Development of Ceramics Technologies

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Abstract

Through the application of ceramic-related technologies, we have been developing a variety of products such as gapless Zinc Oxide (ZnO) surge arresters, Nitrogen Oxides (NO_x) decomposition equipment, fuel cells, and zeolite membranes. We recently commercialized Ceramic Flat-sheet Membranes (CFMs) with physical strength and chemical stability. The CFM has a bilayer structure composed of a base layer having both physical strength and a membrane layer that functions to separate solid components from water. The CFM has different characteristics of a base layer and membrane layer. The manufacturing processes for such CFMs were developed by fully utilizing the control technologies of porous characteristic and sintering property. Due to our manufacturing expertise in producing such high-quality CFMs, we established a system of assuring both filtration performance and a stable supply of ceramic flat-sheet membranes for water treatment plants. Such water treatment plants are considered vital social infrastructures.

1 Preface

To meet the various demands of our customers and solve societal challenges, we proposed ceramic products with multiple functions. This paper introduces a history of our ceramic-related technologies. We also introduce our recent ceramics technologies that mostly focus on the Ceramic Flat-sheet Membranes (CFMs). We developed the CFMs to solve current water processing challenges.

2 History of Our Ceramics Technologies

Aligning with the Paris Agreement adopted by the COP21 in 2015, Japan set a target of 26% reduction of greenhouse gas emissions since 2013. This called for a strong review of our society's current fossil fuel consumption society. This invited world-wide interest on environmentally-friendly "green" technologies. By controlling the composition and structure during manufacturing, ceramics can provide a variety of functions such as energy conversions or catalysts. We succeeded in developing Zinc Oxide (ZnO) elements for gapless ZnO surge arresters in the 1980s. Since, we have been producing many kinds of ceramic products by applying our ceramic-related technologies.

Fig. 1 shows our ceramic technology development and major business and products. In the 1990s, due to air pollution, there was growing interest in solving environmental problems in the world. Amid such concern, we started the development of a catalyst for exhaust gas denitrification equipment

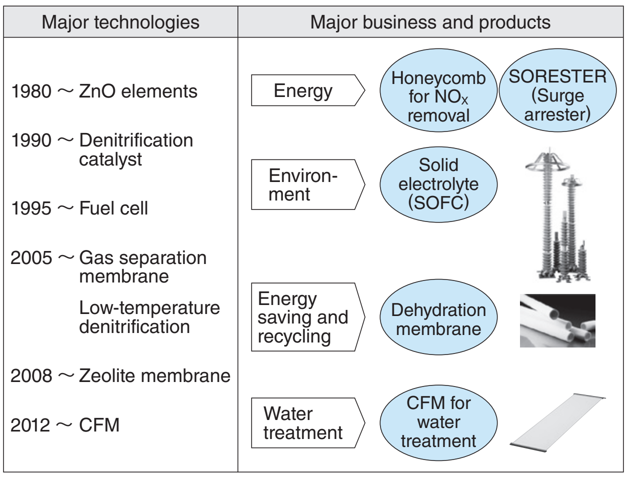

Fig. 1 Our Ceramic Technology Development and Major Business and Products

We developed ceramic products for various applications and built up base technologies along the way.

that is used to remove Nitrogen Oxides (NO_x) emitted from power generating diesel engines. In 2000, we succeeded in the development of a honeycomb type catalyst. We commercialized exhaust gas denitrification equipment with excellent efficiency.

In 1994, we began to develop fuel cells which received industrial attention as a “zero emission” technology. Aiming for a target market of medium- and large-scale power generation market areas for commercial and industrial fields, we embarked on the development of a Solid Oxide Fuel Cell (SOFC) early in this development. SOFC was known to have the highest power conversion efficiency among many other types of fuel cells. While a conventional Zirconium dioxide (ZrO_2) based material requires a high operating temperature of more than 1000℃, we applied a Cerium dioxide (CeO_2) based material to the electrolyte because it can works at a lower temperature. Our SOFC can work under the temperature of 800℃ and it can offer energy-saving and acceptable material options on key components.

In 1999, based on the aforementioned developments, we worked on a technology to separate carbon dioxide from sludge digestive gas and bio-gases to realize fuel refinement and storage. We developed a ceramic type gas separation membrane to concentrate methane gas. In 2003, we conducted verification field tests at a sewage water treatment plant and pig farm for our power generating system. This system combined a newly developed gas separator, a micro gas turbine, and a compact fuel cell unit.

Since 2003, we also developed a Methane To Benzene (MTB) catalyst technology to generate benzene. Benzene is a raw material to produce plastics. In this fundamental research program, we realized the continuous operation for more than 1000 hours at a high yield of more than 10%. At that time, the oil industry was concerned about future depletion of our planet’s fossil fuels, so our research program received attention from the oil industry and many inquiries from major overseas oil companies were forthcoming.

In 2008, by drawing on our zeolite material technology, we developed a zeolite separation membrane which dehydrates a used organic solvent and condenses it to a reusable level. Zeolite is a crystal consisting mainly of Aluminum (Al), Silicon (Si), Sodium (Na), and Oxygen (O). It is possible to produce pores of 0.2 to 1 nm by adjusting the component ratio and crystal structure. These pores can be utilized adequately to separate any different molecular size organic solvent from water, which enables high-concentration condensation and is energy saving. In 2011, we established mass production technology for Zeolite membrane.

In developing our ceramic products, we drew on our Long-standing ceramic production expertise relating to molding, and sintering, and also utilized our appropriate analytical technologies for the ceramics. As a result, CFMs for water treatment were developed and its mass production facility was established in Meiden Nagoya Works, Aichi Prefecture in 2012. CFMs are classified as a Micro Filtration (MF) for water treatment. It has nominal pore size of 0.1 μm. Since ceramics have a high physical strength and is chemically stable, it is applicable to wastewater from petrochemical systems which contains many kinds of mixed chemicals. Our CFMs can be used for processing wastewater from cutting and grinding processes which contain a lot of hard solids.

Our CFMs have high endurance and durability against chemicals and less deterioration, which offers a long operation life. These CFM products are currently used in a variety of fields such as public utility drinking water, sewage treatment plants, and industrial wastewater treatment plants in many countries.

3 Basics of Ceramics

3.1 What is Ceramics?

In general, materials are classified into metals, plastics, and ceramics. Ceramics is a compound formed by covalent bonding or ionic bonding of metallic and nonmetallic elements. It comes in a large variety. Typical ceramic materials are, for example, Aluminum Oxide (Al_2O_3: alumina), ZrO_2, Silicon Nitride (Si_3N_4), and Silicon Carbide (SiC). These materials are applied to a variety of industrial fields, for example, structural ceramic body, and electronic ceramics possessing functions of insulation or energy conversion. Even a similar type of ceramics can have a different function according to its application purpose by adding a small amount of an element and controlling its microstructure. Our gapless ZnO surge arrester is an example of this application utilizing semiconductor characteristics of the ZnO material.

Further, ceramics can be categorized into a dense and porous body. The dense body has excellent mechanical strength and is therefore used as a structural body or an abrasion resistant material. The porous body, however, has many pores inside the ceramics and its strength is inferior to that of the dense body. Despite that, it has functional features such as a light mass, thermal insulation, acoustic absorption, and adsorption. Our CFM is provided with a filtering function to remove solid components in water. It is done by controlling the pore size of porous alumina in the production process.

3.2 Production of Ceramics

The ceramics manufacturing processes generally comprises of four phases: raw material preparation by grinding and mixing, molding to make up a product shape, sintering to harden molds at a high temperature, and post-processing by cutting and polishing. **Fig. 2** shows a flow diagram of manufacturing processes for general ceramics. Raw material preparation is a process to formulate grain size of raw materials, particle size distribution, and components. This process greatly affects material characteristics and quality of a product. The next molding process is selected in conjunction with the product shape and application. There are several methods of molding ceramics like pressure molding, injection molding, extrusion molding, and so on. A pottery wheel to produce tableware is a kind of ceramics forming system. Molded bodies are put in a sintering kiln. These are sintered at a high temperature close to the melting point of the raw material. Our CFMs are also manufactured through the aforementioned processes. In order to realize both mass production and product quality, these processes are made based on our various technical expertise.

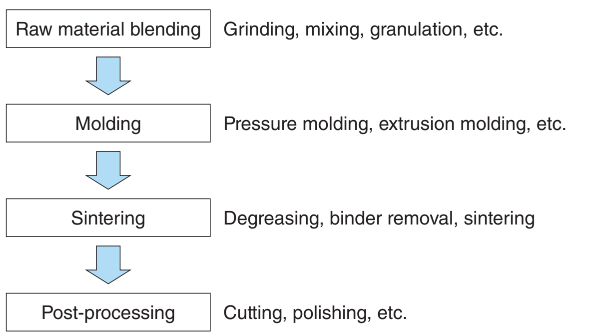

Fig. 2 **Flow Diagram of Manufacturing Processes for General Ceramics**

Ceramics is generally manufactured through multiple stages of processes.

4 Manufacturing and Control Techniques of CFMs

4.1 Factors Required for CFMs

Fig. 3 shows an external appearance of our CFM and **Table 1** shows its specifications. This ceramic membrane is composed of three sections: the ceramic section, the resin section for water stoppage and water collection, and the joint section to connect the two sections. The ceramic section is a bilayer structure consisting of the base layer having enough physical strength and the membrane layer to separate solid components from water. A module containing multiple CFMs is submerged in sewage water to obtain filtered water by using a suction pump. **Fig. 4** shows a cross-sectional image of a CFM by scanning electron microscope. Alumina is the major component of both the base and membrane layers. Using multiple types of raw materials, a pored flat plate structure is formed to the shape of the product and solidified in the sintering process to make up a CFM with high physical strength.

Generally, any membranes used for water treatment function to separate solid components in water. Consequently, as a result of filtering operation, the membrane surface and pore insides inevi-

Fig. 3 **External Appearance of our CFM**

An external appearance of our CFM is shown.

Table 1 **Specifications of the CFM**

Specifications of the CFM are shown.

Item	Specifications
Membrane type	MF, flat-sheet membrane
Raw material	Alumina
Nominal pore size	0.1 μm
External dimensions	W281 × H1046 × T12 mm
Mass (Dry)	1.8 kg
Membrane area	0.5 m^2

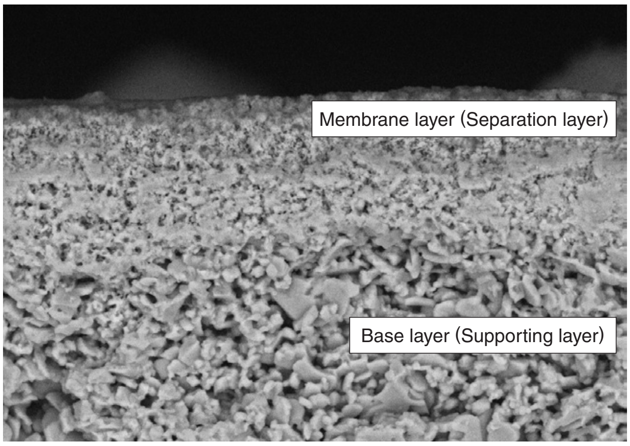

Fig. 4 **Cross-Sectional Image of a CFM by Scanning Electron Microscope**

The CFM has a bilayer structure that is composed of a base layer (lower part) with physical strength and a membrane layer for separating solids in water.

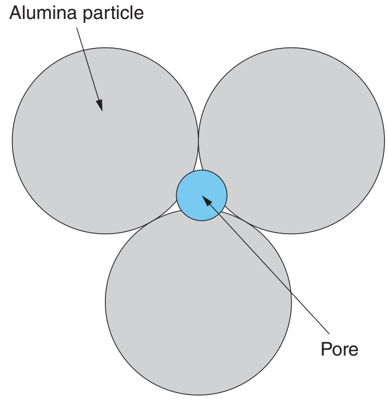

Fig. 5 **Image of Ceramic Pores**

The pore size of ceramics refers to a cubic clearance among constituent particles. The CFM is designed so that ceramic pores can remove turbidity substance of 0.1 μm in size.

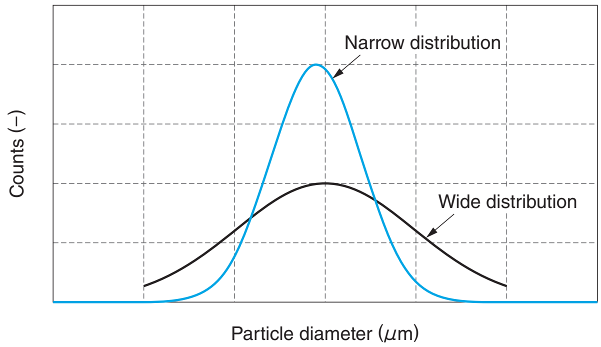

Fig. 6 **Particle Distribution of Ceramic Raw Materials**

The pore size of ceramics depends on a cubic clearance among constituent particles. The CFM is designed so that ceramic pores can remove turbidity substance of 0.1 μm in size.

tably give rise to clogging in flow paths. The velocity of clogging is greatly influenced by the conditions of raw water and filtration flux. It is also changed by the membrane type and material. To obtain a favorable membrane that has minimal clogging velocity during operation, it is important to achieve an efficient pore design and production control on the porous structure. When a membrane is used in a drinking water treatment plant, any breakages of membrane immediately leads to facility shutdown and/or water supply stop, and there will have a negative impact on social infrastructures. For this reason, it is necessary to secure the robustness of the membrane while the membrane secures superb multi-porous property. Especially in large-scale water treatment facilities, tens of thousands of ceramic membranes are generally used. Accordingly, as a membrane supplier, it is necessary to have the capability of mass production of such a high-quality product. As described, manufacturing processes for CFMs are required to assure both mass production capability and production control in making micro-sized porous structures. Such control defines membrane performance characteristics.

4.2 Pore Distribution Control

Fig. 5 shows an image of ceramic pores. The membrane material is designed to make the solid separation function of the CFM with a porous structure with fine pores. Each fine pore is designed to have a diameter of 0.1 μm. The fine pore mentioned here means a cubic clearance among particles that constitute a membrane material. Since the size of a clearance geometrically formed by particles is proportionate to the grain diameter, it is essential to control the diameter of raw material for the control of the fine pore size. According to the purpose of the application, raw material powder for ceramics is manufactured and distributed in a variety of sizes by synthesizing, grinding and classifying, etc.

Fig. 6 shows the particle distribution of ceramic raw materials. The size of raw material powder is evaluated by statistical distribution. In many cases, a typical value of grain diameter is defined by a median value, a center figure of grains lined up in the order from smaller to larger. Even though the median diameters are the same as each other, there are many cases in which the particle distribution is asymmetric, or the width is wider. Accordingly, the sizes of fine pores depend on the individual raw materials with certain distribution. CFMs are made

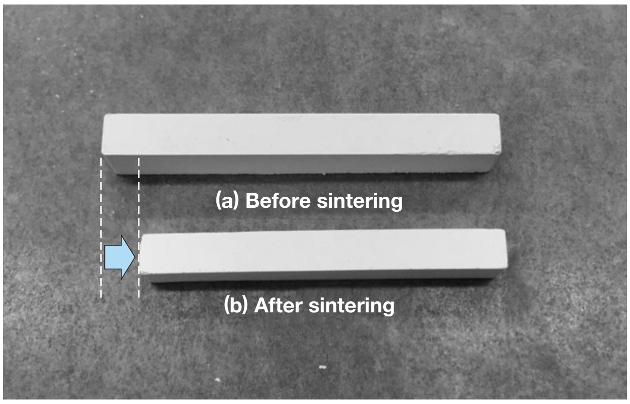

Fig. 7 **Size Change in Ceramics before and after Sintering**

Ceramic size differs in two stages: (a) before sintering (b) after sintering.

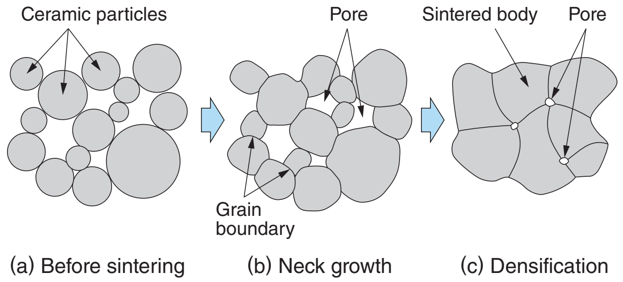

Fig. 8 **Change in Ceramic Microstructure under Rising Temperature Condition**

Along with the rise of sintering temperature, respective particles for composing ceramics before sintering (a) are densified (b) through the process of neck growth.

from such raw material powder to make high precision filtration.

4.3 Sintering Property Control

Fig. 7 shows a size change in ceramics before and after sintering. The most important manufacturing process for a ceramic product is the sintering process. Ceramics changes its size after sintering not only the appearance, but also in microstructure.

Fig. 8 shows a change in ceramic microstructure under rising temperature conditions. The changes occur in chronological order: (a) respective neighboring ceramic particles approach to the melting point, (b) particles then make bonds with each other (neck growth) in order to relieve free energy on the particle surface, and (c) when the temperature rises further, the particles become completely one (densification).

In this process, the volume of the void among particles decrease and ceramics shrink and densify.

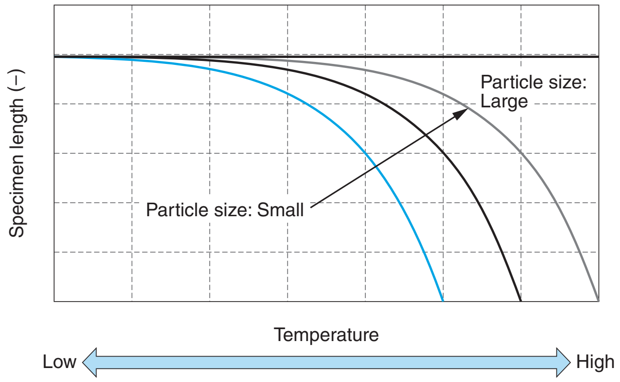

Fig. 9 **Thermal Shrinkage Curves of Ceramic Raw Materials**

Sinterability of ceramic particles depends on particle size. The curves show the shrinkage rapidly begins at certain temperature depending on particle sizes.

In the sintering process, the particle diameter of raw material is also an important factor. Fig. 9 shows the thermal shrinkage curves of ceramic raw materials observed when the temperature gradually increases on raw materials with various particle diameters. It shows that a raw material with finer grain size tends to start shrinking and densification at a lower temperature. For this reason, temperature control is important during the sintering of the ceramic material.

4.4 Sintering Program Design

In the sintering process, the ceramic products are gradually heated from a low to high temperature. This is to prevent product cracking by the combined effects of (1) product expansion due to rapid temperature rise and (2) shrinkage during sintering.

In some cases of molding, a polymer binder may be added in order to improve moldability and shape retainability in the molding process. In such a case, it is necessary to burn off such components during low temperature process stage. The sintering temperature control program is required to be suitable for both sintering of ceramics and removal of binder additives.

Fig. 10 shows an example of the sintering program for ceramic products. The burn-off temperature for the removal of binder additives is maintained at 300 to 800℃ for a long time and then a high temperature is maintained to promote densification again. This temperature controlled program is designed according to the sintering characteristics of the ceramics itself, and the type and content of the binders. A strong two-layer structure of our

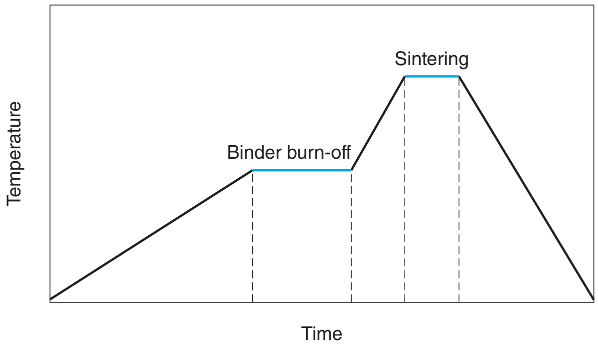

Fig. 10 Sintering Program for Ceramic Products

The sintering program for ceramics is composed of two-stage processes: one for burning off binders at a low temperature and the other for sintering at the highest temperature.

CFMs is obtained by sintering in a state where a base material and a membrane material having different characteristics coexist. In order to realize this, it is necessary to set up the sintering program that is suitable for two kinds of ceramics. Optimal sintering programs are designed based on our technical expertise relating to particle size of ceramic raw material, impurities, mixing ratio of binder and sintering additive components as described in foregoing sections.

5 Postscript

Ceramics are rich in variety and are regarded as an excellent material that can be versatile with many different processes. The characteristics of ceramics can be greatly affected not only by the component and state of raw materials but also by molding and sintering conditions. We are working hard on the R&D programs of our ceramic products to produce and supply much higher quality ceramic products.

Going forward, we will make the best use of our ceramic technologies to solve water processing and energy issues.