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# *JPRS Report*

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HIGH TEMPERATURE MATERIALS

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# SCIENCE & TECHNOLOGY
# JAPAN

## HIGH TEMPERATURE MATERIALS

906C7538 Tokyo DAI 21 KAI KO ON ZAIRYO GIJUTSU KOSHUKAI in Japanese Feb 90 pp 1-42

[Selected papers from the 21st Study Session on High Temperature Materials Technology held 22-23 Feb 90 in Tokyo, sponsored by the Ceramic Society of Japan]

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## Net-Shape Forming Technology

906C7538A Tokyo DAI 21 KAI KO ON ZAIRYO GIJUTSU KOSHUKAI in Japanese Feb 90 pp 85-90

[Article by Hiroaki Nishio, Akira Kato, and Ken Kawashima, NKK Central Laboratory]

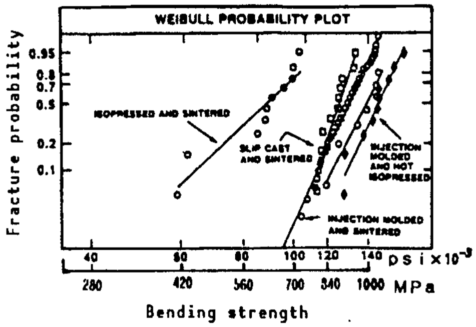
[Text] **1. Introduction**

Injection molding has attracted attention in the production of structural ceramic parts for its high productivity and capability to form complicated shapes by near-net and net-shape formings. It is viewed as one of the major forming technologies. Figure 1 shows the bending strength of a silicon nitride sintered material prepared by four different routes plotted on a Weibull chart.[1] It is known in case of CIP plus sintering in the drawing that the strength is on the low side. With an average strength 710 MPa and Weibull coefficient 9, the dispersion is great. In contrast, increase in strength and decrease in dispersion are recognized in the slip cast plus sintering and the injection molded plus sintering cases. In particular, the best results of average strength 1,000 MPa and Weibull coefficient 20 have been obtained in injection molded plus HIP. As seen here, the injection-molding method has the potential to prepare superior materials. However, this is a sample, and many problems exist in actual development.

### 2. Present Status and Topics of Injection Molding Method

### 2.1 Size Restriction

S. Wada[2] has shown the molding methods applied for parts with various sizes and complications (Figure 2). As seen in the drawing, there is an area in which the combination of size (especially thickness) and complexity fit well in conventional ceramics. However, it seems that many turbine parts do not respond well to these molding methods. The injection molding method, which has been put to practical use in the turbocharger rotor and precombustion chamber, has not succeeded for molding thick, large products with complicated shapes, such as combustors. The development of new molding methods to fill this gap are expected.



Weibull probability plot of bending strength for silicon nitrides prepared by various methods

| | Average strength (MPa) | Weibull coefficient (–) |
|---|---|---|
| CIP plus sintering | 710 | 9 |
| Slip casting plus sintering | 850 | 20 |
| Injection molding plus sintering | 910 | 14 |
| Injection molding plus HIP | 1000 | 20 |

Figure 1. Bending Strength of Silicon Nitrides Prepared Under Various Methods[1]

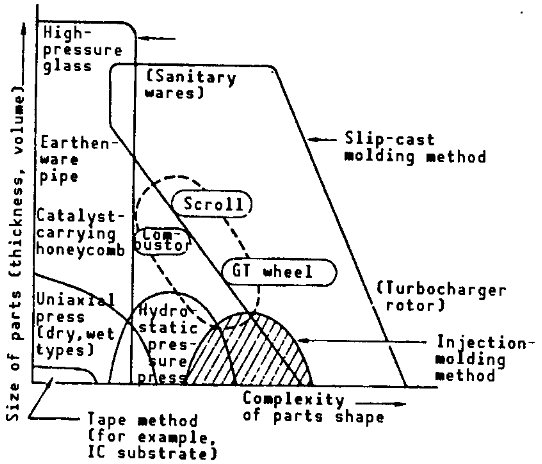


Figure 2. Various Forming Methods of Ceramics and Relationship Between Complexity and Size of Parts[2]

### 2.2 Material Powder Restriction

Degreasing of the injection compact is a risky process in which cracks are easily generated. Securing compact strength has been made by adopting a material powder with a wide particle size distribution for riding across this.[3] This restriction is heavy. The inconvenience that the material powder of the imido thermal composition method, for example, which shows the best mechanical characteristics in compacts of silicon nitride, is not applicable[4] in injection molding because the particle size distribution is small.

## 2.3 Defect Generation Within Compacts

The reliability of a large sectional area (> 12.7 mm) product like the gas turbine rotor is difficult now.[5] One of the reasons for this is because the evasion of flow-mark generation at forming is difficult. An ordinary injection-molding compound shows a Bingham or pseudoplastic flow,[6] and it has a form-maintaining property. Therefore, a large or small jetting generates within the cavity, and a flow mark is left on the compact. Jetting is harmful to compact strength.[7] When jetting occurs from a gate perpendicular to the end face of the square, bar-shaped cavity, the compound reaches the other end of the cavity, bends and piles up, goes back and forth, and fills up the cavity (Figure 3(a) [not reproduced]).[7] This method has been solved (Figure 3(b) [not reproduced]) by enlarging the gate and conducting jetting so that it intersects with the minimum distance direction of the square bar.[7] Ohnsorg, et al.,[8] conducted injection molding of a radial gas turbine rotor and recognized the generation of a flow mark in the blade section. They adopted the measure of enlarging the gate, but a surface defect still remained in the back face of the blade. Therefore, the gate was moved from the conventional nose and to the shaft end on the opposite side. As a result, as seen in the short shot of Figure 4 [not reproduced], the flow mark had moved to the nose part (right drawing), where only low stress was applied in the injection from the shaft end. This was in contrast to the flow mark generating on the blade section (left drawing) in the injection from the nose end, and the problem was tentatively avoided. However, this problem will not be solved unless the flow characteristic of the compound is changed.

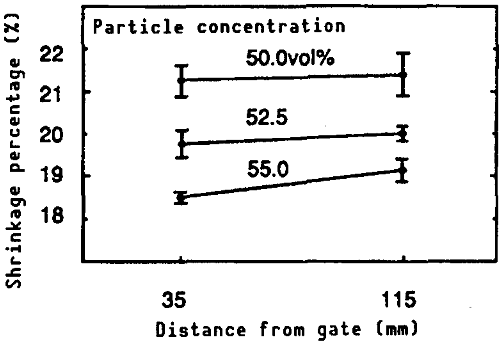


Figure 5. Change of Burning Shrinkage Percentage by Distance From Gate[9]

Sink marks, cracks, and pores are generated by solidification and shrinkage after injection.[7] This problem will be reduced by raising particle concentration and reducing solidification and shrinkage. On the other hand, it has been pointed out that the transfer of pressure maintenance becomes insufficient when the particle concentration is high. The burning shrinkage percentage becomes greater as the distance from the gate increases (Figure 5).[9] Moreover, when the binder melts in the degreasing process, residual stress is released at forming and hairline cracks appear.[10] The solution to these problems is injection pressure. Residual stress can be lowered by reducing injection pressure. This results in changing the flow characteristic of the compound.

Bandyopadhyay, et al.,[11] have recognized cracks along the surface contour in the cross section of a rotor cut after sintering (Figure 6 [not reproduced]). This is because the surface section that had completed degreasing became hard during the process and could not be deformed. With a great amount of binder, the interior separated from the surface when shrinking, and cracks were generated. Quackenbush, et al.,[7] have suggested that the capillary force participation of the binder melted liquid during such a phenomenon. Therefore, this problem may be solved by reducing the surface tension of the binder.

## 2.3 Degreasing Time

It is necessary to conduct degreasing slowly, taking time to evade swellings and cracks of the compact. Degreasing lasting several weeks has been reported.[12] The introduction of a principle replacing ordinary heat degreasing may become indispensable in solving the problem of excessive degreasing time.

## 2.4 Mold Cost

The high-injection pressure of 50~150 MPa brings about a high mold cost. Although small production of multifarious products is popular, injection molding is not able to follow in this wake because of the high mold cost. In other words, the application is limited to a few mass produced parts. This problem is also solved by reducing injection pressure, and it finally arrives at the problem of flow characteristic of the compound as mentioned above.

## 3. SIMSE Process

We attempted to construct a new concept for injection molding. This concept consists of the combination of slurry- (low-pressure) injection molding and supercritical extraction of the organic binder (Figure 7).

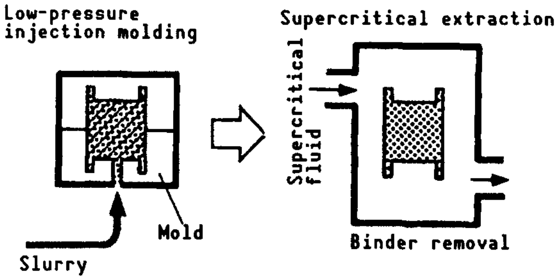


Figure 7. SIMSE Process

The slurry- (low-pressure) injection molding was developed in the Soviet Union during 1946-1960.[13] The binder consists of paraffin, beeswax, and stearic acid. Degreasing is conducted by injection molding of less than 0.1 MPa and heating. Improvement of this molding device was made later by Peltsman.[14] Miyamoto, et al.,[15] have applied this method to engine ceramic molding. Because there are advantages—for example, residual stress that causes defects as a result of

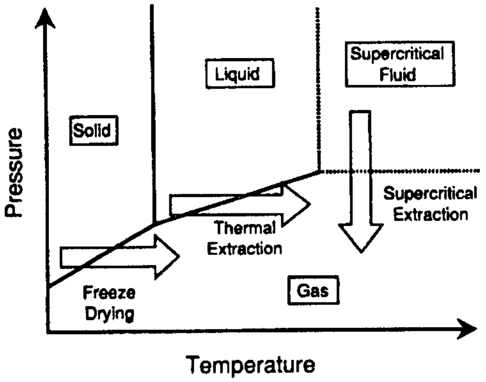


Figure 8. Supercritical Extraction, Thermal Degreasing, and Freeze Drying

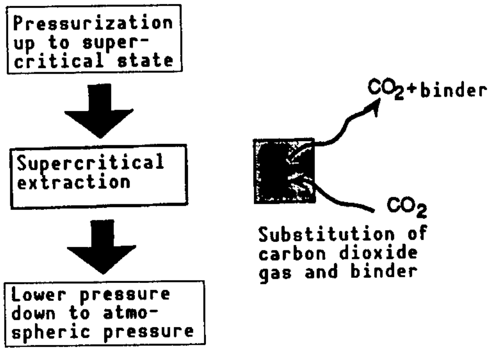


Figure 9. Degreasing by Supercritical Extraction of Injection Compact

low temperature is small and the mold cost is cheap—it has the potential to reduce defects of conventional high-pressure injection molding.

Fluids with pressure and temperature exceeding critical pressure and temperature are called supercritical liquids. They can be made into normal pressure gas without stepping across the boiling line by decompression, that is, without going through a gas-liquid coexistence state. Supercritical liquids, like gases, do not have surface tension. The method for making the dispersion medium filling the particle space within the compact into a supercritical state by pressurizing, heating, and then removing this supercritical state by decompression has been applied to the de-alcoholing of the compact prepared by the sol gel method. Success has been achieved in drying without cracks.[16] It is construed that this success is due to the failure to generate capillary force, which causes transfer of particles. Supercritical extraction (Figure 8), along with freeze drying, are thought to be an effective means of evading the generation of capillary force. Nakajima, et al.,[17] have attempted the method of extracting the organic binder in a compact prepared by pressure molding by a supercritical liquid, and, after replacing it with this supercritical liquid, decompressing and removing it as a gas (Figure 9). It was shown that the degreasing of a 25 mm $\phi$ x 15 mm compact containing 15 wt percent organic binder could be completed in less than 3 hours. When this method can be applied for the degreasing of injection compacts, there is a possibility of solving the difficulty of conventional injection molding methods that accompany degreasing.

### 3.1 Preparation of Slurry

Attention has been given to the following in designing a slurry-dispersion medium.

(1) Extraction is possible by supercritical carbon dioxide.
(2) The rate of heat dependency of slurry viscosity is small.
(3) The solid part concentration is high.

Figure 10 shows the relationship between viscosity and shearing rate of the 48 volume percentage slurry of imide thermal decomposition method silicon nitride powder (Ube Kosan SN-E10). Values of the high-pressure injection molding compound of the same powder and same concentration obtained by Honma, et al., were plotted at the same time. It is known from a comparison of both that viscosity change was small compared with the shearing rate of the slurry obtained. It showed a behavior close to the Newton liquid. The following study was conducted by the slurry-adding sintering assistant and raising the concentration to 54 volume percentage.

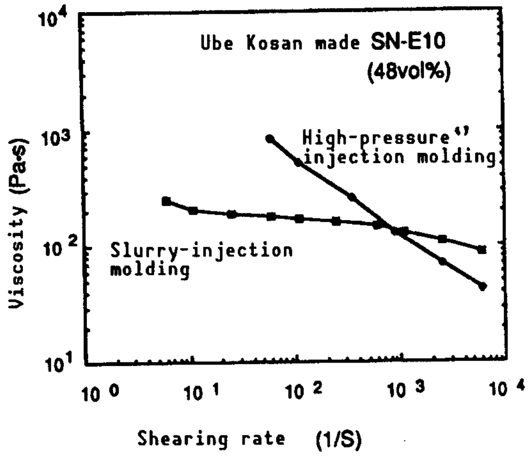


Figure 10. Slurry Developed for Slurry Injection Molding and Rheology of High-Pressure Injection Molding Compound

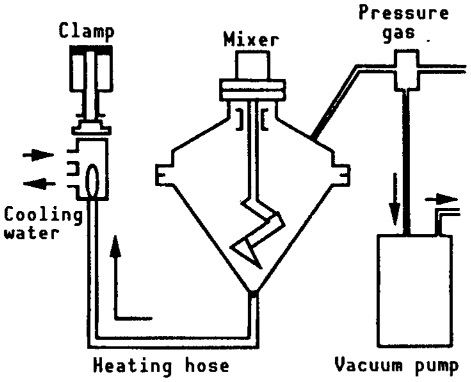


Figure 11. Experimental Device for Slurry Injection Molding

### 3.2 Slurry Injection Molding

The experiment device for slurry injection molding is shown in Figure 11. After heating, mixing, and degassing the material powder organic binder within the sealed agitation tank, pressurization is made to 3~7 kg/cm$^2$ by pressurized nitrogen from the slurry top part. The slurry is then injected into the mold and is solidified by cooling.

Comparison of short shots when injection is made into a rectangular cavity by the high-pressure injection molding method and slurry injection molding method is shown in Figure 12 [not reproduced]. In contrast to jettings that become the cause of flow marks and pores observed in high-pressure injection molding, it is known that slurry developed for the slurry injection molding is gently filled in order from the gate section to the cavity interior.

The ring compact of silicon nitride prepared by slurry injection molding is shown in Figure 13 [not reproduced]. In this ring shape, slurry injected from a side surface separates into two groups, moves along the circumference, and meets again at the opposite side. A weld line was often generated at the point where the slurry meets again when the conventional injection molding method was applied. As the drawing shows, a ring with the surface free from defects was easily available in slurry injection molding. According to the gamma-ray CT image of this ring, the dispersion of the green density was extremely small—2.200 ± 0.008 g/cm$^3$.

### 3.3 Supercritical Extraction of Organic Binder

The main components of the supercritical extraction experiment device are the extractor and the separator (Figure 14). First, the compact is set to the extractor. Liquid carbon dioxide is supplied from the bomb (pressurization is made by a pump) preheated to the prescribed temperature, and introduced into the extractor. The organic binder in the compact is extracted by this supercritical carbon dioxide, flown out to the extractor exterior, deposited by decompression, and accumulated in the separator.

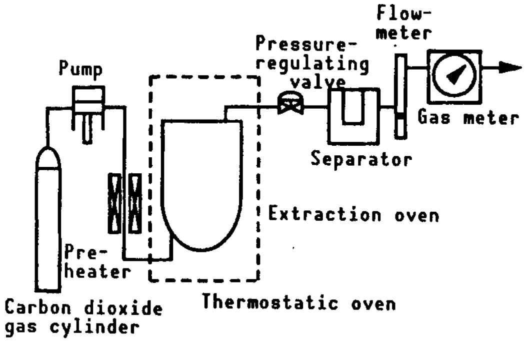


Figure 14. Experimental Device for Supercritical Extraction

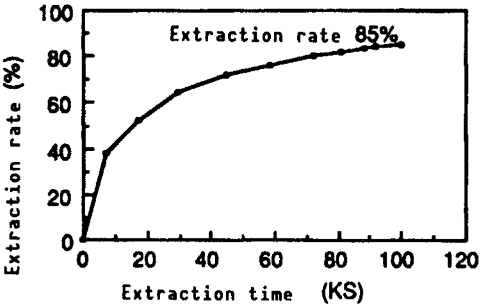


Figure 16. Change of Accumulated Extraction Volume With the Passage of Time in the Supercritical Extraction of Thick Injection Compact (43 mm ϕ x 70 mm)

Figure 15 [not reproduced] shows the external appearance before and after the supercritical extraction of the 43 mm ϕ x 70 mm cylindrical compact. The extraction rate was 85 percent. Despite such a thickness, degreasing could be made without generating cracks. As shown in Figure 16, the change in degreasing rate with time has been shown. Degreasing of 85 percent has been achieved in only 97 ks (27 hours).

### 3.4 Sintering

Figure 17 [not reproduced] shows the bolt and nut prepared by the SIMSE process. The upper drawing in Figure 17 [not reproduced] corresponds to the bolt and nut after slurry injection molding. The middle drawing corresponds to the bolt and nut after supercritical extraction. The bottom drawing corresponds to the bolt and nut after sintering. The fitting of bolt and nut was good for both after molding and sintering. As seen here, compacts by the SIMSE process shrink uniformly in sintering. This is probably due to slurry rheology in which flow marks and pores do not easily generate, low injection pressure with a small stress residual in the compact, and adoption of degreasing by supercritical extraction that does not generate capillary force.

## 4. Conclusion

The SIMSE process is one of the most promising complex form-molding methods and has many advantages over conventional injection molding methods. The advantages of the SIMSE process are:

(1) Thicker and larger molding of parts than conventionally possible.
(2) Small generation of defects in parts.
(3) High dimensional accuracy.
(4) A cheap mold.

This process is applicable from small-volume production up to mass production. Conventional practice to adopt the method of providing machining to the dry compact during trial manufacture. There had been apprehension in predicting performance of parts produced under full-scale manufacture by the injection molding method. This process, however, is also applicable to the trial manufacture stage, and, in comparison with the conventional method, is also advantageous from this point.

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## Slip-Cast Forming Process for Production in Small Quantity, Many Varieties

906C7538B Tokyo DAI 21 KAI KO ON ZAIRYO GIJUTSU KOSHUKAI in Japanese Feb 90
pp 91-99

[Article by Uchimura Katsuji, Shinto Laboratory, Shinto Kogyo Co., Ltd.]

### [Text] 1. Introduction

Molding methods—such as press, extrusion, and injection molding, and casting —are representative of fine ceramics. Each molding method has its advantages and disadvantages, and the optimum molding method must be selected according to function, shape, and production quantity of the intended products. In particular, a method capable of conducting a near-net-shape forming of complex shape and large products and trial manufacturing small quantities of many varieties of low-cost products is desirable.

Because the slip-casting method can be formed comparatively easily by using a plaster mold, expectations are high for this method. However, there are many problems, such as the formability limit of biased and thick shapes, mold durability, contaminations in high-purity materials, productivity, and correspondence to automation in the slip-casting method. Research on pressure molding has been promoted recently. However, many points are dependent on experience and instinct. These include multisegmenting of the mold in complex shape molding, topics on removal of compacts (such as the rapping gradient and mold release method), slurry preparation methods, evaluation method of slurry characteristics, water absorption, and dewatering condition control of molds.

The high-pressure casting method and slurry pressure-injection control system were developed to obtain a homogeneous compact. This is accomplished by forcibly conducting automatic control of water absorption and dewatering of the mold and the water absorbent vacuum retention mold (osmotic V process) with a self-collapsing property that has applied the vacuum shield molding process (V process). Molding of complicated bias-shaped and large products can be done easily by this system. It is a system in which automation is possible without depending on experience and instinct, and it is a new molding process complying with production of a small quantity in many varieties.

Explanations of the basic principle of this process, procedures, system composition, features of formability, and forming characteristic of forming samples using alumina material will be made.

## 2. Osmotic V Process Forming System

### 2.1 System Composition of Process

A system block diagram of the process is shown in Figure 1. The V process forming system consists of a molding system and a slurry injection control system. A vacuum retention mold corresponding to the objective products for the necessary production quantity has been molded, slurry has been injected in this mold in the molding system, and, when the vacuum suction of the mold is canceled after the slurry becomes dehydrated and solidified, the mold is subject to instantaneous self-collapse and the compact can be easily taken out. The slurry-injection control system automatically conducts injection control of the slurry injection flow rate and pressure by conditions set in advance.

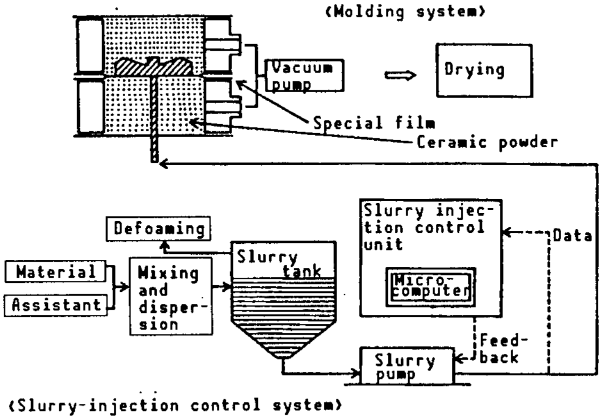


Figure 1. System Block Diagram of Process

### 2.2 Molding Principle and Forming Process for Molds

The molding principle and forming process are shown in Figure 2 and explained below.

(1) After setting the master model (wooden, resin, and metal molds, material quality is not selected) on a master plate in which vacuum suction is possible, a special polymer resin film of several tens of $\mu$m (in which the permeation of slurry solvent is possible) is softening treated, the film is vacuum adhered to the model, and transcription is made.

(2) A flask capable of vacuum suction is placed on the back side and vibration packing of ceramic powder equivalent to the mean particle diameter of 100 $\mu$m as the mold material in the flask is conducted. (It is permissible when it is a powder with a particle size combination that is capable of conducting the finest filling.)

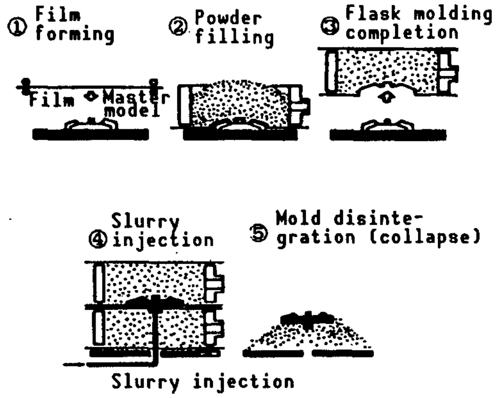


Figure 2. Molding Principle and Forming Process Drawing

(3) A film capable of vacuum sealing is covered on the filled mold material. The mold is sealed by this film and the special film adhered to the model. When vacuum suction of the entire mold is made, a vacuum-packed transcription mold is molded. Molding of the cope is completed when the master model is removed.

(4) The drag is molded in the same manner. When the cope and drag are fitted, the cavity section that should be molded is formed. Slurry is injected and filled in the cavity. The slurry solvent is subject to osmotic vaporization through the special film and dehydrated because the mold interior is of vacuum. The slurry solidifies and a compact is made.

(5) When the vacuum suction of the mold is canceled, the mold is subject to instantaneous self-collapse, and the compact can be taken out easily. The mold material is recovered after collapsing and is reused after drying.

### 2.3 Dehydration Principle of Mold and Its Characteristics

A conceptual drawing of the mold dehydration principle is shown in Figure 3. The theoretical discussion of the dehydration principle is insufficient. However, the film is functioning as the separation membrane of a water perm-selective property because the mold has been vacuum retained. It corresponds to a type of pabepareishon membrane separation.

The distilled water (20°C) absorption rate characteristics of this process mold and an A-class plaster mold in atmospheric pressure are shown in Figure 4. The water absorption rate of the plaster mold becomes smaller with the elapse of water absorption. The mold in this process has an almost fixed elapse characteristic, although the water absorption rate is relatively small.

Although this water absorption characteristic easily generates streaks at thickness gathering at the beginning of casting in the plaster mold, it is also why the mold of this process does not generate streaks.

In addition, the difference of this water-absorption rate characteristic will also greatly affect the homogeneity of compact density, shrinkage percentage,

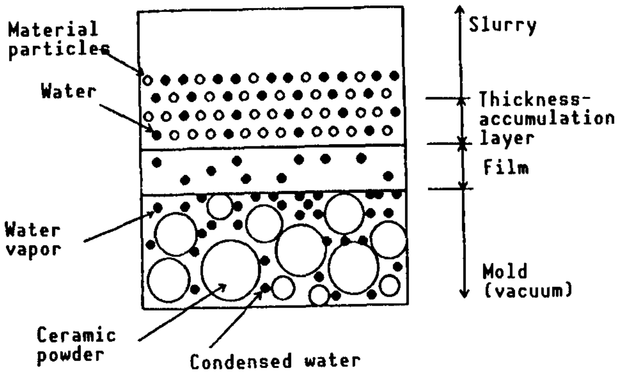


Figure 3. Conceptual Drawing of Mold Dehydration Principle

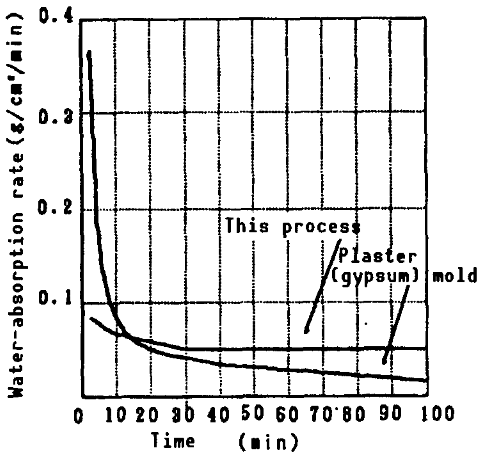


Figure 4. Water-Absorption Rate Characteristics of This Process Mold and Plaster (Gypsum) Mold

and dimensional accuracy in the thickness gathering process conclusively. It is also the reason why biased and thick shapes that are difficult to form by the plaster mold (discussed later) are formable by this process.

### 2.4 Blending Examples, Properties, and Forming Characteristics of Applied Slurrys

It will be formable when the slurry properties are of the properties used in the general plaster mold. However, the properties are closely related to formability, including the thickness gathering characteristic; largely controlled by the characteristic and optimum deflocculant of the starting material, binder selection, and preparation method; and they affect the quality of the compact. The blending examples, properties, and compact characteristic are shown in Table 1.

### 2.5 Comparison of Thickness Gathering and Dehydration Characteristics With the Plaster Mold

The relationship between slurry-injection pressure by the slurry specimen A and thickness gathering rate constant is shown in Figure 5. The thickness gathering rate, compared to that of the plaster mold, is from one-half to one-third. It changes significantly, according to injection pressure and slurry temperature.

Table 1. Slurry Bending Examples, Properties, Preparation Methods, and Representative Molding Characteristics

| Sample No. | A | B | C | D |
|---|---|---|---|---|
| Material quality | Alumina | Easy sintering alumina AL-160SG | High-purity alumina TM-D | Silicon nitride SH-3MF |
| Purity (%) | 90 | 99.5 | 99.99 | Fe 50 ppm |
| Mean particle diameter ($\mu$m) | 2.5 | 0.6 | 0.4 | 0.6 |
| Added assistant | | | | |
| Sintering assistant | $SiO_2$,MgO,CaO | MgO | —— | $Al_2O_3$, $Y_2O_3$ |
| Deflocculant | 0.2 (D-305) Polyacrylic acid $NH_4$ salt | 0.8 (D-305) Polyacrylic acid $NH_4$ salt | 0.5 Polycarbonic acid $NH_4$ salt | 0.5 (D-735) Polycarbonic acid $NH_4$ salt |
| Binder (%) | 0.3 (WE-518) | 1.0 (WE-518) | Sugar-alcohol system | 1.0 (WE-518) |
| Plasticizer (%) | 1.0 | 1.0 | —— | 2.0 |
| Solvent (water) (wt%) | 26 | 20 | 23 | 23 |
| Slurry property | | | | |
| Apparent viscosity (cps) | 950 | 370 | 2450 | 450 |
| Mixing and dispersion method | Ball mill 24 hour, vacuum degasification 30 minutes | | | |
| Compact characteristic | | | | |
| Drying shrinkage (%) | 0.3 | 0.2 | 0.3 | 0.4 |
| Bulk density (g/cm$^3$) | 2.44~2.47 | 2.75~2.80 | 2.38~2.42 | 2.05~2.10 |

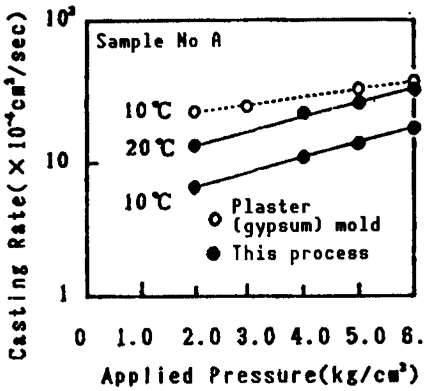


Figure 5. Relationship Between Slurry-Injection Pressure and Thickness-Accumulation Rate Constant

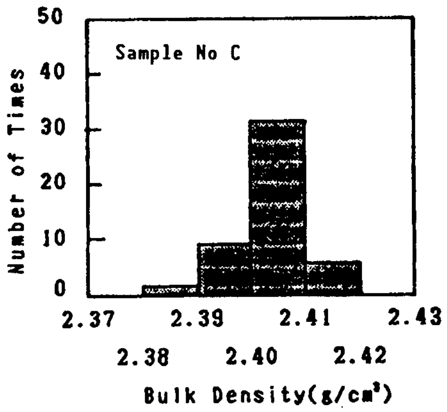


Figure 6. Bulk Density Histogram of High-Purity Alumina Temporary Burnt Compacts

## 2.6 Evaluation of Compact Characteristic of High-Purity Alumina

Four compacts of 60 x 80 x 10 mm that had been formed at the same time in a single mold were samples in the evaluation. The high-purity alumina temporary burnt compacts (800°C) were divided into 48 and cut out into samples of 10 x 10 x 10 mm. The distribution result of the bulk density measured by the Archimedes' method is shown by a histogram (Figure 6). The distribution width is centered at 2.40~2.41 or smaller, the relative density is more than 60 percent and is a homogeneous and high-density compact.

The result of measuring the pore size distribution of the temporary burnt compact by the mercury-injection method is shown in Figure 7. A sharp distribution has been made by the pore size of 0.08 μm, with uniform pore size distribution.

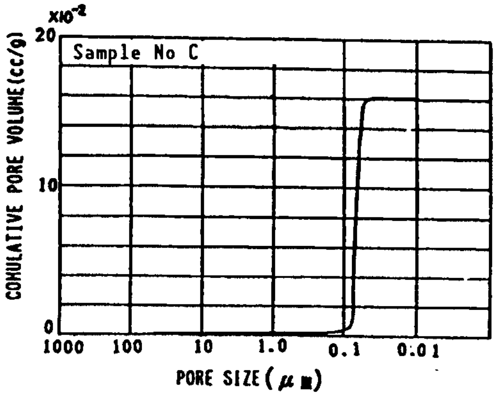


Figure 7. Pore Size Distribution of High-Purity Alumina Temporary Burnt Compacts

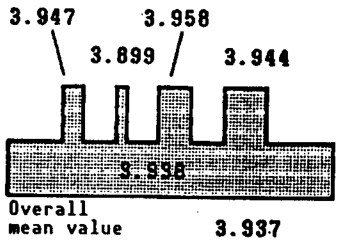


Figure 8. Drawing of Fan-Shaped, Burnt Compact Bulk Density Distribution (High-Purity Alumina)

The bulk density of each part of the burnt body (1,300°C) of the fin shape compact of 100 x 100 x 10 mm provided with fins of 1, 2, 3, and 4 mm is shown in Figure 8. The density of the 1-mm section is relatively slightly lower. However, it is for all practical purposes a homogeneous compact, and it can be said that homogeneous forming is also possible in biased-thickness-shaped products.

The microstructure system photo of the broken-out section of the bending samples burnt at 1,250°C and 1,300°C observed by SEM [scanning electron microscope] is shown in Photo 1 [not reproduced]. The crystal particle size is at the 1.0 $\mu$m level, and they are homogeneously uniform.

Table 2 shows the physical and mechanical characteristics of the entire burnt body. Unlike conventional casting characteristics, these values have achieved low-temperature burning and high strengthening and have become high-level characteristics.

Table 2. Physical and Mechanical Characteristics of Entire Burnt Compact

| Characteristic item | Burning temperature (°C) | |
|---|---|---|
| | 1250 | 1300 |
| Porosity (%) | 0.86 | 0.13 |
| Coefficient of water absorption (%) | 0.22 | 0.03 |
| Apparent specific gravity (g/cm$^3$) | 3.88 | 3.96 |
| Bulk density (g/cm$^3$) | 3.85 | 3.95 |
| Three-point bending strength (MPa) | 578.5 | 619.0 |
| Weibull coefficient (m) | 5.65 | 9.14 |
| Fracture toughness (KIC) (MPam$^{1/2}$) | 3.30 | 3.33 |
| Vickers hardness (GPa) | 18.4 | 18.9 |

## 2.7 Compact Shape and Characteristics

The transcription of the model is easy and superior from the forming principle in this process. Even those that require multidivision or the use of a core when it is of an ordinary forming method can be made readily of monolithic forming.

The hole and cup shapes shown in Photo 2 [not reproduced] are examples of monolithic formings made without using a core. Moreover, because the water-absorption principle of the mold differs from that of the plaster mold, which uses the capillary phenomenon, the density of the thickness gathering body is homogeneous. The formation of biased-thickness-shaped, thick-shaped, and thin-shaped products is possible.

In addition, because it adopts the method of collapsing the mold, it is suitable for production in small quantities but many varieties. It is not necessary to consider the draft and mold-releasing property. Forming an inversed taper shape is also possible by devising the model. Forming of large-sized products and sludge-disposal hollow products in which the removal and handling of the compact is difficult are also possible.

Photo 3 [not reproduced] shows a large-sized rotary-vane-shaped model and a surface-plate-shaped model formed without taking draft into consideration.

## 3. High-Pressure Casting Method and Slurry-Injection Control System

With the development of porous resin types in recent years, the pressure-casting method has promise as a method capable of comparatively easily forming complicated, large-shaped products that are difficult to form by injection-molding methods. There are problems, such as time required for forming compared with other molding methods. In addition, crack generation and deformations easily occur by nonuniform dry shrinkage in thick products and bias-thickness-shaped products. To put this forming method to practical use as a high-accuracy, precision forming method, the dehydration rate in the dehydration and thickness gathering process, characteristic of this forming method, should be consciously controlled. It is important to develop a plan for obtaining a homogeneous compact by departing from forming that is dependent on conventional model water-absorption capacity experience. This system optionally controls injection pressure and injection rate as factors greatly affecting the formability and forcibly changing the dehydration rate. Its goal is a forming system in which control of homogeneous density is possible and which links to high productivity and high-accuracy precision forming. Execution examples that have analyzed for the composition and pressure control effect of this system are explained later.

### 3.1 Mold Structure

The structural cross section of the mold is shown in Figure 9. Air holes have been provided so that the slurry solvent can be forcibly vacuum extracted, through-flow dried, and mold released without being controlled by the water-absorbing property using the capillary phenomenon. The sample size is 70 $\phi$ cylinder x 25 mm thickness. The material quality of the mold is plaster (Nitto plaster, C-2000).

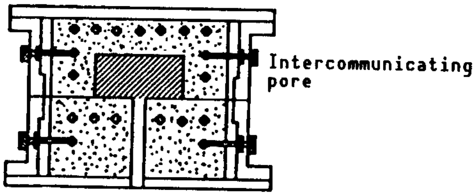


Figure 9. Structural Cross Section of Mold

### 3.2 Slurry Preparation Method and Condition

Two types of sample slurrys were used with the material particle size and slurry viscosity greatly differing as set conditions. Material blending, preparation condition, and properties of the sample slurry shown in samples A and B of Table 1 have been used.

### 3.3 Forming Device and Condition

Figure 10 shows a system block diagram of a high-pressure casting device. It is a plunger injection system by ac servomotor driving. The function of the system is to automatically control the dehydrating rate by selectively programming the injection pressure and injection rate in the computer in advance. Another function is that of online monitoring of the injection amount of the thickness gathering and solidification condition, injection pressure, and injection elapse time in order. The forming process drawing is shown in Figure 11.

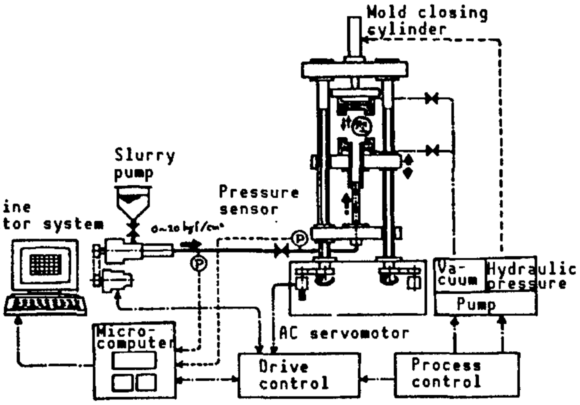


Figure 10. System Block Diagram of Molding Device

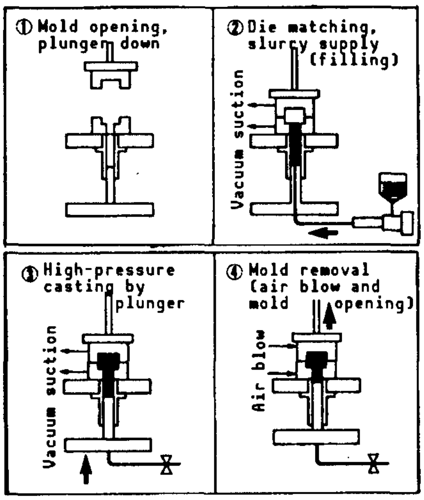


Figure 11. Drawing of High-Pressure Casting Process

The forming condition was fixed by conducting the mold water-absorption action by vacuum dehydration only. By changing the slurry-injection pressure and injection rate, the difference in dehydration condition was analyzed for compact characteristics, injection measurement, and control data.

### 3.4 Evaluation Method by Compact

The moisture, drying shrinkage rate, density (Archimedes' method), and hardness distribution (micro Vickers) of the sample cross section of the compact were measured. After forced drying the compact for 12 hours in 110°C, it was cut and smoothed and a sample for obtaining hardness was made. After temporarily burning the compact for 10 hours at 1,000°C, it was cut out and the sample for obtaining the density made.

### 3.5 Samples for Forming

#### (1) Relationship Between Injection Pressure, Thickness Gathering Time, and Drying Shrinkage Rate

In Figure 12, the case when the slurry-injection pressure has been changed. It shows the relationship between the required thickness gathering time and drying shrinkage rate for obtaining the compact of 70 ϕ x 25 t. The thickness gathering time differs significantly, according to the slurry properties. The drying shrinkage rate becomes smaller as the injection pressure becomes higher. It is thereby known that injection pressure plays a great role in formability.

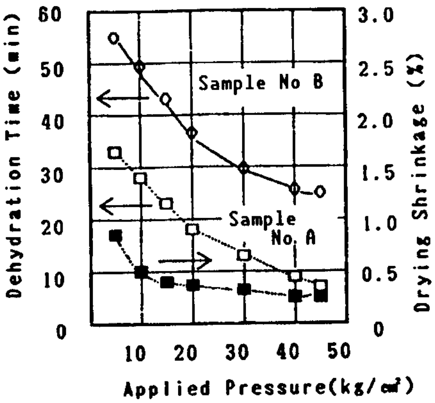


Figure 12. Relationship Between Applied Pressure, Dehydration Time, and Drying Shrinkage Percentage

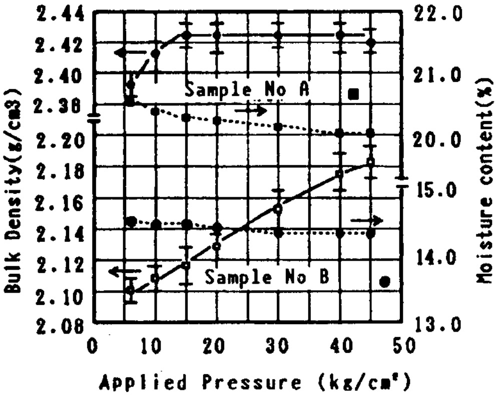


Figure 13. Relationship Between Applied Pressure, Compact Bulk Density, and Moisture Content

#### (2) Relationship Between Injection Pressure, Compact Bulk Density, and Moisture

In Figure 13, the compact density of sample A with a greater particle size has increased with the injection pressure. There is no change in sample B with a small particle size at more than 15 kg/cm$^2$. Moisture has decreased with the injection pressure, but change is insignificant.

### (3) Density Distribution of Compact by the Constant Pressure Dehydration Method

There are generally many cases when pressure casting is conducted by constant pressure dehydration. Density distribution of the compact central cross section is shown in Figure 14.

The density of the compact surface section is low and that of the center part and casting part are high. Unevenness in density easily occurs between the inner and outer sides in thick-formed products. This is believed to be the cause of cracks generated by uneven shrinkage when drying.

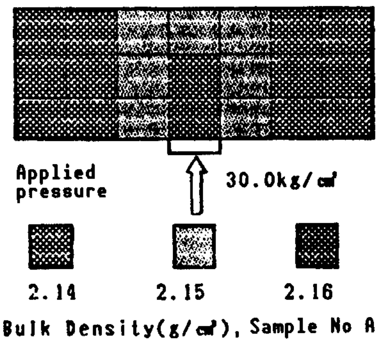


Figure 14. Compact Bulk Density Distribution by Constant Pressure Dehydration

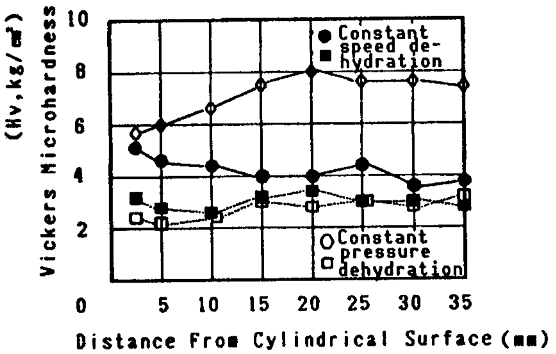


Figure 15. Compact Hardness Distribution by Difference Between Constant Pressure Dehydration and Constant Speed Dehydration

### (4) Homogeneity of Compact by Differences in Dehydration Method

Figure 15 compared by hardness distribution the homogeneity of the compact according to the differences between conducting constant pressure dehydration and constant speed dehydration. It shows the radial Vickers hardness distribution of the compact central cross section. The dehydration method difference of sample B with small particle size conspicuously appeared as the hardness difference of the compact internal and external sections. It is also clear that it has become of a homogeneous hardness distribution by conducting constant rate dehydration.

## 4. Conclusion

There is a potential that products with shapes thought difficult to form in the past can be easily formed by using this process. It is thought that the flexibility of shape has expanded and that structural designing, which takes into consideration material characteristics, will become possible. Moreover, high-productivity forming is possible by conducting high-pressure casting. However, when conducting pressure injection of slurry, the forming of a homogeneous density is controllable by conducting a forced constant rate dehydration control rather than a forming dependent on experiences and instinct in line with the water-absorption property of the mold. It is thought that casting will also be reconsidered. Furthermore, it is believed that the preparation and evaluation methods of slurry will become the most important points in casting formability. However, there are still many points to be studied. Putting the casting method to further practical use will occur when studies on material processing based on the surface chemistry of materials progress.

## New Slip-Casting Method

906C7538C Tokyo DAI 21 KAI KO ON ZAIRYO GIJUTSU KOSHUKAI in Japanese Feb 90 pp 101-112

[Article by Sumihiko Kurita, Tohru Eguchi, and Takahiro Fukuds, Fine Ceramics Division, Koransha Co., Ltd.]

[Text] **Abstract**

"K-process" is a new technology for forming advanced ceramics into near-net shapes without using plaster mold. With conventional slip-casting methods using plaster mold, the mold for some complicated shapes must be designed so as to divide them into several parts. The drawing taper of the mold must be taken into account. Cracks of distortion problems sometimes occur when removing the mold.

Koransha has developed "K-process" to form near-net shape ceramics in complicated configurations without such problems. We use a mixture of powder and liquid solidified as a mold instead of plaster. The solidified mold retains the designed shape and has the property of absorbing liquid. After molding ceramics slurry, the solidified mixture mold disintegrates at increased temperature. Near-net shape green bodies remain without problems.

We have achieved a sintered density in complicated shapes as high as the highest levels seen from conventional methods using a plaster mold, but with a smooth surface condition.

### 1. Introduction

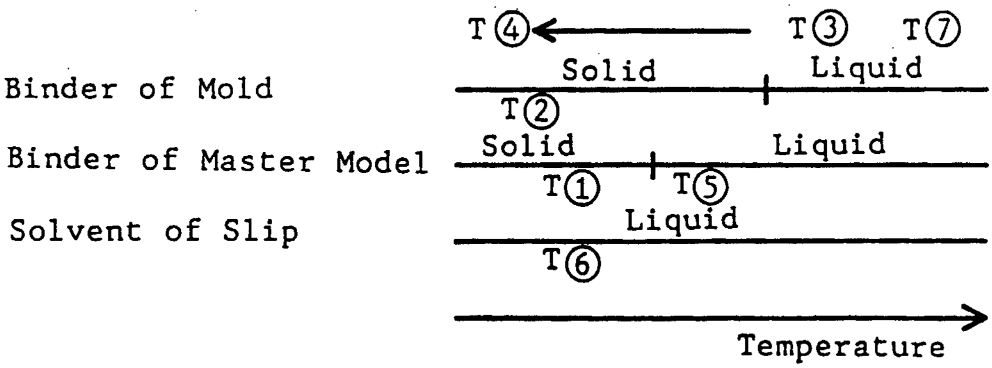
Koransha has applied the slip-casting method technology that it has fostered over many years in porcelains to fine ceramics. It is now engaged in commercializing its technology. To achieve this, it has developed additives (dispersant, binder) for slipping and a unique dispersion technology, improved the green density, and by atmospheric sintering made the density of the material equivalent to more than 99 percent of the theoretical density. As a result, the application of the slip-casting method, which has many advantages, is now used to engineer ceramics and has become the main current of our fine-ceramic molding method. Because there had been demands for the forming of complicated shapes having an inverted taper and high-dimensional accuracy in recent years, we had been engaged in the development of a new slip-casting method. This report explains the new slip-casting method (K-process) and discusses examples using the forming method.

## 2. New Slip-Casting Method--Principle and Flowchart of K-Process

The defects of the conventional slip-casting method using the plaster mold were that mold division was necessary for complicated shape products, operation efficiency was extremely bad, and deformations and crackings of green moldings occurred frequently.

Liquid was added to powder and solidified as a mold in place of the plaster mold. The mold with a water absorption property retained the designed shape by this solidification force, and, after molding the ceramic slurry, the mold disintegrated as temperature increased. A method for taking out the complicated shape product at once (K-process) was developed.

The principle of the K-process is shown in Figure 1, and a flowchart of the K-process is shown in Figure 2.



* T①,T② ..... follow the working temperature of the process in Fig.2 respectively.

Figure 1. States Change of Binders and Working Temperature in K-Process

When the equilibrium temperatures of the solid and liquid phases of mold and master model binders and solvent of slip are selected as shown in Figure 1, the new slip casting (K-process) of Figure 2 becomes possible by setting the working condition of (1)~(7). The temperatures of T(1)~T(7) in Figure 1 correspond to each working temperature at (1) through (7) in Figure 2.

First, the master mold is prepared at the T(1) temperature, and powder that becomes the material of the mold is cast at the T(1) temperature. A binder with a solid/liquid equilibrium temperature higher than that of the binder of the master model is impregnated from T(3) at the working temperature set at T(4). After the mold is prepared, the temperature rises to T(5), and the

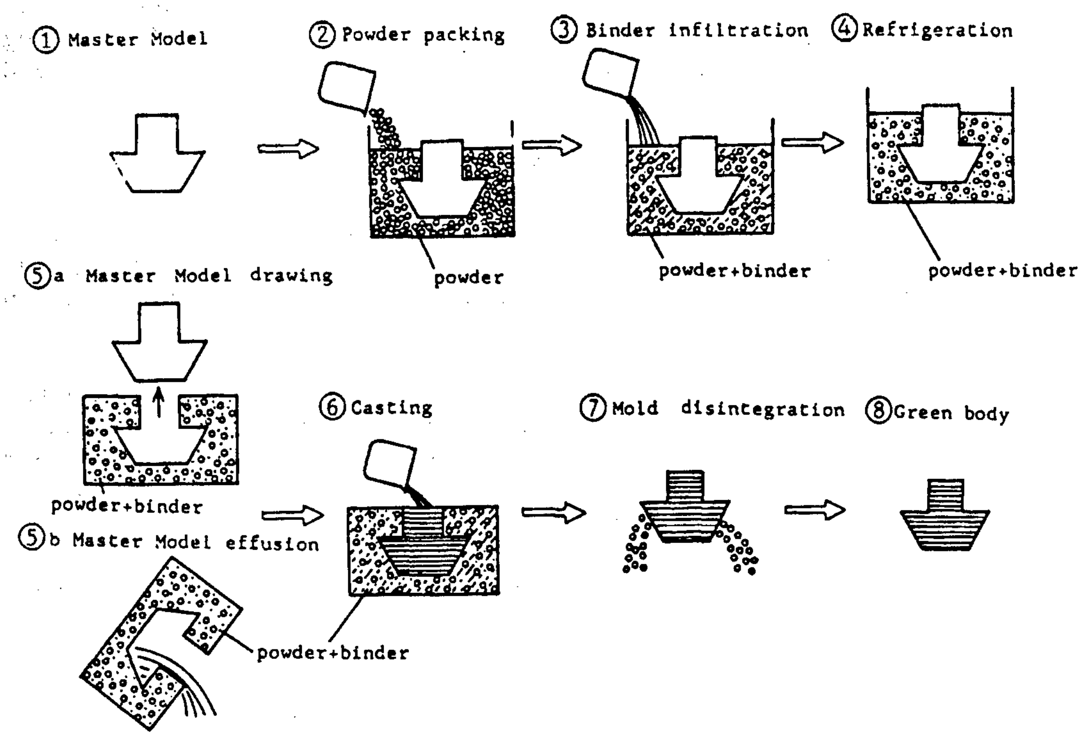


Figure 2. Flow Chart of K-Process

master model is melted and flows out and a cavity is made. The ceramic slurry of T(6) temperature, which has dispersed into a solvent constantly possessing a liquid condition in the working temperature range, is flown into the mold cavity. After thickness gathering, the mold disintegrates at the temperature of T(7) and mold removal is made. These series of processes are the K-process (patent applied for). The master model effusion (5(b)) is the mainstream in the process of (5). There are times, however, when the rubber master model drawing (5(a)) is used, according to shapes.

### 3. Research Execution Examples--Water, Alcohol System

Various materials used in the R&D of this process are shown in Table 1.

Table 1. Materials Used in This Report

| | |
|---|---|
| Mold, master model | Polyethylene (average particle size — 20 μm) |
| Ceramic powder | $Si_3N_4$, $Y_2O_3$, $Al_2O_3$, deflocculant, binder |
| Binder of mold, master model<br>Solvent of slip | $H_2O + C_2H_5OH$ |

## 3.1 Selection of Binder, Slip Solvent, and Working Temperatures

The mold binder, master model binder, and solvent of slip have been made of the water plus ethyl alcohol system. The solidification temperature and viscosity were measured, and the composition ratio satisfying each set condition was studied.

The freezing starting temperature of water plus ethyl alcohol system is shown in Figure 3. The uniform liquid, solid, and mixed states were observed according to temperature and composition in this system. A uniform solidification state was shown up to some 10 volume percentage ethyl alcohol. A sherbet-shaped unequal solidification occurred when more than 20 volume percentage was added.

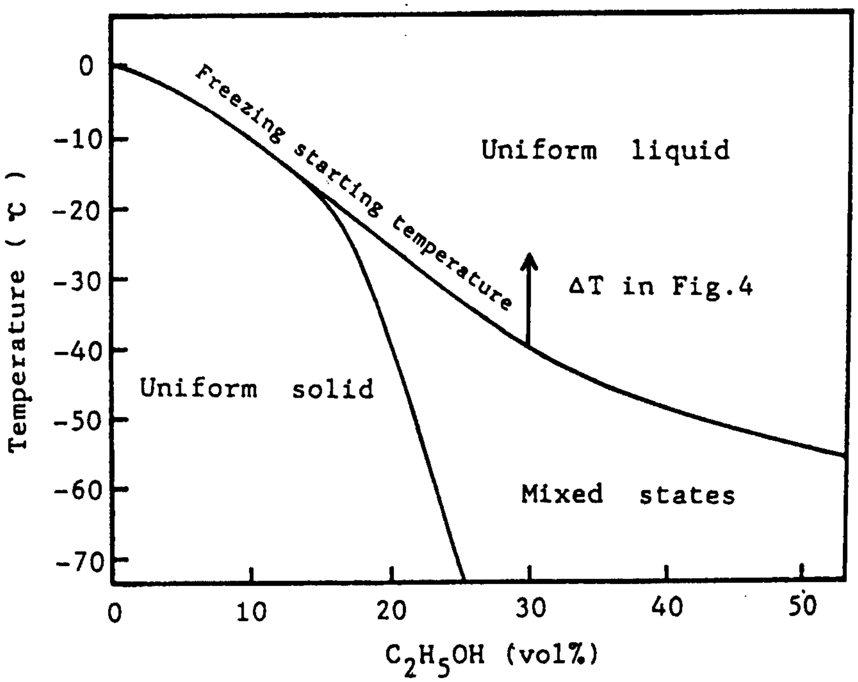


Figure 3. States of Binder at Low Temperature

It could not be handled as a rigid body, although a temperature of -70°C was maintained when it became more than 30 volume percentage. Therefore, it was decided to use water only for the mold, water plus ethyl alcohol 15 volume percentage for the master model, and water plus ethyl alcohol 30 volume percentage for the solvent of slip.

The viscosity values of a system that has mixed the prescribed $Si_3N_4$ powder to water plus 30 volume percentage ethyl alcohol and the solvent are shown in Figure 4. Moreover, the difference between freezing and casting temperatures has become ΔT.

The freezing starting temperature of this solvent is -40°C. With this temperature as a reference, the Δ of Figure 3 was measured in the axis of abscissas.

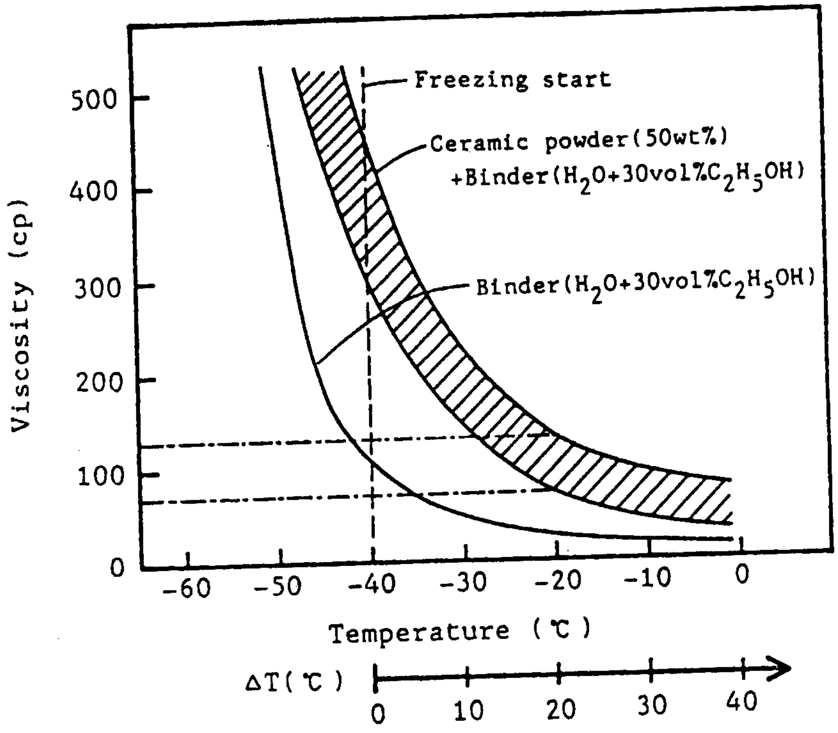


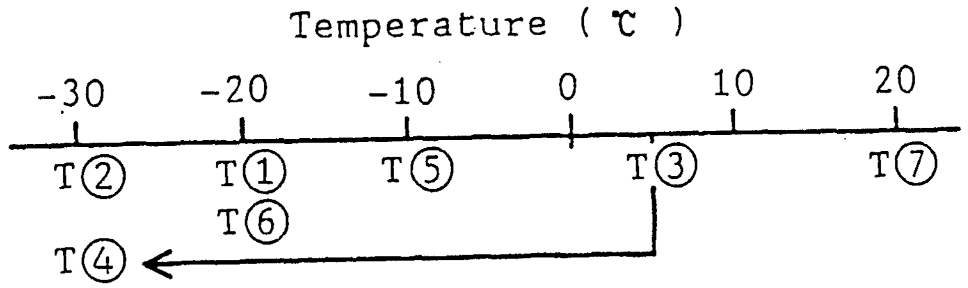
Figure 4. Viscosity of Binder and Slip

The viscosity values of the solvent and slip were measured in the axis of ordinates. According to this, ΔT became 20°C—there was no effect in the solid phase at −20°C, and the viscosity value of the solvent was about 6 cp. Moreover, $Si_3N_4$ powder was added so that the solvent quantity (solvent/powder plus solvent) became 50 percent. The result is shown by a broken line. The viscosity value rose with the $Si_3N_4$ powder addition, becoming an area of about 100 cp at the same temperature. At this viscosity value, as a slip was possible. Therefore, the slip-casting temperature was set at −20°C by taking into consideration the solid-phase effect and operation efficiency. With this temperature as the reference, the ratio of temperature, water, and ethyl alcohol of each process shown in Figure 2 was determined. The results are shown in Figure 5.

### 3.2 Preparation of Master Model and Mold

The material of the master model was polyethylene (PE) fine powder. Water plus ethyl alcohol 15 volume percentage was used for the binder. The percentage of PE and binder had a weight ratio of 1:2.

The same PE and water as the master model was used for preparing the mold. For studying the suction capacity of the slip solvent by the mold in the latter casting process, the ratio of PE and water was changed and the porosity of the mold and mechanical strength at low temperature were measured. The results are shown in Figure 6.



| | |
|---|---|
| Binder of Mold | $H_2O$ |
| Binder of Master Model | $H_2O + 15vol\% C_2H_5OH$ |
| Solvent of Slip | $H_2O + 30vol\% C_2H_5OH$ |

* T①,T② ....... follow in Fig.1,Fig.2.

Figure 5. Working Temperature of K-Process

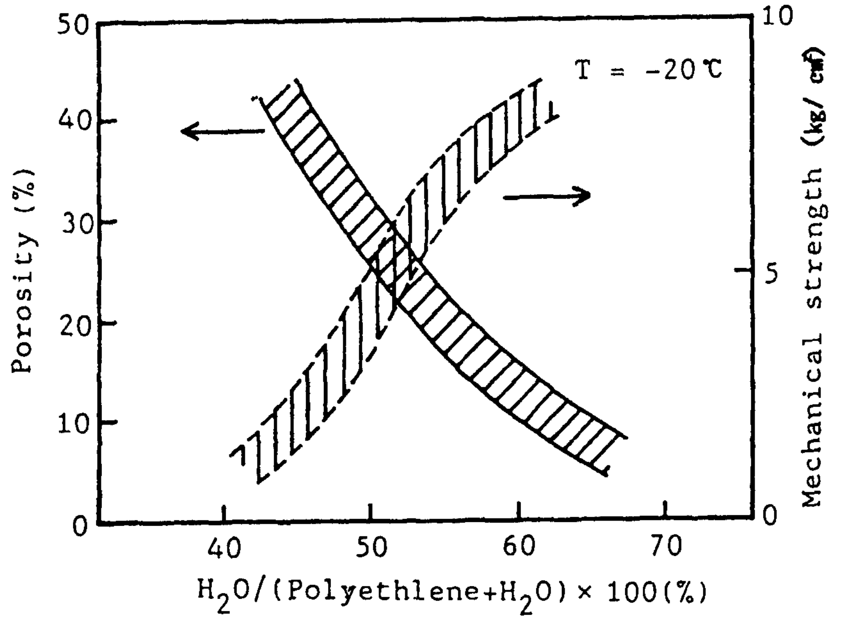


Figure 6. Porosity and Mechanical Strength of Mold

The moisture content (water/water plus powder) was set at 55 percent as a balance between porosity and mechanical strength. The porosity was 20 percent and about one-half that of a plaster mold. The mechanical strength was 7 kg/cm and one-half that of a plaster mold.

### 3.3 Preparation Conditions of Slip

The casting temperature was set at -20°C in 3-1. Viscosity was measured by this set temperature by adding a solvent (water plus alcohol 30 volume percentage) such as $Si_3N_4$, and additional dispersant and binder. The results are shown in Figure 7.

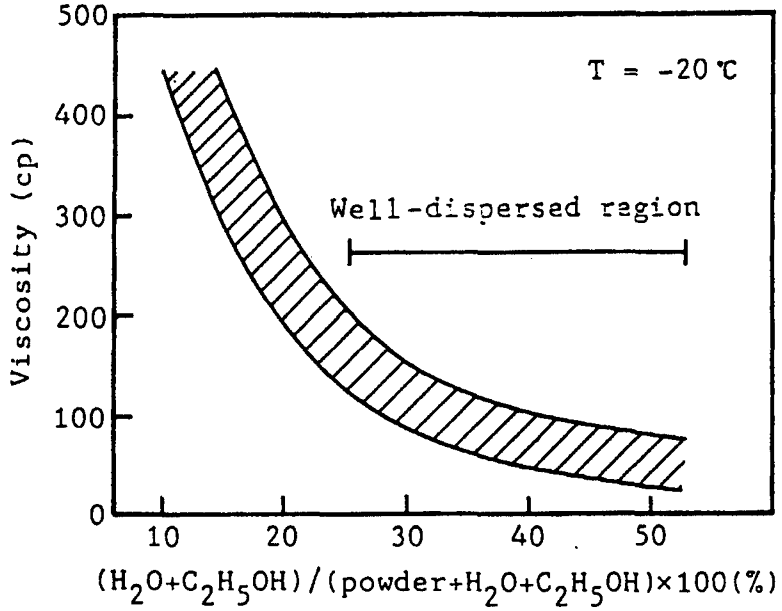


Figure 7. Viscosity of Slip

The powder dispersed up to the solvent quantity (solvent/powder plus solvent) of 25~50 percent. The viscosity value of the slip entered the value of 100 cp ± 30 cp, which is the slip-casting reference value of our company. It was made a slip with the solvent quantity (solvent/powder plus solvent) of 35 percent by taking workability and yield into consideration.

### 4. Execution Results and Problem Points

Photos of each process are shown in Photo 1 [not reproduced]. Because the mold naturally disintegrates, which is the intent of this process, green bodies of high dimensional accuracy and complicated shapes that are free from deformation and flaws have been available. Several evaluations have been conducted in these green bodies and those obtained by conventional plastic mold. The results are shown in Table 2. Although the thickness gathering rate becomes about one-fourth of that when using the plaster mold in this K-process, other characteristics compared favorably with those of the plaster mold.

The structure of the sintered material formed by the K-process is the same as that of the plaster mold, as shown in Photo 2 [not reproduced].

Table 2. Properties of Green and Sintered $Si_3N_4$ Materials

| Item | | Plaster mold | K-process |
|---|---|---|---|
| Green body | Density (g/cm$^3$) | 1.80 | 1.80 |
| | Accumulative rate (mm/sec) | 12 | 3 |
| Sintered body | Density (g/cm$^3$) | 3.21 | 3.21 |
| | Bending strength (kg/mm$^2$) | 100 | 100 |

As explained above, moldings with complicated shapes that could not be made conventionally could be formed under the same quality level as slip casting using the plaster mold—and be free from cracks and deformation by using this K-process. A slight problem is that the thickness gathering rate of the K-process is one-fourth that of the plaster mold. Mold removal is a problem in complicated moldings. Because the plaster mold requires assembly, disassembly, and removal of the mold by hand, compared with the K-process which uses natural disintegration of the mold, there is a labor savings. Thus, the K-process has a big advantage when considering the process as a whole.

## 5. Conclusion

The K-process is capable of preparing moldings of the same quality as slip castings of the conventional plaster mold. In addition, the K-process (Figure 8), characterized by the effusion of the master model and natural disintegration of the mold, has the following advantages.

(1) Compacts of complicated shapes can be made.
(2) Mold release is easy.
(3) Compact free from burrs and cracks can be made.
(4) Recycling of the mold material is possible.
(5) Dimensional accuracy of the compact is high, and there is no mold wear.

The working temperature which is below the ice temperature, and the high degree of temperature control required, are problems with the K-process. The current K-process is a first response using water and alcohol in the binder. A new K-process with working temperature of room temperature is now under R&D.

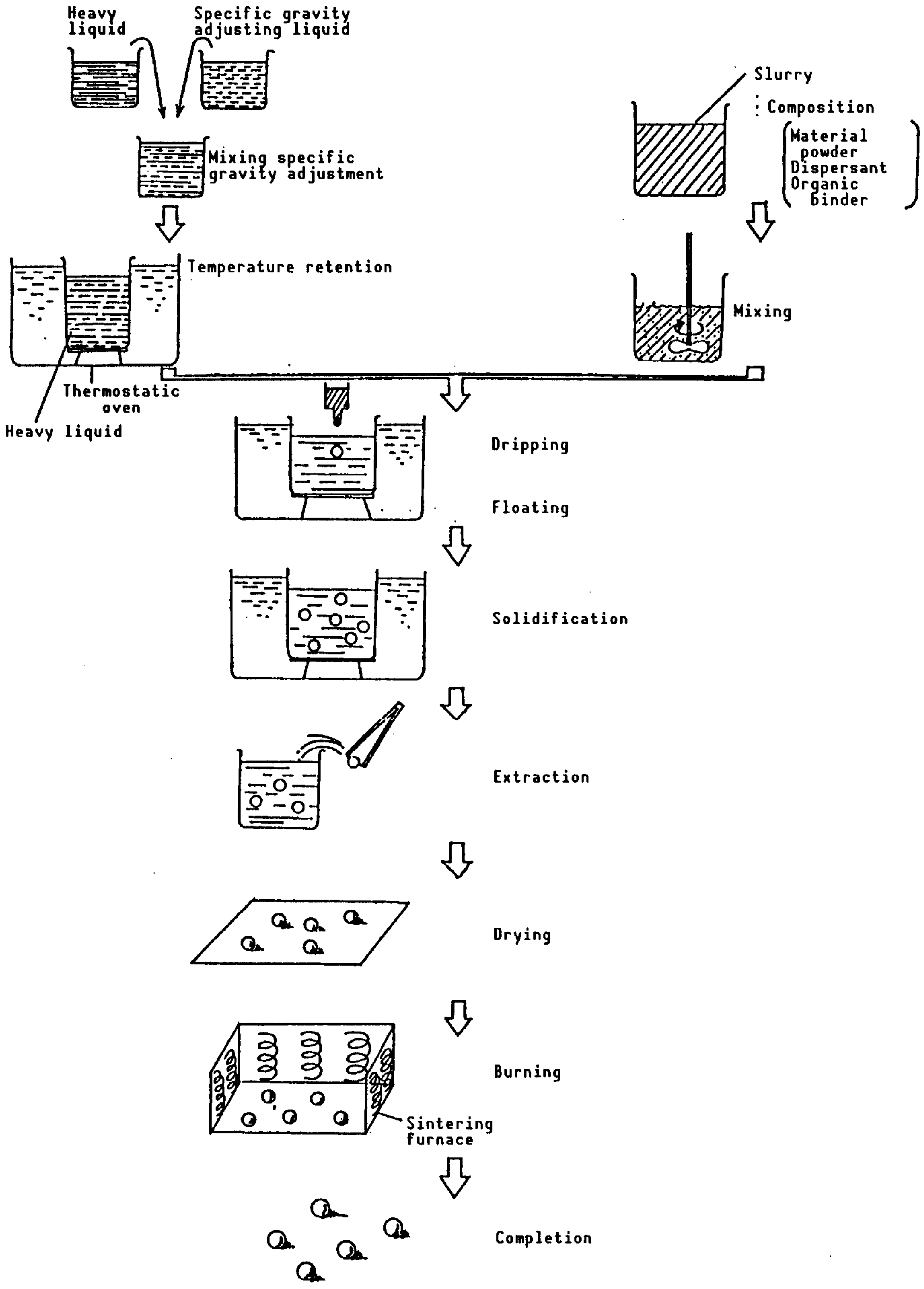


Figure 8. Floating Molding Method: Flowchart of Spherical Bodies

# Casting Technology for Large-Sized Alumina Products

906C7538D Tokyo DAI 21 KAI KO ON ZAIRYO GIJUTSU KOSHUKAI in Japanese Feb 90 pp 113-121

[Article by Yuji Hirose, Basic Research Laboratory, Toji Kiki Co., Ltd.]

## [Text] 1. Introduction

The method of casting slurry into a porous plaster mold, dehydrating and solidifying slurry by the capillary force of the plaster mold, and obtaining compacts had been industrialized as the forming method of household ceramics. products include tableware, vases, washbowls, flush toilets, etc. This process has been going on for about 100 years.

Casting is generally classified into sludge casting and solid casting from forming.

When slurry is poured into a mold, a fine layer or cast, is formed along the mold by the water absorption action of the mold. The thickness of this fine layer, which equals the standing time after pouring the slurry into the mold interior, is generally called the thickness gathering (accumulation) time. This time increases in proportion to the square root. The slurry-casting method discharges excessive slurry when the prescribed thickness has been formed. After standing for a time, mold releasing occurs and the compact is taken out. The solid-casting method does not discharge slurry and allows accumulation of all slurry in the mold. It is suitable for preparing thick compacts. When comparing the casting method with other forming methods for ceramics, the following advantages and disadvantages can be listed.

| Advantages | Disadvantages |
|---|---|
| 1. Complicated shapes can be formed. | 1. Not suitable for mass production of simple shapes and small-sized products. |
| 2. Forming of large-sized products is possible. | |
| 3. Forming equipment is inexpensive. | 2. Area for the equipment is necessary. |

Because of the advantages mentioned above, casting has come into favor for the forming of fine ceramics as well as ceramics. Forming of large-sized alumina products by using casting is also being done by our company.

## 2. Casting Process

The casting process is shown in Figure 1. The material is pulverized, together with water and deflocculant, up to the prescribed particle size with a ball mill until it becomes a slurry. Agitation of slurry is made by an arc for a fixed period for stabilization (aging). After moisture and viscosity have been adjusted, it is subject to vacuum defoaming. A plaster mold provided with mold treatments, such as mold lubricant application, is assembled in advance and slurry is poured into it. A cast is formed along the mold surface by the water absorption of the mold. There are cases in which excessive slurry is exhausted upon reaching the prescribed thickness (sludge disposal process) and cases in which all slurry is accumulated in the mold.

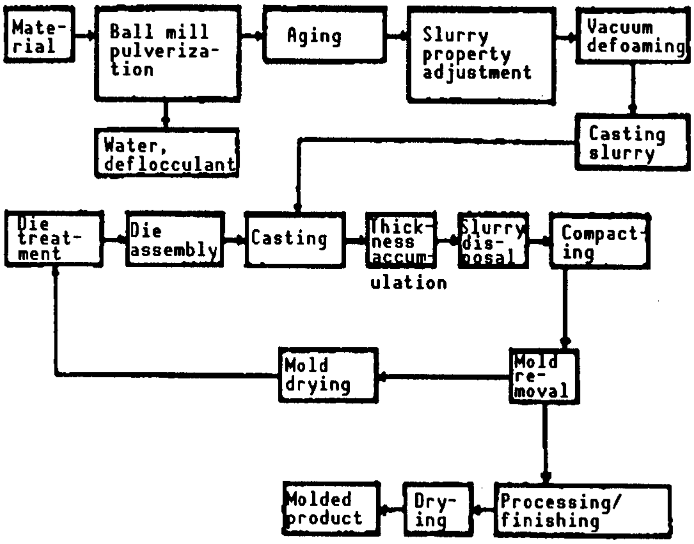


Figure 1. Casting Process Drawing

Because the water absorption of the mold against the cast in the mold continues, the moisture in the accumulated layer further reduces and the casted body (cast) increases in hardness. The cast shrinks and separates from the mold (earth compaction process). The casted body is released from the mold. After a greensand treatment and finishing, the cast is dried. The plaster mold is dried and used repeatedly.

## 3. Plaster Mold

The plaster mold is classified into $\alpha$-type hemihydrate and $\beta$-type hemihydrate gypsum by the burning method. A feature of the $\beta$-type hemihydrate gypsum is that it consists of a fine crystal field of sets that disperse into fine particles when cool water is added and strongly agitated. Therefore, the water-carrying capacity (water/plaster x 100) is high and the available hardened body is of low density and inferior in strength and wear resistance. On the other hand, it is suited to atmospheric casting of ceramics because of its high water-absorption property.

Our company has taken advantage of the fact that the water-absorption property is great and is utilizing the plaster mold. It is using the $\beta$-type hemihydrate gypsum for casting of large-sized alumina products.

The crystal structure generated by the hydration of a hemihydrate gypsum is affected by the water-carrying capacity, temperature of plaster slurry, strength of agitation (agitation rate, time, blade shape, blade size), and water quality. These details are not covered by this article.

An example of the pore-sized distribution when the water-carrying capacity is 75 percent and an example of the thickness accumulation rate constant against the slurry temperature are shown in Figures 2 and 3, respectively.

```
        Incremental volume (CC/G) vs. pore diameter
                    100% = +0.308455E + 000

        0%          20%          40%          100%
        I............I............I............I
  +5.96-*
  +4.66-*
  +3.65-*
  +2.86-*
  +2.24-*
  +1.75-****************************************
  +1.37-***********************
  +1.07-**************
 +0.839-*********
 +0.657-******
 +0.514-****
 +0.402-***
 +0.315-**
 +0.247-**          Intrusion (pressurization) data summary
 +0.193-**
 +0.151-**                Total intrusion volume "    +0.6786 CC/G
 +0.118-**                       Total pore area "   +11.6024 SQ-M/G
+0.0926-**         Medium pore diameter (volume) "    +1.7095 µm
+0.0725-**         Medium pore diameter (area)   "    +0.0200 µm
+0.0567-*          Average pore diameter (4V/A)  "    +0.2339 µm
+0.0444-*                           Bulk density "    +0.9474 G/CC
+0.0347-*            Apparent (skeletal) density "    +2.6533 G/CC
                   % Capillary = +85.5636
```

Figure 2. Pore-Sized Distribution of Plaster (Gypsum) Mold

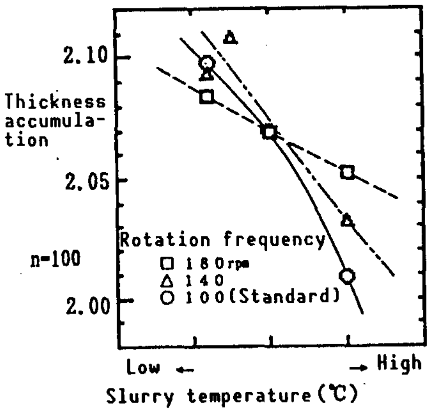


Figure 3. Relationship Between Slurry Temperature and Thickness Accumulation

## 4. Properties Demanded in Casting Slurry

To obtain superior casting products it is necessary to adjust the following various properties to suitable values.

(1) Fluidity of slurry
(2) Thickness accumulation rate
(3) Mold releasing property of cast
(4) Shape retaining property
(5) Workability

However, there are many mutually confusing and extremely complicated factors affecting these slurry properties. Factors when preparing the slurry have been listed in Table 1. Although much research has been done on the relationship between these factors and slurry properties, a direct correspondence has not been made yet.

Table 1. Preparation Factors Affecting Slurry Properties

1. Brand and blending composition of material
2. Type, volume, and corrosion of soluble salts resulting from materials and water
3. Ball mill pulverizing conditions—mill size, charging of material and spherulite, spherulite size, moisture content, and deflocculation time
4. Type, adding content, and adding time of deflocculant
5. Agitation rate and time in aging
6. Moisture content, particle size, and temperature of slurry
7. Using percentage of excavated debris

1) Decomposed products of vegetation contained in materials

Control of slurry properties can be more easily accomplished by selecting certain basic characteristic values as parameters. These parameters can be used to obtain a correlation between preparation factors and slurry properties, determine what values the basic parameters should have to obtain required slurry properties, and move the preparation factors to attain this purpose. The following are the basic characteristics controlling slurry properties.

(1) Shape and particle size distribution of particles composing the base system.
(2) Dispersion state of particles in slurry.
(3) Hydration property of particles.

We have selected the following three basic parameters as those that can be expressed as numerical values. They are slightly lacking in strictness, but measurement can be easily made, and they are used for slurry control.

| | |
|---|---|
| (1) Particle filling rate: | Particle volume percentage in dried base. |
| (2) Specific surface area: | Specific surface area calculated from thickness accumulation rate of slurry. |
| (3) Particle hydration property: | Water film thickness of particle calculated from the moisture at thickness accumulation of the casted body. |

Among these, particle filling rate and specific surface area are especially important parameters because they essentially control the base properties. The corresponding relation between these parameters and properties demanded in the slurry are qualitatively shown in Figure 4.

| | Flowability | Thickness accumulation property | Mold-removing property | Shape-retention property | Workability |
|---|---|---|---|---|---|
| Particle-filling rate ↗ | ↘ | ↘ | ↗ | ↗ | → |
| Specific surface area ↗ | → | ↘ | ↗ | ↗ | → |

Figure 4. Changing Trend of Slurry Properties When the Particle Filling Rate and Specific Surface Area Have Been Enlarged

Because the green base material strength increases as the particle filling rate of the base material increases and the specific surface area of the base material increases when the latter process is considered, it excels in formability such as mold-releasing and shape-retaining properties and workability. Burnt shrinkage is small in the sintering stage, and sintering is also easy. These become especially important factors for large-sized products.

Care is necessary, however, as the thickness accumulation rate decreases and the thickness accumulation moves in the undesired direction in the base slurry with a large particle-filling rate and specific surface area.

## 5. Particle Size Distribution

Studies on making the particle-filling rate and special surface area values suitable is necessary when preparing casting slurry. Generally, the particle-filling rate is from 55~70 percent, and the specific surface area is from 1~5 x $10^5 cm^3/cm^3$.

Particle size distribution and the deflocculant condition of the material during preparation cause the particle filling rate and specific surface area to fluctuate greatly. The Furnas experiment (Figure 5) and Andreasen close-filling grain-size curve (Figure 6) provide data on particle size distribution.

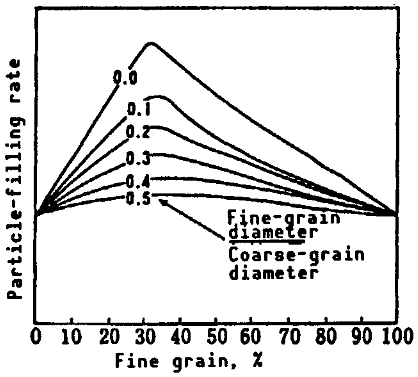


Figure 5. Filling of Dried Powder Consisting of Two Components of Coarse and Fine Grains

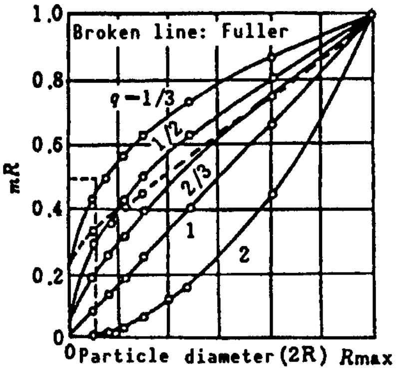


Figure 6. Dense Filling Particle Size Curve of Andreasen

Figure 5 shows a case in which dried powder consisting of two components, coarse and fine grains, has been filled. It has been shown that the maximum value of the filling rate exists when the fine particle is 30~40 percent, and that the filling rate increases as the particle size difference of coarse and fine grains become larger.

On the other hand, Figure 6 shows by the following equation that the continuous particle system becomes dense when the maximum particle diameter is made $R_{max}$. The optional particle diameter is made R and q is one-half to one-third. There are many production methods for alumina materials generally sold, such as those by the Bayer's process, the ammonium salt decomposition method, and the vapor phase synthesis method. When an alumina material by the Bayer's process is used as an example,the crystallite size differs according to the temporary burnt temperature. There are many cases where the so-called primary particle size ($\alpha$-alumina) is decided.

Figure 7 shows the pulverizing time and particle size distribution change of alumina. In comparing it with the Andreasen curve, the percentage of the fine particle portion is insufficient.

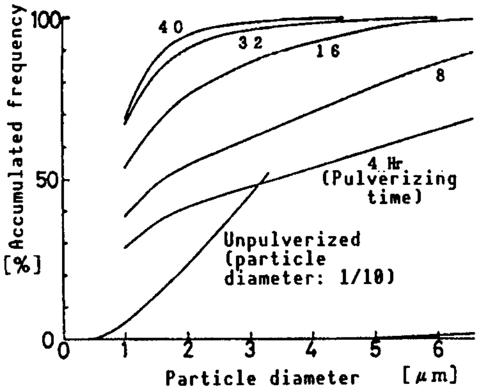


Figure 7. Particle Size Distribution Change of Alumina

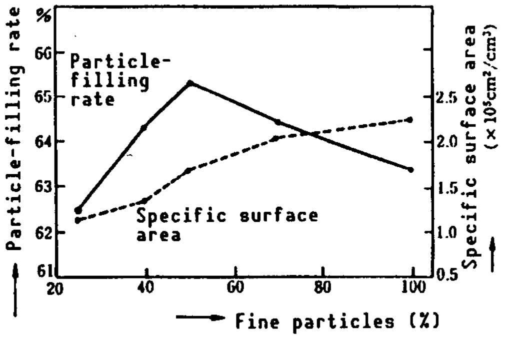


Figure 8. Relationship Between Fine Particle Quantity, Particle Filling Rate, and Specific Surface Area of Alumina Casting Base

Figure 8 shows the relationship between the particle filling rate and specific surface area against the fine particle proportion in case of two types of alumina with different particle sizes. The mean diameter is 3 μm for the coarse grain and 1.3 μm for fine grain. Each slurry has the maximum deflocculation state by hydrochloric acid. The maximum value of the particle filling rate is 50 percent for fine particles in this case, but the curve well resembles the Furnas result.

The specific surface area increased almost in proportion to the amount of fine grains.

It is clear from these results that a fine grain portion of 40~50 percent, with a large particle size difference between coarse and fine grains would make the particle filling rate large. Moreover, the smaller the fine grain size and greater the fine particle quantity, the larger the specific surface area.

## 6. Deflocculation Condition

Because fine particles are easily subject to cohesion, even when a suitable particle size distribution has been obtained by material blending and adjustment of pulverizing conditions, a required particle filling rate and specific surface area will not be available unless a suitable deflocculant is added and the fine particles are dispersed sufficiently. Deflocculation condition is the second important preparation factor for greatly changing the particle filling rate and specific surface area. Details on the deflocculation theory are not covered in this article. In simple terms, however, when electrostatic resiliency works among the particles in the slurry and each particle stably maintains a dispersed condition, it is called the deflocculation condition.

The following conditions are necessary for enlarging the electric charge of particles and deflocculating the slurry. Now, for alkali deflocculation, the following must be considered.

(1) Substitution of negative site anions to monovalent ions, such as $Na^+$ and $NH_4^+$.

(2) Make pH of weak alkaline and substitute the positive site anions to $OH^-$ ions.

(3) Make the ion concentration in the solution and especially the concentration of polyvalent ions such as $Ca^{2+}$ and $Mg^{2+}$ as small as possible.

There are numerous types of deflocculants. Because the optimum deflocculant differs according to the base, its selection is important in casting. Deflocculants can be largely classified into three groups by their operations.

(1) Those working as acid or alkali, such as NaOH, $NH_4OH$, and HCl.

(2) Inorganic salts forming insoluble salt and complex salt against polyvalent cation, such as soda ash, water glass, and polyphosphate.

(3) Those forming organic polyanion, such as CMC salt, lignosulfonic acid, and polyacrylic acid.

Many oxides can be deflocculated by acid or alkali. Which deflocculation of oxidity of alkalinity is better differs according to the base. Because the plaster mold used in casting is easily affected by oxidity, there are many industrial cases when casting is made in the alkali range.

Because the inorganic deflocculant disappears in the burning process, the effect exerted on the sintered material purity is small, and it is widely used in the fine ceramics field.

Various types of salts, including the Na salt, $NH_4$ salt as polyacrylic acid, are used as organic deflocculants. Many are polymers having a carboxyl group or sulfonic group, and they deflocculate in water and generate polyanions. These anions collect the polyvalent ions and advance the Na or $NH_4$ substitution and, because they themselves become absorbed, apply an electric charge to particles. A superior deflocculation action is shown.

The deflocculation force changes greatly with molecular weight and decreases as molecular weight increases. A quantity showing the maximum deflocculation or slightly smaller is generally selected as the addition quantity of deflocculant.

## 7. Casting for Large-Sized Alumina Products

The casting method for large-sized alumina products is a general plaster mold. Forming is possible by making the particle filling rate and specific surface area proper values by adjusting particle size distribution and deflocculation condition of the base.

### 7.1 Particle Filling Rate

When a dried compact is burned at 1,500~1,700°C, a compact in which the particle filling rate is 55~70 percent generates volumetric shrinkage little over about 45~30 percent at burning. Shrinkage is from 24 percent to 20 percent in area. The empty weight of the compact becomes 270 kg by the 1,000 square surface plate. It is clear that frictional resistance with the setter in shrinkage will increase considerably. It is necessary to set the particle filling rate of the base as high as possible, together with studying the oven packing method, for reducing this frictional resistance.

### 7.2 Formability

The relationship between moisture, strength, and deformation of the base after mold release has been shown for alumina base and ceramic base (Figure 9). The strength of the alumina base after mold release is greater than that of the ceramic base. It excels shape-retaining property: however, deformation is small, and it is fragile. Compared with clay bases, the following problems in formability exist.

(1) Cracks easily generate at mold removal, and forming of products with complicated shape is difficult.

(2) Because cracks generate as a result of shrinkage difference stress when the moisture-reduction rate at drying is not uniform, control of drying conditions is difficult.

(3) Greensand processing, such as drilling and cutting, are difficult.

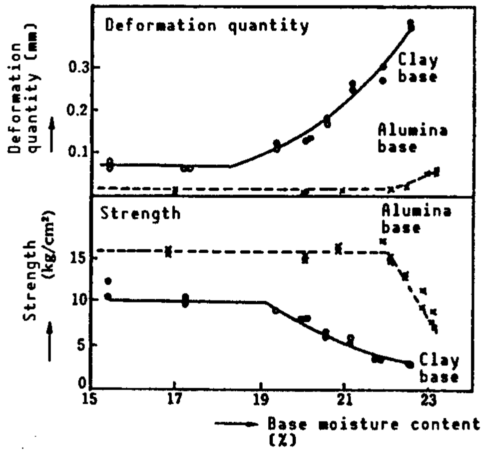


Figure 9. Relationship Between Moisture Content, Strength, and Deformation Quantity of Clay Base and Alumina Base

A back system, which has added the minimum required clay soil as the plasticity endowing agent and organic binder for solving these problems, has been developed as the large-sized products casting base. Shrinkage stress by the compact interior water distribution in the earth-compacting process has been relaxed through plastic deformation. Moreover, the mold release is better and the mold-releasing property is improved.

### 7.3 Base Physical Properties

Table 2 compares the physical properties of large-sized products casting base with those of other materials.

Table 2. Comparison of Physical Properties of Large-Sized Alumina Ceramics and Metal Materials

| | | Large-sized alumina ceramics | | | Cast iron | Stain-less | Aluminum | Stone material gabbros |
|---|---|---|---|---|---|---|---|---|
| | | AC 270 purity 87% | AC 203 purity 90% | AC 291 purity 99% | FC25 | | | |
| Specific gravity | | 3.4 | 3.5 | 3.8 | 7.8 | 7.9 | 2.7 | 3.0 |
| Water absorption | % | 0 | 0 | 0 | 0 | 0 | 0 | 0.03~0.3 |
| Bending strength | kg/mm$^2$ | 32 | 32 | 32 | 40 | 35 | 17** | 3~5 |
| Young's modulus | ×10$^4$ kg/mm$^2$ | 2.4 | 2.7 | 3.5 | 1.1 | 2.0 | 0.7 | 0.3~0.9 |
| Specific rigidity | ×10$^7$ mm | 7 | 7.7 | 9.2 | 1.4 | 2.5 | 2.5 | 1~3 |
| Thermal expansion coefficient* | ×10$^{-7}$/℃ | 43 | — | — | 110 | 173 | 230 | 80 |
| Thermal conductivity | cal/cm·sec·℃ | 0.04 | 0.05 | 0.06 | 0.11 | 0.04 | 0.49 | 0.003 |
| Corrosion resistance (Erosion degree 90℃) mg/cm$^2$·day | 30% NaOH | 0.6 | — | 0.2 | 0.5 | 0.5 | — | — |
| | 67% $HNO_3$ | 0.1 | — | 0 | — | 0.2 | — | — |
| | 95% $H_2SO_4$ | 0.1 | — | 0 | — | 0.7 | — | — |

* 15~25℃ ** Tensile strength

It has the following characteristics compared to metallic materials when used as industrial machinery members.

(1) Light weight is possible because the specific rigidity is high.

(2) Thermal variation is small because the thermal expansion coefficient is small.

(3) Strength under high temperature is great.

(4) Because it is a brittle body, it is fragile and weak against shocks.

(5) Because there is no plastic deformation under ordinary temperature, it excels in dimensional stability. Finishing precision can be made high.

(6) It is hard and difficult to wear, and processing is difficult.

(7) It excels in corrosion resistance and is strong against rust.

## 7.4 Forming Method for Large-Sized Products

The casting method of large-sized products using the plaster mold is shown in Figure 10. It corresponds to large-sized products and products with complicated shapes made by the slurry-casting method, solid-casting method, junction-molding method, and a combination of these methods.

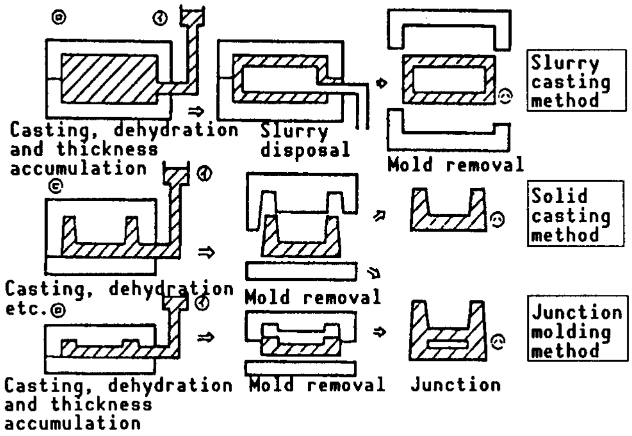


Figure 10. Production Method for Large-Sized Alumina Products

When cast thickness is more than 20 mm as the thickness of a compact, the compact interior moisture content (or moisture-decreasing content) between the section facing the mold and the cast inner wall differs greatly in places. It is susceptible to crack generation at drying by the shrinkage difference (stress). A guideline for compact thickness is 20 mm in the slurry-casting method, 40 mm in the solid-casting method, and about 90 mm in the junction-molding method.

Possible production dimensions are as follows:

| | |
|---|---|
| • Width | 1,500 mm maximum |
| • Length | 3,000 mm maximum |
| • Height | 600 mm |
| • Disk | $\phi$ 1,500 mm |
| • Cylinder | $\phi$ 200 x $\ell$ 800 mm |

The following positive achievements have been obtained:

| | | |
|---|---|---|
| Static pressure guiding block: | 110 x 2,750 x 40t mm | (AC-270) |
| Large-sized precision surface plate: | 1,000 x 1,000 x 200t mm | (AC-270) |
| Stage plate: | 1,090 x 1,090 x 45t mm | (AC-203) |

## 7.5 Forming Design

I have listed as one of the characteristics of alumina ceramics that specific rigidity was high. There are many cases when the compact shape is designed of a rib structure to further decrease weight. The result is further high rigidity and the prevention of softening deformation at burning. This design takes advantage of the casting-method characteristic. It is important to design the thickness of the rib gathering point to a rib shape so that it is equal or close to the rib thickness (Figure 11).

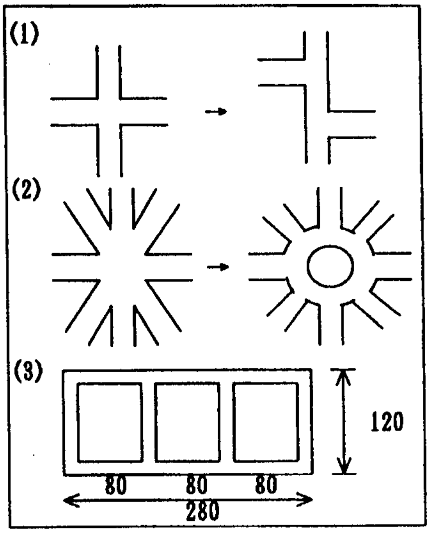


Figure 11. Design Examples for Rib Structures

Always provide an extract taper for a rib structure by rapping and establish all angular sections of the mold by as large an R as possible.

There are those shown in Figure 12 as the softening deformations at burning and since the method of deformation differs according to the burning method (oven packing method), thickness, etc., in case of the rib structure for preventing this, studies complying with the product shape are necessary in case of the structural design.

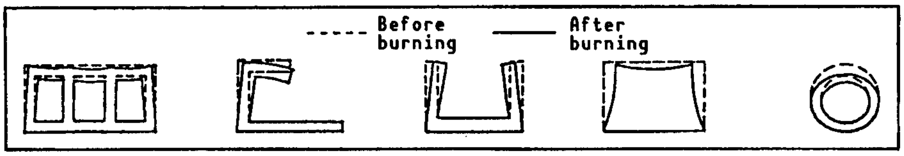


Figure 12. Shape Deformations Before and After Burning Process

### 7.6 Dimensional Tolerance of Compact

The shrinkage of drying, the shrinkage at burning, and burning deformation need to be considered when setting the dimension of the burning body for compact dimension. At present, a dimensional dispersion of 0.5~1.5 percent and a deformation of 1~3 mm/1,000 mm are suggested because of burning shrinkage of about 40 percent in volume.

It is desirable that dimensional changes against set values in the compact be as small as possible.

### 7.7 Plaster (Gypsum) Mold

The plaster mold is prepared by defoaming and mixing gypsum powder and water uniformly and pouring it between the master die and molding flask. The plaster mold is about 1,400 square x 500t for the 1,000 square surface plate. Because it interferes with handling when only the strength of the gypsum material is used a reinforcing material is used whenever necessary. Together this results in adopting a sufficient thickness for increasing strength. Iron reinforcing rods will be assembled in a form complying with the shape of the compact and buried within the plaster mold.

The mold structure basically consists of the cope and drag. There are also cases where the middle or drum mold of the rib structure section is inserted according to the compact shape. These molds are dried well and mold assembly is conducted so that there is no leakage of casted slurry. A simplified molding machine is necessary because the weight of the molds amounts to only several hundred kilograms. Casting is conducted under ordinary temperature and atmospheric pressure, and, when injecting slurry into the mold, a casting rate control is necessary so that air is not sucked in.

### 7.8 Drying of Compacts

The typical relationship between base shrinkage amount and moisture is shown in Figure 13. The base consists of the particle sold phase and water at point A in the drawing. A water screen exists between particles. Because water between particles decreases when moisture decreases, the distance between particles decreases and the base shrinks. Fellow particles directly contact at point B in the drawing. Air is substituted after moisture reduction, and shrinkage of the base does not occur.

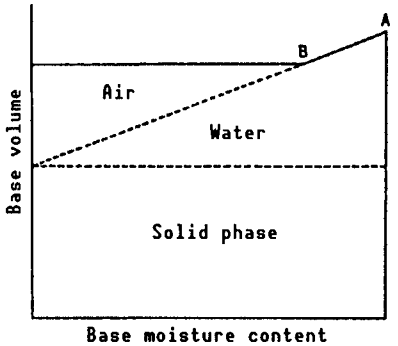


Figure 13. Relationship Between Volume and Moisture Content of Base

The component at point B is called the shrinkage critical moisture. It is necessary to dry uniformly so that a moisture difference does not generate in the compact until reaching the shrinkage critical moisture for holding down the drying limit. Therefore, it is necessary to adopt the following steps. First, the moisture difference in the thickness accumulation and slurry-disposal processes must be as small as possible. Next, get rid of the generated moisture difference as soon as possible because the base is capable of plastic deformation. And last, refrain from generating a moisture difference during the drying process.

After the compact has shrunk and the mold has separated in the compacting process, remove the mold. Because immediately after the mold is released, the compact is in a soft condition (deformation can be generated by depressing the compact with the fingers), it is necessary to prepare a receiving mold to prevent deformation by the empty load. The compact will pass the drying process, and, after slow drying in room temperature, it passes through (30°C) and high-temperature drying (45°C) until it is fully dried.

When the thickness greatly differs in places in a compact, it is necessary to develop a means so that moisture differences are not made and the generation of cracks is prevented during the drying process.

### 7.9 Casting Examples of Large-Sized Alumina Products

The following large-sized alumina products are possible with casting.

- Guide axis
- Large-sized surface plate
- Static pressure guiding block
- Insulating ring
- Lapping machine disk
- Others

## High-Pressure Injection Molding for Ceramics

906C7538E Tokyo DAI 21 KAI KO ON ZAIRYO GIJUTSU KOSHUKAI in Japanese Feb 90 pp 123–132

[Article by Katsuyoshi Saito, Industrial Laboratory, Kyoto City]

[Text] **1. Introduction**

The process of high-pressure injection molding of ceramics is shown in Figure 1. Following are the main technical points of this process.

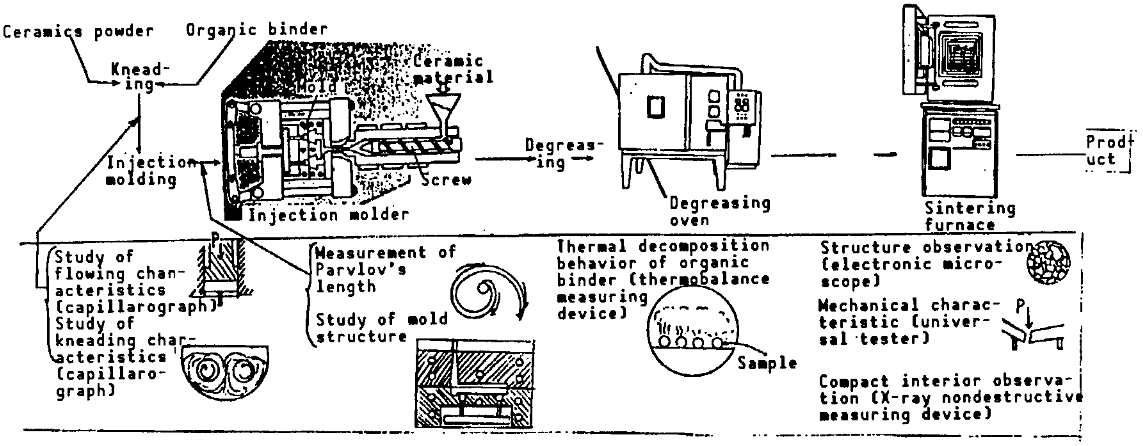


Figure 1. Injection–Molding Process

(1) Design of a mold and an expensive means of developing a mold with superior precision.

(2) Selection of binders with an easy mixing property, good formability, and superior degreasing property.

(3) Determination of how fast degreasing method can be made without defects.

## 2. Selection and Actual State of Binders

Binders consist of the bonding agent, lubricant, and plasticizer. A surface-treatment agent is used for powders with an inferior moisture acceptance.

In selecting binders, emphasis should be placed on formability and degreasing properties. A method using triangular coordinates follows.

A bonding agent with superior flowability on the upper part of the triangular coordinates is shown in Figure 2. Bonding agents include polyethylene polypropylene, polystyrene, EVA resin, and EEA resin. A bonding agent with a superior degreasing property is placed on the left side. These bonding agents include polystyrene, APP, ethyacryl resins (butyl and isobutyl), polyacetal, and cellulose system. Those on the right side are lubricants and those having a lubricating action. These are the waxes and stearate. The plasticizers are generally D.B.P. and D.O.P. A fixed volume has been put out to the coordinates exterior, and the addition content is 5~20 percent of the bonding agent.

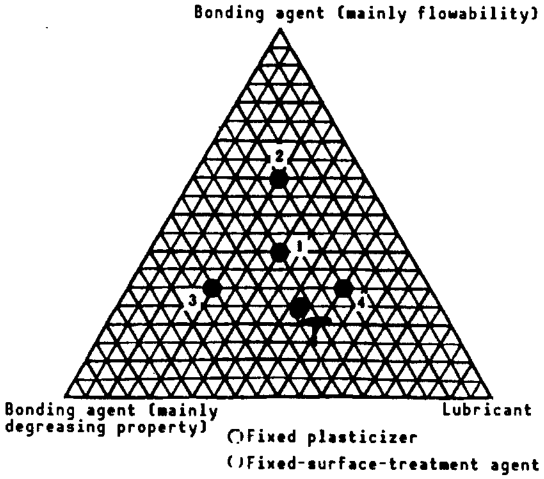


Figure 2. Combined Triangular Coordinates of Binders

For example, EVA resin was used for the bonding agent (mainly flowability), polybutylmethacrylate was used for the bonding agent (mainly degreasing property), stearate was used for the lubricant, and dibutylphthalate was used for the plasticizer. The arrangement of central point 1 was made in the triangular coordinates, and the results by mixing, forming, degreasing, and burning were observed. When superior results are obtained, further studies will be made near central point 1. If defects are found, similar studies will be made on left side point 3, upper point 2, and right side point 4. In the sample arrangement, point 2 showed good formability, but it was susceptible to a defect in degreasing. Point 4 has extremely good formability but the compact was easily destroyed because it was too soft. Flowing is difficult at point 4 unless the forming temperature and pressure are high, but the degreasing property is superior. Superior results are available at point 1 because it is well harmonized.

When only results with defects are available in all points of the triangular coordinates, studies the combination of types of bonding agents and lubricants mentioned above should be changed.

The problem next is how much binder should be added quantitatively. It is better to calculate the adding content by capacity (volume) rather than weight. In other words, when the specific gravity of binders equal to a specific gravity 4 is made 1 (actually, it is calculated more minutely and figures to the second decimal point are obtained) in the case of alumina, alumina of 100 g and binders of 25 g are heated and mixed (volume ratio is 1:1). There is no problem when it has a glutinous condition, but, when it has a crisp condition, further binder should be added. The composed products are pulverized into pellets and powdered condition. Flowability is obtained in advance by heating with a high-chemical-system flow tester, capillarograph, and melt indexer.

The high-chemical-system flow tester should have an outflow of more than 0.05 $cm^3/sec$ when the pressure of the 1 x 10 mm $\phi$ nozzle is 30 $kgf/cm^2$. (The temperature is optional.) The apparent viscosity is less than 1000 poise (optimal temperature) in the shearing rate range of 100~1,000 $sec^{-1}$, with the 1 x 10 mm $\phi$ nozzle in the capillarograph. The load should be 6,200 g. The temperature should be 180°C. Outflow should be more than 30 g/10 minutes.

Forming, degreasing, and burning are conducted when the heated flowability is sufficient, and a product or sample is prepared. When the volume ratio of the powder binders is more than 50:50 percent, it is most likely that defects will generate easily in degreasing.

The volume ratio of powder binders should be changed gradually and tested.

The addition content of binders is related to the tap density and specific surface area of the powder. The volume of binders becomes great for those with too large a specific surface area, which is not suitable. A specific surface area of less than 10 $m^2/g$ is generally preferable in injection-molding powders. Studies on binder quality and quantity should be conducted.

The volume ratio of the powder and binders in the alumina system will work at 60:40 percent. A volume ratio of 45~55:55~50 percent will work in the zirconia system, and a volume ratio of 52~54:48~46 percent will work in unoxidized substances (SiC, $Si_3N_4$).

Generally speaking, however, degreasing would also be easy when all powders are formed at the ratio of about 60:40 percent. Particle size adjustment of powders and using surface treatment agents are needed.

Stability in mixing and forming and instability in degreasing are demanded in binders. This totally contradictory fact is needed in a single process. Binders are a compromise, an important point to consider when selecting them. Moreover, there are no equations or theories yet calculated—all selections of binders are the result of trial and error. Therefore, "know-how" is of great importance.

As an example, one ceramics manufacturer studied 100 points for alumina, zirconia, and $Si_3N_4$ triangular coordinates by arranging the EVA resin, acryl resin, denatured wax, and D.B.P. system binders. The manufacturer obtained superior results by the arrangement of 2:3:4:1. Point T is shown in Figure 2.

In addition, superior results have been obtained by adding the EVA resin (VE633), acryl resin (CB-1), and denatured wax (Selna ND-793) in the triangular coordinates and arranging D.B.P. and Orikokus KD-140 (Kyoeisha Fat and Oil Co., Ltd.) to improve the wetness of the surface.

### 3. Kneading

The purpose of kneading is to uniformly and effectively provide the minimum required coating of binders to each grain of the powder. The laboplast mill, which is shown in Photo 1 [not reproduced], was used as the principle (Figure 3) for testing and small quantity production in heating and kneading. The laboplast mill has been enlarged for practical use. The kneading operation is conducted by using a pressure-kneading kneader.

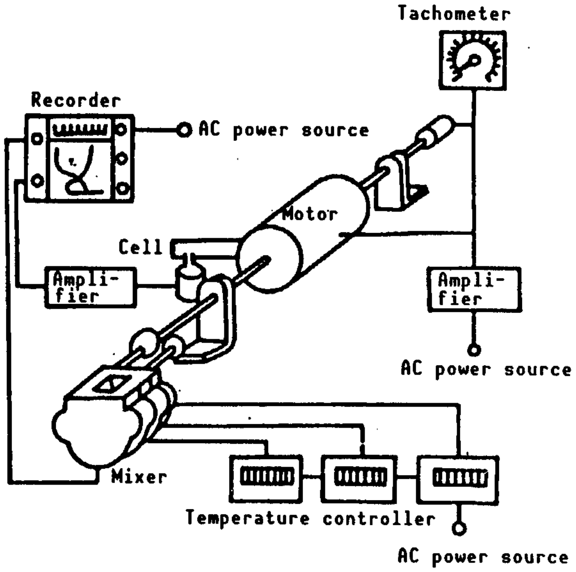


Figure 3. Principle of a Laboplast Mill

Because the change of shearing torque (kg·cm) for the kneading time and internal temperature can be continuously measured by this laboplast mill, various data are available (Figure 4).

Curve A is the most standard type. This curve is shown when the powder is wetted well by binders and the powder is close to a globular shape or adopts the ordinary densest filling distribution. Curve B occurs when the torque value lowers with time. This curve is seen when used binders are decomposed by heat and are of low molecular weight. Curve C, on the contrary, is seen when a chemical reaction occurs in the interior of the binders by the heat of the used binders or when the binders and powder have reacted. For curve D the powder has been crushed into extremely fine powder. This curve is seen in those having a squarish form, those with a gourd shape, and those in which the kneading torque becomes high because the binders do not wet well with the powder. The kneading torque lowers after a certain period. Curves A, B, C, and D occur when binders have been tentatively inserted sufficiently into the powder. Those showing a torque value that does not lower even after the elapse of time or slightly rises as shown in curve E occurs when the addition content of binders is of small quantity. Although it has apparently been kneaded tentatively, a friction between the powders generates, and the equilibrium state slightly rises without the torque value reducing because each grain of powder has not been coated sufficiently by binders. The point at which the torque value becomes fixed within a certain time is the point at which sufficient kneading has occurred. There may be problems under microobservation. Suffice it to say that a rule of thumb is that kneading is complete when it becomes fixed.

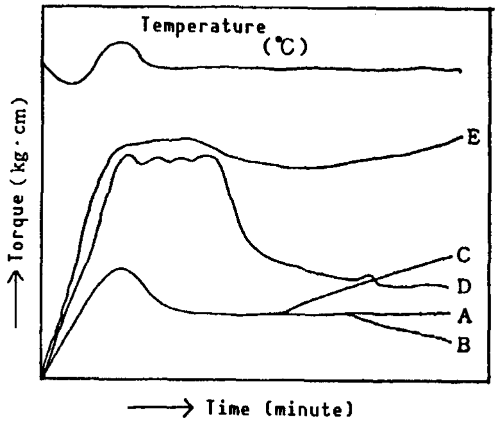


Figure 4. Kneading Behavior of a Laboplast Mill

## 4. Flowability

Composed products using alumina, polybutylmethacrylate (PBMA), polystyrene (PST), atacticpolypropylene (APP), and stearate (ST) are shown in Table 1. They have been kneaded at 160°C for 40 minutes by the laboplast mill. The flowing characteristic of the composed products was measured by a capillarograph.

Table 1. Composition (wt%) of Composed Products

| Item | $Al_2O_3$ | Pst | PBMA | APP | WAX | St | Total |
|---|---|---|---|---|---|---|---|
| A' | 100 | 3.30 | 3.30 | 9.44 | — | 0.46 | 116.5 |
| B' | 100 | 3.30 | 3.30 | 4.72 | 4.72 | 0.46 | 116.5 |
| C' | 100 | 3.30 | 3.30 | — | 9.44 | 0.46 | 116.5 |

The apparent viscosity for the shear rate of the composed products measured by the capillarograph is shown in Figure 5. Generally, forming is possible when the shear rate is less than $10^4$ poise at $10^2$~$10^3$sec$^{-1}$. Parvlov's mold (Figure 6) is frequently used as a guideline for actual injection molding. When measuring the flow length of various composed products, the formable length is more than about 10 cm. Moreover, the activation energy of flow was 9~28 Kcal/mol at the shear rate of 1.2 x $10^2$~6 x $10^2$sec$^{-1}$ of the capillarograph. An activation energy of more than 10 Kcal/mol is necessary.

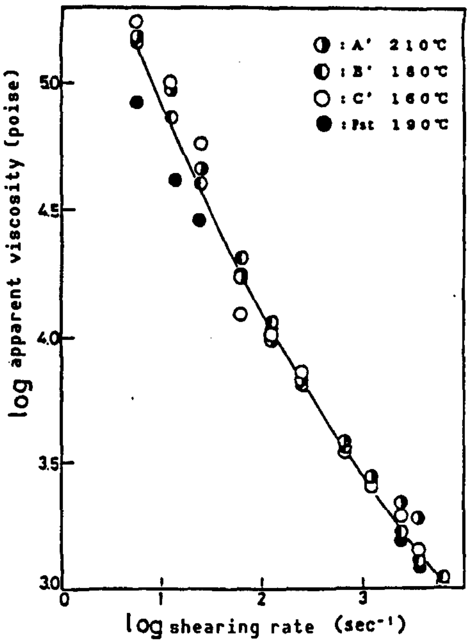


Figure 5. Change of Apparent Viscosity Against Shearing Rate

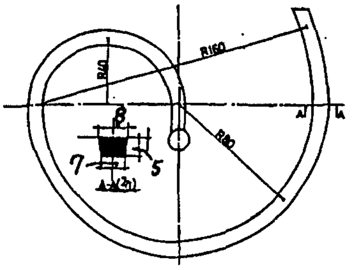


Figure 6. Parvlov's Mold

## 5. Degreasing Method

### (1) Atmospheric Pressure

The thermal decomposition curve of binders by the differential thermobalance becomes a reference for deciding the degreasing program. From among Figures 8 to 10, select from two to four types and make it a curve so that thermal composition curve becomes gently-scoped while referring to the item of binder selection.

### (2) Pressurization

The reduction effect of the heating decomposition gas capacity (Figure 11) is available by pressurization. Because the product (PV) of the generating gas capacity at a certain temperature and the gas pressure is fixed, the generating gas capacity is reduced to one-fifth in comparison to that at atmospheric pressure, where the pressure force is 5 kg/cm$^2$G. The pattern sample (Figure 11) consisting of the $Si_3N_4$ compact (cutter blade) of 12t x 30W x 85 mm (35 g), $Si_3N_4$ (Denka SN-9FW) at 70.5 percent, $Y_2O_3$ at 4.7 percent, $Al_2O_3$ at 3.2 percent, thermoplastic resin (PE·PP) at 13.7 percent, stearate at 2.5 percent, wax at 4.9 percent, and plasticizer at 0.5 percent was good. Thirty-four of 62 samples conducted by the Tokai Konetsu Kogyo Co., Ltd., were good.

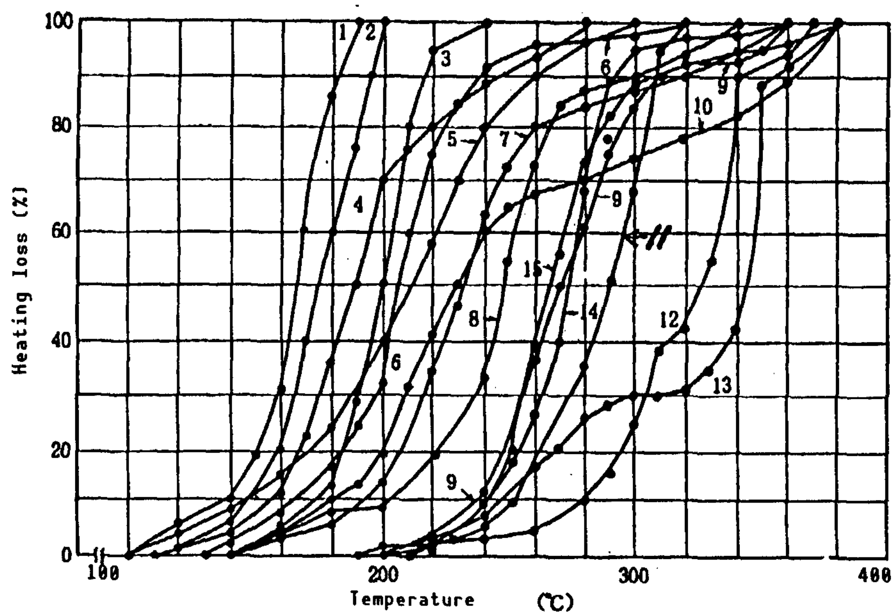


Figure 8. Thermal Decomposition Curves of Binders by Differential Thermobalance (in air, temperature up rate 2°C/min)

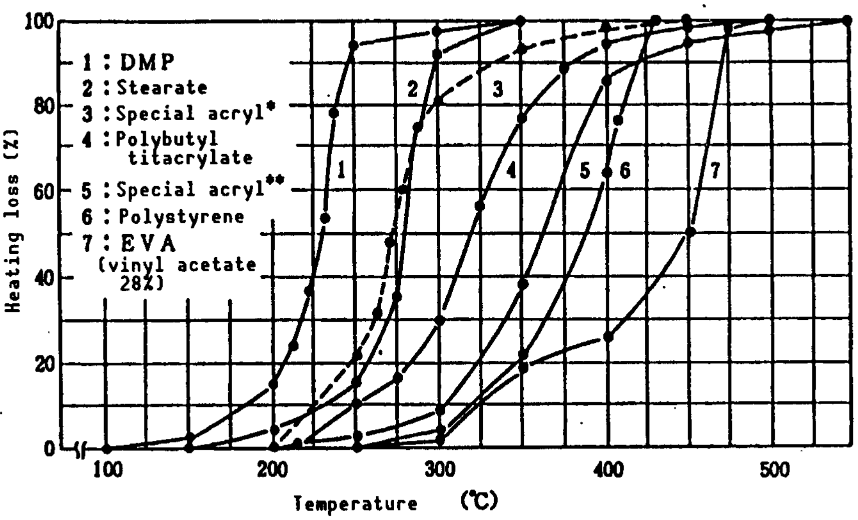
1. DEP
2. DBP
3. DOP
4. Stearate
5. Liquid polystyrene
6. Paraffin wax
7. APP (low molecular)
8. APP (high molecular)
9. Styrene oligomer
10. Micro wax #200
11. Polystyrene
12. High-density polyethylene
13. Ethylene-vinyl acetate copolymer;
14. Polypropylene
15. Butyl polymethacrylate

**(3) Decompression**

When direct decompression is made, the binder swells like a "millet cake." Therefore, after removing 10~20 percent by the volume percentage of binders in advance by other atmospheric extractions, the decompression method is effective. Those that have been degreased by 20~30 volume percentage by atmospheric pressure in advance can be degreased up to 500°C in 2~4 hours at the decompression of $10^{-2}$~$10^{-1}$ torr in the furnace of Shimadzu Corp. (thickness 3~5 mm).

**(4) Extraction**

According to U.S. Patent No 4,197,118 of 8 April 1980, low-molecular-weight polyolefin is used for the binder, and extraction is made by using trichlene solvent (Figure 12). A green body with the thickness of 420/1,000th inch is degreased in about 120 hours.



* MMA / BMA / /CHMA / DOP
** BA / IBMA / AA

Figure 9. Thermal Decomposition Characteristics of Binders

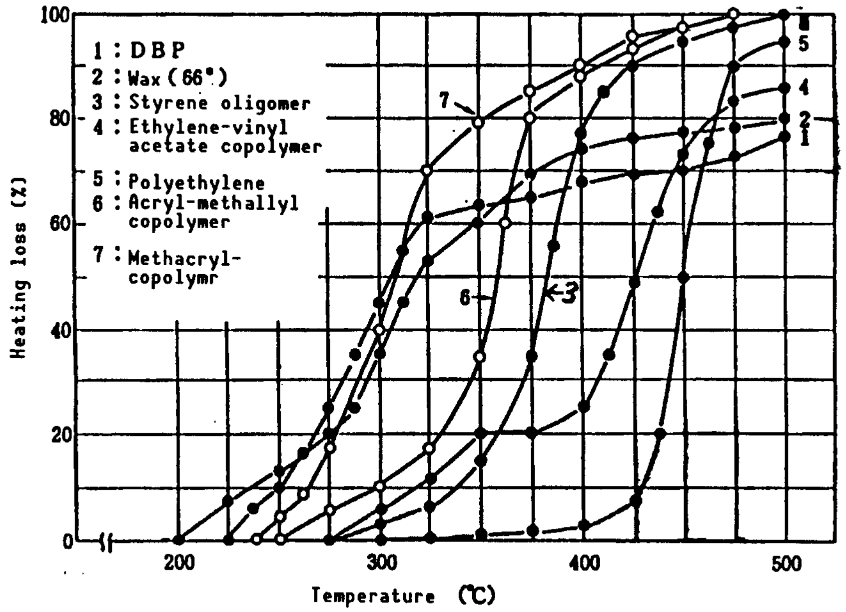


Figure 10. Thermal Decomposition Curves of Binders by Differential Thermobalance (in Ar gas, temperature up rate 3°C/minute)

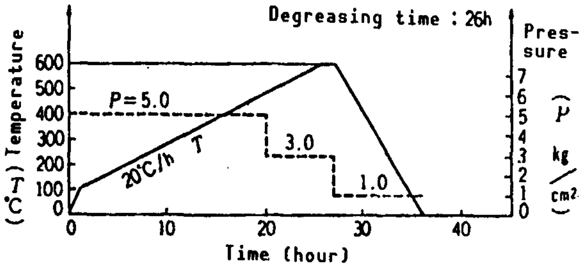


Figure 11. Pressure Degreasing Pattern Example

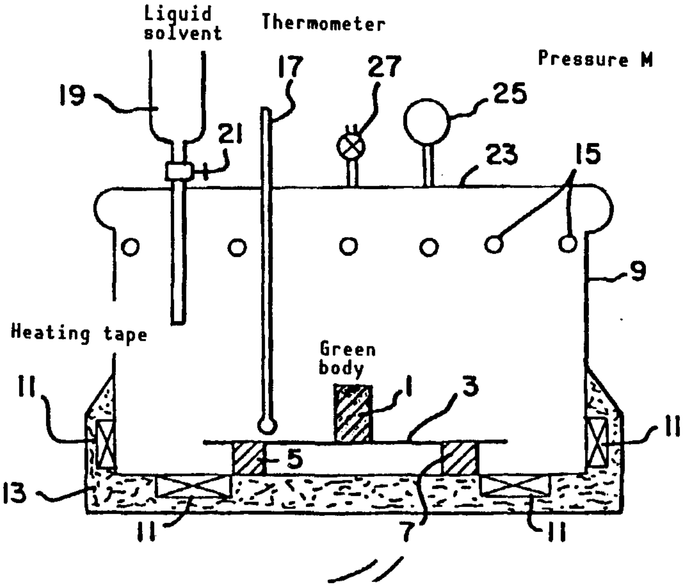


Figure 12. Extraction Degreasing Device

Moreover, according to patent application No 47774 of 1982, stearate and DBP were extracted by hot water (100°C) from those that had been formed by APP, stearate, and DBP binder. Atmospheric degreasing was made after this, and superior results were obtained.

**(5) Supercritical Gas**

That is an application of the extraction technology by the supercritical gas fluid. The advantages are short extraction time (2~3 hours), effectiveness for thick products, low-temperature degreasing, small strain, and an unoxidized atmosphere. However, there are disadvantages such as having a high initial cost, being of a batch type, and being subject to the application of the high-pressure gas regulations. Experimental samples, results of an alumina compact of 325 mmϕ x 15 mm containing 15 weight percentage of stearyl alcohol and stearate as binders are as shown in Table 2.

Table 2. Degreasing Test Results (Sumitomo Heavy Industries, Ltd., Catalog)

| Binder | Liquid | Temperature (°C) | Pressure kg/cm$^2$ Ct | Degreasing rate (%) | Time (hours) |
|---|---|---|---|---|---|
| Stearyl alcohol | $CO_2$ | 45 | 200 | 70.2 | 2.2 |
| Stearyl alcohol | Freon 12 | 120 | 120 | 94.7 | 2.8 |
| Stearate | $CO_2$ | 45 | 200 | 85.0 | 2.5 |
| Stearate | Freon 12 | 120 | 120 | 99.0 | 0.7 |

## 6. Sintering

Oxides are generally sintered in air. Temperature ranges from ordinary temperatures up to 1,000°C at the rate of 400°C per hour and from 1,000°C up to 1,620°C at the rate of 120°C per hour. Temperature is held an hour and a half at 1,620°C. Then temperature is lowered to 600°C at the rate of 400°C per hour and left to cool (for alumina). For zirconia, temperature ranges from ordinary temperatures up to 1,000°C at the rate of 400°C per hour and from 1,000°C up to 1,550°C at the rate of 200°C per hour. Temperature is held for 2 hours at 1,550°C. Then temperature is lowered to 600°C at the rate of 200°C per hour and left to cool. Sintering of nitrides are generally conducted in $N_2$ gas of 10 atmospheric pressure at 1,800°C for 30 minutes. It is generally conducted under the $N_2$ gas atmosphere.

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2. Saito, K., "Basic and Application Technologies of Fine Ceramics/Metal Powder Forming Binders," published by IPC Edition Department, 10 December 1988.

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## Low-Pressure Injection Molding for Ceramics

906C7538F Tokyo DAI 21 KAI KO ON ZAIRYO GIJUTSU KOSHUKAI in Japanese Feb 90 pp 133-142

[Article by Hiroki Miyamoto, chief, Organic New Material Research Section, Industrial Technology Laboratory, Osaka City]

### [Text] 1. Introduction

Because high-density sintered materials such as alumina, zirconia, and silicon nitride have superior heat-resisting properties, corrosion resistance, and high-strength properties, expectations are that they will be developed as new materials usable under severe conditions in which metal and plastic materials are difficult to use. These superior materials also are usable immediately upon being provided with intended shapes. Research has been conducted in the low-pressure injection molding method at our laboratory as the forming technology for this purpose. Explanations on the preparation of material slurry, mold structure, slurry flow in mold, and characteristics of prepared alumina and silicon nitride ceramics follows.

### 2. Low-Pressure Injection Molding Method

An organic binder with paraffinic was, which flows easier than the polymer system organic binder used in ordinary injection molding method in low-pressure and low temperature, is used as the main component in the low-pressure injection molding method. A slurry consisting of the paraffinic system binder and ceramic powder is heated to about 80~100°C and mixed. This slurry is then injected into the mold at low pressure (3~5 atmospheric pressure) and formed by cooling solidification.

The characteristics of this low-pressure injection molding method are that after processing is not necessary, products with complicated shapes can be formed with good dimensional accuracy, and mass production is possible. Moreover, when comparing it with ordinary injection molding methods (several hundred to 2,000 atmospheric pressures), it has advantages. For example, contact surface friction with the ceramics slurry is small because it is of low pressure. It is inexpensive, and mold life is about 10 times longer.

The process for obtaining a sintered material from the material powder of ceramics is as shown in Figure 1.

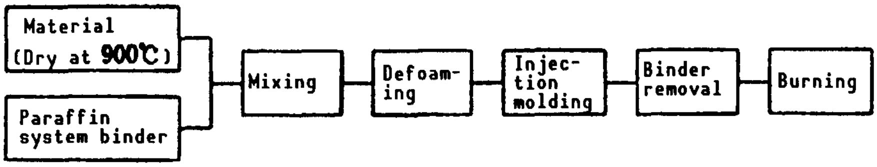


Figure 1. Process Flow of Low-Pressure Injection Molding Method

A schematic drawing of Peltsman's molding machine is shown in Figure 2. The mixture of material powder and organic binder is heated and melted in tank at 80~100°C. After defoaming with a vacuum pump, the slurry is injected at 3~5 atmospheric pressure into a mold heated in advance by hot water. A compact is obtained by cooling and solidifying with cooling water while maintaining pressure.

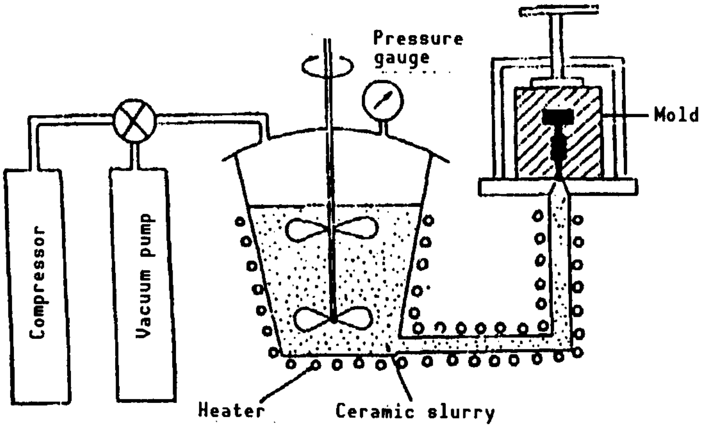


Figure 2. Peltsman-Type Molding Machine

## 3. Preparation of Alumina Sintered Material

### Kneading Method and Effect of Mold Structure

The molding example for $Al_2O_3$ powder is shown in Table 1. The binder volume is 12~20 weight percent. (It is difficult to obtain an accurate sintered material when it becomes more than 50 volume percentage in a material difficult to sinter, such as SiC.) Because binder volume is great, a long time is required for binder removal. When the temperature increase rate is too fast, defects, such as sagging and bulging, generate. When the thickness is 5 mm in the NE-146 15 weight percent binder volume, binder removal is conducted in the $Al_2O_3$ powder bed at 5°C/h in room temperature to 230°C, at 2°C/h in 230°C~400°C, and at 5°C/h in 400°C~550°C.

Although the same ceramics material powder and organic binder are used, the available bending strength and Weibull coefficient will differ greatly according to the mixing method of powder and binder. Examples will be discussed for the four types of mixing methods shown in Figure 3. Methylethyl ketone was used as the solvent in types C and D. The solvent was evaporated at

Table 1. Blending Quantity of Binders and Proper Injection-Molding Conditions

| | |
|---|---|
| $Al_2O_3$: AL-160G4 produced by Showa Light Metal Co., Ltd., (mean particle diameter 0.6 μm) (dried at 900°C) | 850 g |
| Organic binder: Serna NE-146 made by Chukyo Yushi Co., Ltd.,<br>(Paraffin wax 70%: long chain, molecular weight 300~500<br>Microcrystalline wax 20%: Branching, molecular weight 500~700<br>Dispersant: 10%) | 150 g |
| Plate-shaped mold: 50 x 50 x 3 mm, 50 x 50 x 5 mm (injection port 4 mmϕ)<br>Proper injection molding conditions | |

| Compact thickness | Tank temperature | Pipe temperature | Injection time | Injection pressure |
|---|---|---|---|---|
| 3 mm | 100°C | 90°C | 20 hours | 5 kgf/cm$^2$ |
| 5 m | 100°C | 90°C | 30 hours | 5 kgf/cm$^2$ |

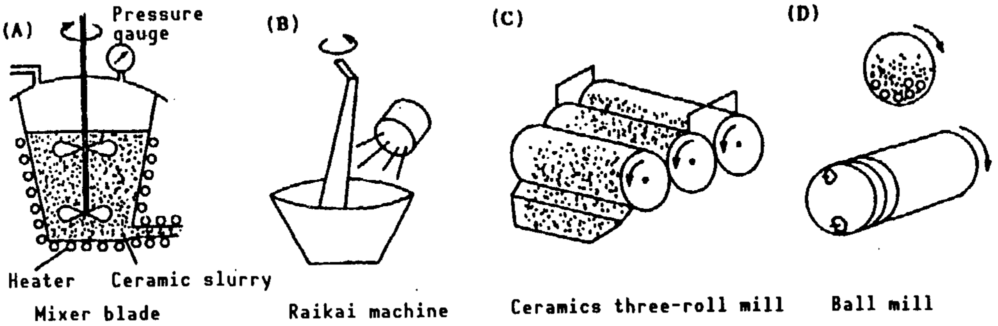


Figure 3. Mixing Methods

70°C after mixing and made into a ceramics slurry. Properties of the slurry are evaluated by the presence of spinnability and undispersed particles (Table 2) and viscosity. The ball mill method (D) has the best dispersion. The mean bending strength and Weibull coefficient adopt the maximum values. It has been shown that dispersion of powder particles controls the characteristics of sintered materials.

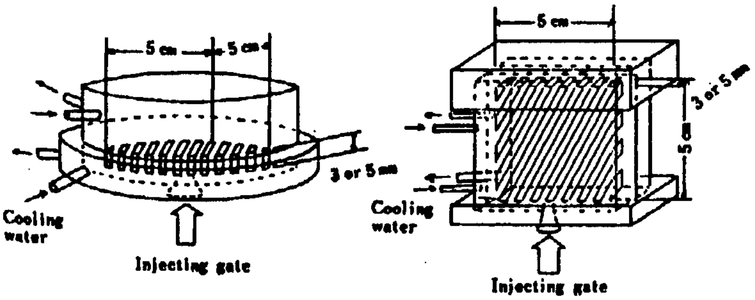
Improvement of bending strength is possible from 40.0 kgf/mm$^2$ to 46.2 kgf/mm$^2$, and the improvement of the Weibull coefficient is possible from 6.9~14.5 by changing the horizontal-type mold (Figure 4-1) to a vertical type mold (Figure 4-2) and reducing as much as possible defects, such as bubbles, at forming (Figure 5).

Table 2. Properties of Ceramic Slurry

| Mixing method | Mixing time | Spinnability | Undispersed particles |
|---|---|---|---|
| Mixer blade | 5~6 hours | Good | Many |
| Raikai machine | 4 hours | Superior | Few |
| Ceramic three-roll mill | 15 minutes | Superior | Few |
| Ball mill | 24 hours | Superior | Nil |

Table 3. Mixing Methods and Mean Three-Point Bending Strength of Alumina Sintered Material

| Mixing method | Mean bending strength | Weibull coefficient |
|---|---|---|
| Mixer blade | 22.1 kgf/mm$^2$ | 3.7 |
| Raikai machine | 28.3 kgf/mm$^2$ | 4.6 |
| Ceramic-three roll mill | 32.5 kgf/mm$^2$ | 5.2 |
| Ball mill | 40.0 kgf/mm$^2$ | 6.9 |



(1) Horizontal-type mold (2) Vertical-type mold

Figure 4. Schematic Drawing of Mold

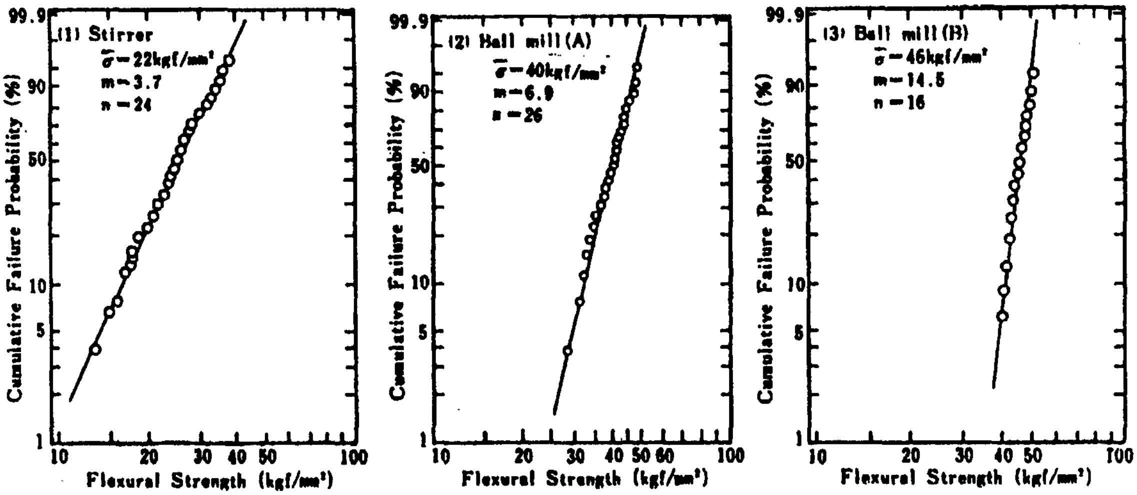


Figure 5. Weibull Plot of Alumina Sintered Materials by Three Types of Preparation Methods
(1) Horizontal-type mold, mixing by mixer blade
(2) Horizontal-type mold, mixing by ball mill
(3) Vertical-type mold, mixing by ball mill

### (4) Preparation of Silicon Nitride

#### Slurry Flow in Mold

The experimental process of sintered material preparation is shown in Figure 6.

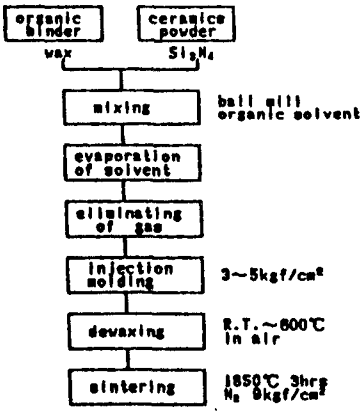


Figure 6. Process To Prepare $Si_3N_4$ Ceramics by Low-Pressure Injection Molding Method

The binder E-146, deflocculant E-503, and amine system activator F-219 made by Chukyo Yushi Co., Ltd., were added to the material powder. This powder had 5 weight percent $Al_2O_3$ and 5.3 weight percent $Y_2O_3$ added as sintering assistants to $Si_3N_4$ (made by Nippon Denko Co., Ltd.; N4-F mean particle diameter is 0.91 μm). Pulverizing was done by ball mill with methylethyl ketone as the solvent. The addition volume of the binder is 17~20 weight percent. After pulverizing for 24 hours by the ball mill, the solvent was evaporated at about 70°C and made into slurry. Plate-shaped compacts were prepared by the Peltsman's molding machine. Binder removal was conducted at room temperature to 150°C at 5°C in air, at 2°C/h in 150~250°C, at 5°C/h in 250~600°C, and held at 600°C for 1 hour. Sintering was conducted in 9 atmospheric pressure of $N_2$ for 3 hours at 1,850°C. Characteristics of compacts formed by the injection molding conditions of Table 1 are shown in Table 2.

Table 1. Conditions of Molding

| Temperature of tank | Temperature of pipe | Molding time | Holding time of pressure | Molding pressure | Temperature of mold |
|---|---|---|---|---|---|
| 88°C | 70°C | 30 sec | 60 sec | 3~5kgf/cm$^2$ | 85~90 °C |

Table 2. Properties of Green Compacts

| Content of E-146 wt% | Molding pressure kgf/cm$^2$ | Bulk density g/cm$^3$ | Apparent porosity % | Water absorption % | Shrinkage | | |
|---|---|---|---|---|---|---|---|
| | | | | | Length % | Width % | Thickness % |
| 17 | 3 | 2.21 | 0.02 | 0.01 | 0.80 | 0.82 | 0.20 |
| | 5 | 2.21 | 0.09 | 0.04 | 0.74 | 0.74 | 0.20 |
| 20 | 3 | 2.15 | 0.06 | 0.03 | 0.95 | 0.86 | 1.22 |
| | 5 | 2.15 | 0.06 | 0.03 | 0.86 | 0.86 | 1.14 |

Table 3. Properties of Sintered $Si_3N_4$ Ceramics

| Content of E-146 wt% | Molding pressure kgf/cm$^2$ | Bulk density g/cm$^3$ (%) | Apparent porosity % | Water absorption % | Shrinkage | | |
|---|---|---|---|---|---|---|---|
| | | | | | Length % | Width % | Thickness % |
| 17 | 3 | 3.22(98.7) | 0.27 | 0.08 | 17.1 | 18.1 | 16.4 |
| | 5 | 3.22(98.7) | 0.06 | 0.02 | 16.8 | 17.6 | 17.0 |
| 20 | 3 | 3.22(98.7) | 0.19 | 0.06 | 18.4 | 19.5 | 20.0 |
| | 5 | 3.23(98.8) | 0.01 | 0.01 | 18.7 | 19.7 | 21.0 |

Table 4. Flexural Strength of $Si_3N_4$ Ceramics and Their Weibull Constants

| Content of E-146 wt% | Molding pressure kgf/cm$^2$ | Average of flexural strength kgf/mm$^2$ | Weibull constant |
|---|---|---|---|
| 17 | 3<br>5 | 74.8<br>86.7 | 7.2 |
| 20 | 3<br>5 | 80.9<br>77.1 | 5.6 |

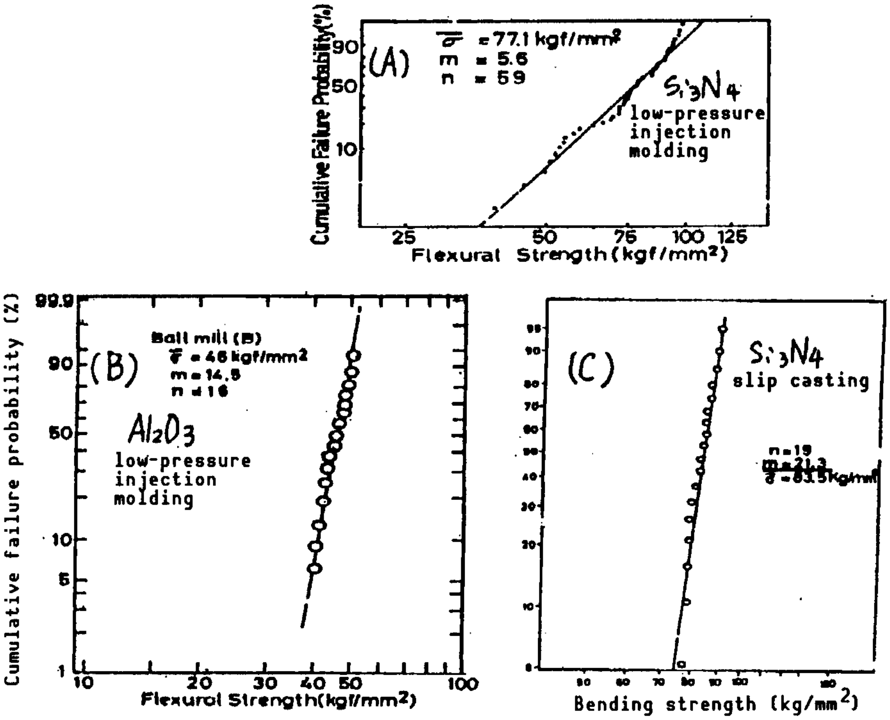


Figure 7. Comparison of Weibull Plot of $Si_3N_4$ With Other Methods

The shrinkage percentage in the length direction is about 0.8 percent. The bulk density and shrinkage percentage of the compact is shown in Table 3. The bulk density is 3.22 g/cc, and it has reached about 98.7 percent of the theoretical density. The Weibull plot of bending strength of those with a binder volume of 20 weight percent is shown in Figure 7. The mean bending strength is 77.1 kg/mm$^2$, and the Weibull coefficient is 5.6. The characteristics are inferior when comparing it with silicon nitride's mean bending strength of 83.5 kg/mm2 and Weibull coefficient of 21.3, has been prepared under the same sintering condition using the slip-cast method and the same material. The mean bending strength is 41.6 kg/mm$^2$, and the Weibull coefficient is 14.5 for alumina ceramics prepared by a similar low-pressure injection molding method. Because the density of the sintered material is almost the same as that of the slip-casting method, there are special problems in the sintering process. Therefore, defects that have been introduced are caused by forming. Because the slurry flow in the mold cannot be observed from the exterior, it is necessary to determine whether or not it is of an optimum injection molding condition. It may be that the reason why a comparatively high strength and Weibull coefficient have been obtained for alumina is because the injection molding conditions discovered by trial and error were suitable. Deciding the optimum injection molding conditions would become easier when the slurry flow in the mold can be seen directly. Therefore, a mold was devised which in one side was made of tempered glass (Figure 8 [not reproduced]). The slurry flow at injection molding was recorded by video.

A recording of the slurry flow using this mold is shown in Figure 9 [not reproduced]. Normal, uniform filling is not achieved when a turbulent flow condition—the slurry temperature and pressure are too high—exists. Bubbles are incorporated into the compact in such cases. When such a turbulent flow condition does not occur, uniform filling is achieved under suitable injection molding conditions. Behavior of the flow of $Si_3N_4$ into the mold is shown in Figure 10 [not reproduced].

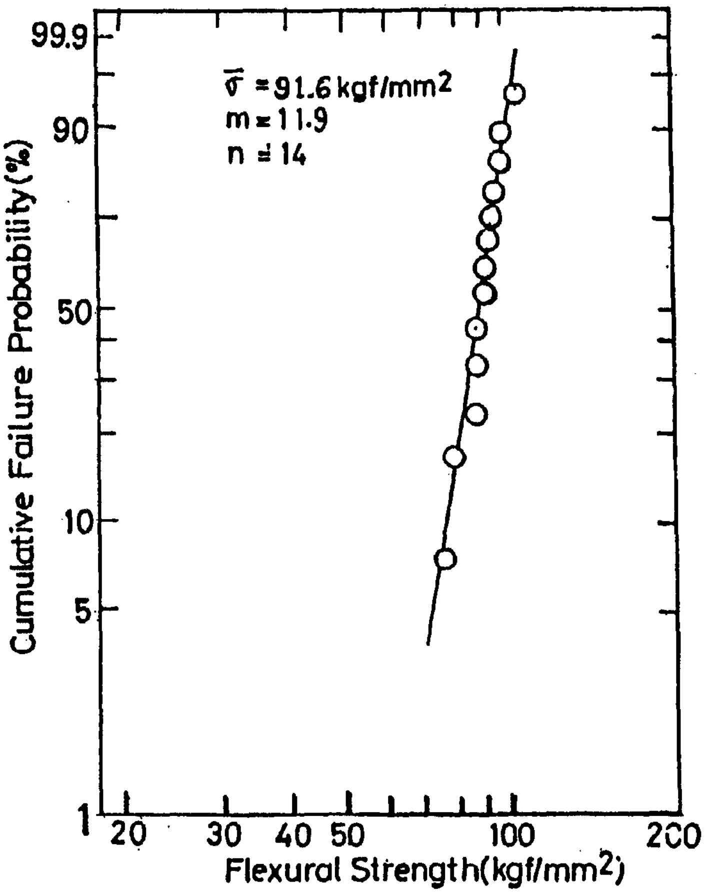


Figure 11. Weibull Plot of $Si_3N_4$ Sintered Material That Has Been Low-Pressure Injection Molded by Uniform Filling

The Weibull plot of the three-point bending strength of a uniformly filled compact with the binder removed is shown in Figure 11. Clearly, the characteristics were drastically improved. The mean strength was 91.6 kg/mm$^2$, and the Weibull coefficient was 11.9.

## 5. Conclusion

The low-pressure injection molding method had been used mainly for the preparation of ceramics that did not require high mechanical strength, such as insulating ceramics that used materials with a high particle size. Therefore, as the forming technology of engineering ceramics, it had not been studied as well, compared to ordinary high-pressure injection molding methods. There are practically no concrete examples of practical applications in Japan. Nevertheless, the low-pressure injection molding method shows the following superior characteristics.

1. Because the injection pressure is low, mold wear is extremely small. Expensive mold material and sintered and special steels, which are difficult to process, are not necessary. It is suited to small quantity production with many varieties.

2. The device cost is inexpensive.

3. Because the mold can be made compact and light weight, heating and cooling of the mold are easy, and it is easy to discover suitable injection molding conditions.

4. It is possible to observe directly the slurry flow at injection molding, and it is extremely easy to decide the optimum injection molding conditions.

5. Binder removal is comparatively easy with the wax system binder.

6. Low speed and uniform filling free from phenomena such as jetting is possible and the introduction of defects to prepared compacts can be controlled. Therefore, ceramics with a high Weibull coefficient can be prepared.

When taking these characteristics into consideration, the low-pressure injection molding method is a promising manufacturing technology of future engineering ceramics.

- END -

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