense ceramic membrane, the principle of penetration and separation is more complex [32]. In the porous ceramic filter membrane, their application and separation mechanism with the ceramic filter membrane pore size corresponds to, as shown in Table 2.

Table 2. Ceramic Filter Membrane Classification

Types（IUPAC Classification [37]）	Pore Size（nm）	Mechanism	Application
Macroporous	>50	Sieve	Microfiltration, Ultrafiltration
Mesopore	2~50	Knudsen Diffusion	Ultrafiltration, Nanofiltration, Gas separation
Microporous	<2	Microporous Diffusion	Gas Separation
Dense	—	Diffusion	Gas Separation, Reaction

The ceramic filter membrane is usually composed of several layers of one or more different ceramic materials, generally composed of macroporous support, mesoporous interlayer and microporous (or dense) top layer, as shown in Figure 1, the bottom The support provides mechanical strength while the intermediate layer bridges the support with the top sheet (the separation behavior actually occurs in the top sheet) and acts as a transition. Common materials for the preparation of ceramic filter membrane are Al2O3, TiO2, ZrO2, SiO2, or the combination of these materials. Figure 2 shows the pore characteristics of a four-layer alumina film. It can be seen from the figure that the aperture of the top separation layer, the intermediate transition layer and the bottom support are 6 nm (mesoporous), 0.2 to 0.7 μm and 10 μm, respectively. Vos and Verweij reported a more complex multilayer film consisting of a layer of alpha-alumina macroporous support, two layers of gamma-alumina mesoporous intermediate transition layer and a layer of microporous silicon oxide layer [33]. As shown in the transmission electron micrograph of Fig. 3, it is seen that a very

thin layer of silicon oxide has a thickness of only about 30 nm and a pore size of only 5A. The TEM micrograph further indicates that the silicon oxide layer is deposited on the top of the gamma-Al2O3 layer. The boundary between silicon oxide and γ-Al2O3 is clearly visible. From the figure, the boundary width of the first layer γ-Al2O3 and the second layer γ-Al2O3 is about 250 nm.

1. 改进过的分离层 (致密或<2 nm)
2. 分离层(2~50 nm)
3. 中间过渡层(50~1000 nm)
4. 多孔支撑体(1~15 μm)
1 + 2 + 3+ 4 纳滤或气体分离膜
2 + 3 + 4 超滤膜
3 + 4 微滤膜

Figure 1. Schematic diagram of the principle of asymmetric composite film
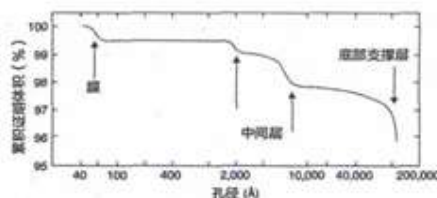

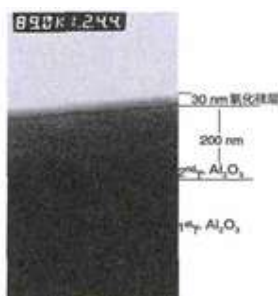**Figure 2.** Pore size distribution of four-layer alumina film / support composites [35]

Figure 3. TEM micrographs of Si (400) film γ-Al2O3 layer and partial cross section of silicon oxide layer [43]

The above-mentioned ceramic filter membrane can only be realized by a multi-step, as shown in Fig. 1, first to prepare a support to provide mechanical strength to the film, followed by the application of one or more intermediate transition layers on the support, a layer of microporous separation layer. Each step contains a high-temperature sintering process, making the ceramic filter membrane preparation costs are relatively high. If multiple steps can be combined into one step, the production time and cost of the ceramic filter membrane can be greatly reduced. Li et al. There have demonstrated that the layered ceramic filter membrane can be combined into one step by phase conversion [34]. They used this process to prepare an asymmetric ceramic filter membrane, the SEM micro-morphology shown in Figure 4. It can be seen that a thin layer of skin is integrated on the porous support of the same ceramic material.

Most of the ceramic filter membrane products on the market are made in a disc-like or tubular configuration, and they are usually assembled into flat and frame membrane modules using discs or flakes, or they are assembled into tubular membrane modules using membrane tubes. In order to improve the specific surface area, that is, the unit volume of the membrane unit has a greater separation area, people have developed an alumina multi-channel integral film unit, as shown in Figure 5 [35], these integral film unit can be integrated as a module The Hsieh's research results show that for a single tube, the specific surface area is about $30 \sim 250$ m^2/m^3; for multi-channel monolithic membrane unit, the specific surface area of about $130 \sim 400$ m^2/m^3; and for honeycomb multi-channel As a whole membrane unit, the specific surface area reached 800 m^2/m^3 [36]. CeraMem has also developed a similar module, as shown in Figure 6.
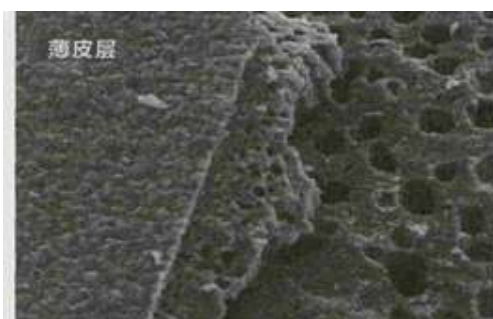
Figure 4. SEM micrograph of layered ceramic filter [44]
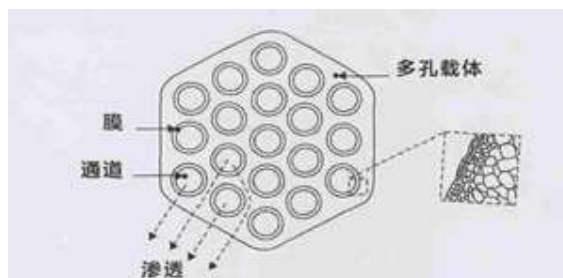
Figure 5. Section of the bulk multi-channel membrane unit [45]
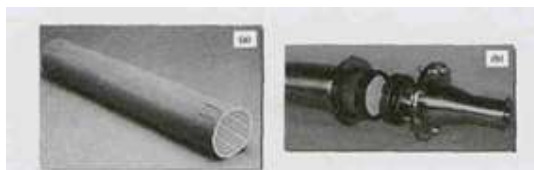
Figure 6. Multi-channel ceramic module: (a) membrane unit diameter 142 mm, length 864 mm, membrane area 10.7 m2; (b) with a simple compression seal design of the membrane unit installed in the stainless steel shell (CeraMem)

Similarly, the frame-and-frame ceramic module can be obtained by assembling a plurality of diaphragm cells (made of ceramic sheets). In this way, a disk or sheet film of high bulk density can also be obtained, the principle of which is shown in Fig. It can be seen that the feed fluid flows into the porous spacer sandwiched between the two sheets of thin film. The fluid passes through the membrane and flows out of the system through the septum compartment compartment, which provides space for fluid through the membrane pool. A detailed description of this frame-and-frame ceramic system can be found in other literature [38].

The hollow fiber ceramic filter membrane module shown in Fig. 8 has a high bulk density compared to a specific surface area of about 30 to 500 m^2/m^3 of a frame ceramic filter membrane or a tubular ceramic filter membrane, and a specific surface area of a hollow fiber ceramic filter membrane module Can be as high as 130 ~ 400 m^2/m^3 or so. The biggest difficulty in preparing a hollow fiber ceramic filter membrane is to overcome the inherent physical brittleness of the ceramic material. According to the specific application requirements, hollow fiber ceramic filter membrane can be made porous or dense form. Hollow fiber ceramic filter membrane has been widely studied and applied in gas separation, membrane reactor, solvent recovery and so on [39-42].

4. Membrane separation process

The membrane process has become a unit of operation that is universally recognized in the various industrial processes. These membrane processes are driven by pressure diff erence, concentration diff erence or electric fi eld, and can be distinguished according to the type of driving force, the size of the molecule, or the type of operation. Common membrane processes are reverse osmosis, microfiltration, pervaporation, ultrafiltration, gas separation, dialysis, nanofi ltration, electrodialysis, membrane contactors and membrane reactors. This chapter focuses on reverse Osmosis, nanofi ltration, ultrafi ltration and microfi ltration Make a brief introduction.

4.1. Reverse osmosis and nanofiltration

The reverse osmosis (RO) and nanofi ltration (NF) processes allow only certain types of substances (solvents) to pass selectively, while other species such as solutes are partially or completely retained. Solute separation and solvent permeation are characteristics of the membrane, which depend on the structure of the membrane material and the fi lm. The main diff erence between reverse osmosis and nanofi ltration is that reverse osmosis can block all solutes, including monovalent ions, while nanofi ltration membranes can only block polyvalent ions and have no selectivity for monovalent ions.

As shown in Fig. 9, permeation is a natural phenomenon in which water passes from one end of the membrane low solute concentration across the membrane to the other end of the high solute concentration (Fig. 9a) until the osmotic equilibrium is reached (Fig. 9b). In order to induce water backflow, a mechanical pressure is applied at one end of the high solute concentration (Fig. 9c) to provide a reverse pressure diff erence greater than the equilibrium pressure diff erence, thus allowing the separation of pure water from the solution. This phenomenon is called reverse osmosis. Applications of reverse osmosis processes include: desalination, wastewater treatment and ultrapure water preparation.

Reverse osmosis is a perfect membrane technology that is used to handle a wide variety of water. Currently on the market have been commercial only high polymer Polymer reverse osmosis/nanofiltration membrane. High-molecular polymer reverse osmosis/nanofiltration membrane in the application process encountered the main problems are: (1) due to the fluid properties of the feed fluid caused by excessive pollution; (2) resistance to chlorine and other oxidants Poor; (3) the corresponding waste in the process of extensive pretreatment; (4) the lack of the ideal surface charge to reduce the potential of pollutants. In these respects, the ceramic filter membrane is more advantageous than the commercially available polymer film. In reverse osmosis and Nanofiltration applications, the most important is the excellent resistance to chlorine, antioxidant, radiation resistance, solvent resistance and high thermal stability, high chemical stability and longer reliable life. However, high cost, low assembly density and poor permeability select ability make commercially available ceramic filter membrane technology economically difficult to maintain for reverse osmosis/nanofiltration applications. In recent years, the preparation of ceramic nanofiltration membranes has been studied and reported by titanium dioxide [46-49], zirconium oxide [50-52], silica-zirconia [53,54], hafnium dioxide [55,56] and γ-alumina [5]. Most of these nanofiltration membranes are prepared by sol-gel method to separate non-aqueous solvents, wherein the metal oxide layer overlying the mesoporous ceramic support determines the final pore size. The pore size of the membrane is controlled by selecting the appropriate colloidal solution at the final coating stage. It is reported that the molecular weight of these membranes is between 200 and 1000 g/mol.

4.2. Ultrafiltration and Microfiltration

Ultrafiltration is a membrane process in which colloidal particles or large molecular weight solutes are separated from the solvent using a porous membrane. In the ultrafiltration process, the mechanism of solvent separation from solute/colloid is similar to that of reverse osmosis/nanofiltration. Therefore, the interception of the solute depends on the pore size and pore size distribution of the membrane, and the interaction between the membrane surface and the solvent/solute. All solvent transfer is mainly affected by

The membrane and the control of the mass transfer resistance at the boundary of the solution. Therefore, even low concentrations of residual substances can also have a profound impact on solvent penetration.

Although there is no precise definition of the boundaries between ultrafiltration and microfiltration, as shown in Figure 10, as a membrane process, the microfiltration is similar to the conventional filtration process, separating the discrete particles from the solution. It can be seen that there is no clear dividing line between coarse filtration and microfiltration, about a few microns to 0.1 microns. Microfiltration is used to separate small insoluble particles, bacteria and yeast cells from liquid culture and water. Traditional depth filters, which are usually composed of fiber matrices, are also used to perform similar tasks, but the mechanism of separation is that the separated material is trapped in the fiber and adsorbed on its surface. There is no clear 'hole' for depth filtration, but the voids between the fibers are larger than the smallest residual particles. Therefore, the intercept rate of the depth filter is a statistical function. On the other hand, the microfiltration membrane has a clear pore size and is separated based on the sieving effect. Because the membrane pore size is large enough, the solvent is usually passed through the membrane pores through convection. The flow rate of the solvent flowing through the membrane is proportional to the differential pressure of the transmembrane and, if the membrane pore is assumed to be cylindrical, can be described by the Hagen-Poiseuille equation.

There are many polymers used to prepare ultrafiltration membranes and microfiltration membranes, such as cellulose acetate, Nitrocellulose, Polyacrylonitrile, Polyamide, Polyethersulfone, Polyimide, Polysulfone, polyvinyl alcohol, Vinyl fluoride, and so on. Ceramic filter membranes have also been developed for ultrafiltration and microfiltration. Since the upper limit of the temperature of the polymer film is much lower than 200 ° C, ceramic filters are developed to meet practical application requirements in order to produce films with better chemical resistance and high temperature resistance. In addition, most of the above-mentioned polymers cannot be present in a solvent such as benzene and toluene for a long time. Materials for the preparation of ceramic ultrafiltration membranes and microfiltration membranes are mainly alumina, titanium oxide and zirconium oxide, because these materials can withstand high temperatures and harsh chemical environments. Ceramic ultrafiltration membrane and microfiltration membrane is mainly used in dairy products, food, pharmaceutical, biological, paint, paper and water industry. A detailed discussion of the application of ceramic filters in these areas can be found in other literature [57].

Ultrafiltration and microfiltration operation in two ways: (1) dead end filter; (2) cross-flow filter. As shown in Fig. 11, dead-end filtration is only applicable to the treatment of very low solids suspensions, while cross-flow filtration is suitable for high concentrations because the deposits on the membrane surface are washed away by parallel flow of the membrane.

5. Ceramic filter membrane preparation method

Conventional ceramic filter membranes (multilayer films) are typically formed by film coating on a film support by dip coating, sol-gel, CVD or EVD processes, and are accompanied by repeated calcination. The hollow fiber ceramic membrane is characterized by the preparation of the support and the filter layer of the integrated molding firing, as

shown in Figure 12. This method involves a three-step process: (1) preparation of spinning suspensions; (2) spinning of ceramic hollow fibers; (3) sintering. The detailed process of the three steps is as follows: (1) the characteristics of the spinning suspension, including particle and particle accumulation, particle dispersion and rheology of the suspension (first step); (2) phase transformation mechanism and it's The relationship between the asymmetry and the pore structure of the matrix (the second step); and (3) the sintering process, ie, the evolution / elimination of calcination, pyrolysis and surface porosity. In this chapter, the preparation methods are discussed respectively, and the preparation of Al2O3, TiO2 and various perovskite hollow fiber ceramic membranes is briefly introduced.

5.1. Sol-gel method

Sol-gel method was first used by Leenaars et al. To develop ceramic ultrafiltration membranes[58]. Sol-gel method is one of the most important processes for preparing ceramic filter membrane. The advantage is that the pore size of the membrane can be controlled arbitrarily, especially for small holes. As shown in Figure 13, there are two main routes to prepare a sol-gel film:

(1) Colloidal route, metal salt and water mixed to form a sol, coated on the membrane support, thus forming a colloidal gel.

(2) A polymer route in which the organometallic precursor is mixed with an organic solvent to form a sol and then coated on the film support to form a polymer gel.

Sol is a colloidal solution of dense oxide particles, such as Al2O3, SiO2, TiO2 or ZrO2. Leenaars et al. developed a γ-Al2O3 film with a pore size of 4 to 10 nm from Boehmite sol [59]. Since the apertures of these membranes are in the ultrafiltration range, they are used for the separation of colloidal particles from large molecular weight solutes or are used as membrane supports to develop films with smaller pore sizes.

For gas separation based on the molecular sieve effect, a ceramic filter membrane with a pore size of less than 1 nm must be used. In this case, the γ-Al2O3 film prepared from the above sol can be used as a support, and a molecular sieve film is prepared on the support by a polymer sol route. It should be noted that in the polymer sol route, the pore size of the resulting film is determined by the degree of branching of the inorganic polymer, as shown in Fig. It can be seen that the low degree of branching leads to smaller pores. The SiO2 polymer sols containing low-branching clusters [60] have been prepared using acidic hydrolysis of the corresponding silicon alkoxides, which exhibit high selectivity for gas separation.

Because the sol size of the sol is very small and is prepared by the hydrolysis and coagulation of their corresponding Alkoxides, the local charge of the metal in the Alkoxide affects the hydrolysis behavior of the Alkoxide. The local charges of transition metals such as Ti or Zr carried in their alkoxides are higher than those contained in Si in Orthosilicate. The hydrolysis rate of transition metal Alkoxides is much faster than that of Silanolates. In addition, the characteristics of R ligand in the Alkoxide, the degree of oligomerization of the initial Alkoxide, the possibility of coordination of the metal coordination in the hydrolysis process, and the pH value all affect the hydrolysis behavior. The sol also undergoes gelation during the drying process. After the heat treatment, a ceramic filter film was prepared.

5.2. Impregnated coating method

Fig. 15 is a schematic view of the process of impregnating the coating film. The most critical factor in the coating process is the viscosity and coating speed or time of the particulate suspension. When the substrate is exposed to an atmosphere with a relative humidity of less than 100%, the drying process is carried out simultaneously with the dip coating. In a multi-step process, the first layer of the impregnated film is first calcined and then repeated, impregnated, dried and calcined for a complete cycle. For example, if an alumina film having an average pore size of 100 nm is to be obtained, it can be prepared by a suspension of submicron alumina powder having an average particle size of 500 nm [61].

5.3. Chemical Vapor Deposition

Chemical vapor deposition is a process of modifying the surface properties of a film by depositing a layer of the same or different compound on the surface of the material by a chemical reaction occurring between the components surrounded by the gaseous medium under certain temperature conditions. Figure 16 shows a CVD system comprising a system for measuring the reaction gas and a carrier gas mixture, a heating reaction chamber and an exhaust gas management system. The gas mixture (typically from hydrogen, nitrogen or argon, and reactive gases such as metal halides and hydrocarbons) is fed to a reaction chamber heated to the target temperature. Over the past few decades, various types of CVD methods have been developed. These methods include medium temperature CVD, plasma assisted CVD, and laser CVD. However, all CVD systems require a mechanism to handle the chemical reaction product. These products contain a variety of reactive and potentially hazardous ingredients and particulates that must be eliminated before the gas is discharged into the atmosphere. In addition, since most of the CVD process is carried

out at below atmospheric pressure, it is necessary to prevent the pumping device from being eroded by hot corrosive gases. In one aspect, the reaction between the various components takes place in the gas phase on the hot substrate and a solid layer is deposited on the surface of the substrate. On the other hand, the surface film may also be deposited by the reaction between the surface of the substrate and one or more gas phase components. One example is the formation of a layer of nickel-aluminum compound film on the surface of nickel which is achieved by the reaction between aluminum Trichloride at high temperatures and hydrogen from the vapor in the nickel surface. Therefore, such a film may be referred to as a conversion film.

5.4. Preparation method of hollow fiber ceramic filter membrane

At present, polymer hollow fiber membranes are widely used in many aspects, including filtration, desalination, gas separation, pervaporation and biochemical reactions. However, it is almost impossible to find such a membrane configuration in ceramic filter applications, possibly due to a lack of viable methods for preparing ceramic filters with such hollow fiber geometries. The development of a method for preparing a hollow fiber ceramic filter membrane is clearly interesting because the hollow fiber ceramic filter membrane will demonstrate its advantages in strong bases, strong acids and high temperatures, so that existing polymer Hollow fiber membrane. A typical example is distillation, in this process compared to random distillation or distillation [62], hollow fiber membrane can play a better separation effect, and the yield is higher. The above-mentioned ceramic filter membrane preparation method is not suitable for the preparation of hollow fiber ceramic filter membrane. Although many attempts have been made to produce silica glass hollow fiber membranes for gas separation [63], these films are too fragile and cannot be used in large-scale industrial applications. In recent years, Tan et al. [64] and Liu et al. [65] have successfully produced alumina and perovskite hollow fiber ceramic filters by phase transformation, which consists of three steps: (1) Liquid preparation; (2) spinning of ceramic hollow fiber precursors; (3) sintering. The preparation of the ceramic filter membrane by the phase inversion process is usually carried out simultaneously with the support of the membrane, and many factors can affect the performance of the final film.

The preparation of the spinning suspension comprises the following steps: (1) mixing the solvent with the dispersant; (2) adding the pretreated particles to dissolve and dispersing; (3) adding the polymer binder and the plasticizer ; (4) degassing the suspension before spinning the membrane precursor. Among them, the peptizing effect is a very important step because the soft agglomerates in the spinning suspension affect the pore size and permeability coefficient of the final membrane [66].

The main constituents of the spinning suspensions used to prepare the hollow fiber ceramic filter membranes are ceramic powders, additives and solvents. In the choice of ceramic powder, to consider the important factors are particle size and its distribution, as well as the shape of particles. These factors affect the porosity, pore size and distribution of the final membrane [67]. Inhibitors / dispersants, binders, plasticizers, Defoamers, pore-forming agents, antistatic agents, chelating agents, fungicides and other additives give the necessary properties of the spinning suspension. In the process of preparing the hollow fiber ceramic filter membrane by the phase inversion process, it is required that the organic binder is not only reversible, but also must be burned during the calcination process, leaving the ashes and tar. The amount of organic binder should be as little as possible, but cannot affect the conversion performance of the suspension. The solvent used must be able to dissolve the additives and binders and have a higher exchange rate with the non-solvent (coagulant). The effluent rate of the solvent and the rate of influx of the coagulant will affect the cross-sectional structure of the membrane precursor and even the final membrane product [68].

The preparation of the spinning suspension is still in the development stage and the general rules so far are considered to be favorable for the preparation of spinning suspensions:

(1) The content of the dispersant must be maintained to ensure the stability of the suspension;

(2) The solvent content must be kept to a minimum to maintain the uniformity of the suspension;

(3) The ratio between the organic component and the ceramic powder must be as low as possible;

(4) The ratio of plasticizer to binder must be adjusted so that the membrane precursor is flexible and flexible.

The spinning of the ceramic hollow fiber precursor can be carried out in the spinning apparatus as shown in Fig. The hollow fiber precursor is spun through the spinneret, and there is a tube inserted into the orifice of the spinneret. As shown in the illustration in Figure 17, the outer and inner diaphragms of the nozzle are 3 mm and 1.2 Mm. The extrusion rate of the spinning suspension is controlled by a nitrogen pressure (or gear pump) and a control valve. Non-solvent (usually water) is used as an internal and external coagulant at room temperature. The spinneret is arranged so that the primary fiber precursor can be extruded vertically into the coagulation bath. After the phase is converted and coagulated, the fiber precursor is introduced into a washing bath and then dried.

6. Conclusions

The future development of the field of ceramic filter membrane will focus on the following aspects: (1) to further improve the separation of ceramic filter membrane material separation accuracy and separation stability, so that in the field of liquid separation to achieve continuous high efficiency filter, (2) the development of high-temperature and high porosity of the high-temperature ceramic separation membrane material, so that the efficient use of resources and environmental protection and other fields to achieve high-temperature gas-solid separation process of long-term Stable operation; (3) to achieve low-cost production of ceramic filter membrane, combined with the construction of the practical application of the membrane material design and preparation methods, so as to ceramic filter membrane in the application process to provide bottlenecks to solve the problem; Preparation of membrane materials that can resist strong acid and alkali corrosion, improve the separation stability of ceramic filter membrane, and expand the use range of ceramic filter membrane in industry. To play the advantages of ceramic filter membrane, so that it can contribute to social and economic development, we must address: (1) large-capacity ceramic filter membrane support strength and acid and alkali resistance; (2) Ceramic filter membrane resistance is too large, it is difficult to achieve high throughput and high selectivity and other issues.

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