Porosity of dental gypsum-bonded investments in setting and heating process

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The porosity of gypsum-bonded investments for set and heated compacts was measured and theoretically computed quantitatively, because porosity is an effective factor for determining the strength, setting/heating expansion, and permeability of compacts at casting. A helium gas pycnometer was used to measure the solid volume of fine powders, powder-water mixtures, and porous compacts. The compositions of the conventional cristobalite investment and rapid-heating type investment were estimated from the measured solid densities of the as-received powders and the set investments. The porosity and water content of the set investments were determined from the experimental data. Excess water content in the set investment was calculated in relation to the elapsed time from the start of mixing with water. The experimental porosities of the set and heated investments were about 40% for dry set compacts and about 50% for fired compacts, which well agreed with the numerically computed estimations, respectively.

Keywords: Gypsum-bonded investment, Porosity, Calcium sulfate, Refractory

INTRODUCTION

Gypsum-bonded investments have long been used in dental casting systems^{1,2)}. However, the exact porosity of such investments has not been reported except in qualitative discussion in texts³⁻⁵⁾; that is, the porosity of these materials for dental stones has only been estimated using the assumed or quoted solid density of components. Advanced powder technology has improved the handling properties of gypsum products such as dental investments and helped in the fabrication of high-precision casting molds by an easy method. For the handling process in preparing porous products, the control of the pores in a compact is a key technology, that is, the apparent volume, which is the sum of the solid volume and pore volume, and the pores are effective factors for determining dimensional accuracy, strength, and permeability⁶⁻¹¹⁾. However, the solid volume is difficult to measure by the Archimedes method using water and other solutions, because gypsum is soluble in the solutions and has precise micro-nano spaces.

Helium gas is inert and mono-atomic, and its atomic diameter is 0.3 nm. Therefore, it can pass through a narrow space of sub-nanometer order. A gas pycnometer can measure the solid volume of not only porous materials but also solid-liquid mixtures and fine powders¹⁴⁾. The solid volume of a gypsum product, which has open and closed pores of micro-nano spaces in a compact structure, can be used to measure and calculate the porosity of gypsum products. It is easy to measure the exact solid density compared with using equipment with mercury, and has advantages on treatments.

In this study, the solid density of two types of investment powder, *i.e.*, a conventional cristobalite investment and a rapid-heating type investment, was

measured. The porosities of the set and heated compacts were measured in relation to the setting reaction and heating process. The experimental results are discussed with the theoretical analogy of the calcium sulfate (CS) reaction with water. Theoretical analogy developed in this study may be a powerful tool for designing mixtures with different additive powders to gypsum and for estimating a reasonable W/P ratio by applying the numerical calculation used in this study.

MATERIALS AND METHODS

A commercial gypsum-bonded dental investment for casting (A: Cristobalite Micro II, GC, Tokyo, Japan) and a commercial gypsum-bonded rapid-heating type investment (B: Cristobalite PF, Shofu, Kyoto, Japan) were used. Table 1 shows the specifications given by the manufactures. The weight and solid volume of the as-received powders; *i.e.*, A and B, were respectively measured using a microbalance with 0.01 mg accuracy (AUW220D; Shimadzu, Kyoto, Japan) and a gas pycnometer (AccuPyc 1330, Shimadzu, Kyoto, Japan) within 0.02% accuracy for 1 cm³. From these values, the solid density of the powders was calculated. The particle size of the powders was measured using a laser diffraction particle size analyzer (PSA) with injection type dry measurement (SALD-7100; Shimadzu, Kyoto, Japan). The composition of each sample was analyzed qualitatively using X-ray diffraction equipment (XRD: MiniFlex; Rigaku, Tokyo, Japan).

The solid densities of the as-received powders for the commercial dental stone (Newplastone II, GC, Tokyo, Japan) and six types of cristobalite and quartz, which were mixed with a refractory component of a commercial investment, were measured. For the dental stone, the

solid densities of the CS dihydrate and anhydrate were determined from the set and heated compacts, which were mixed with water. The measured solid densities were used in the theoretical calculation.

According to the specifications of the manufactures, the as-received investment powders were mixed with distilled water using the P/W ratios shown in Table 1. The mixed slurry was poured into a polyethylene mold with an internal diameter of 10 mm and a height of 10 mm. The top and bottom sides of the mold were clamped with a glass plate for 30 min, and the sample was kept in ambient air without the mold. The density ρ of the compact was calculated from the weight and outer dimensions of the compact measured using a digital caliper. The solid density ρ_s of the compact was calculated from the weight of the compact and the solid density which was measured using a gas pycnometer. The porosity P was computed from the density ρ and solid density ρ_s : $P = 1 - \rho/\rho_s$. For preparing of dry set sample which is set sample with low excess water content, the sample were kept in ambient air for one day. The dry set sample heated at the rate of 5°C/min to indicated temperatures of up to 700°C and cooled to room temperature. The indicated temperatures were selected 50°C apart to each in considering of dehydration of CS and transforming temperature range of silica. The solid density and porosity of all samples were measured at room temperature (CS anhydride sample: fired compact).

Solid density measurement

The sample set in the cell, and charged helium gas at the pressure P_1 . After P_1 became a stable; *i.e.*, lower than 34.5 Pa/min, the valve between the cell and the reserve room was opened. Then, the pressure in both rooms balanced at P_2 .

When P_1 and P_2 can be measured, the sample volume can be calculated using the following equations.

$$P_1 (V_C - V_S) = P_2 (V_C - V_S + V_E) \quad (1)$$

$$V_S = V_C - P_2 V_E / (P_1 - P_2) \quad (2)$$

Here, V is the volume, and subscripts S , C and E refer to the volumes/spaces of the solid sample, cell, and reserve room, respectively.

In this system, helium is used as the charging gas. The gas pass go through a sub-nano meters space in the compact/powder because helium is an inert gas and its atomic diameter is 0.3 nm. If the exact weight of the material can be measured, we can calculate the solid density of the material. The data were obtained the average of five measurements. The standard deviation of the solid density was 0.001 g/cm³, and the duration of measurement was about 2 to 30 min for each measurement, depended on sample physicochemical stability.

RESULTS

The solid density and particle size of the as-received powders are shown in Table 2. Measured data are the average of three measurements of randomly sampled powder from the same batch. Here, the essential ingredients of the investment were identified as α -hemihydrate of stone, quartz, and cristobalite by XRD analysis. The average particle sizes of investments A and B were 11.63 and 11.56 μ m, respectively. However, three peaks of relative frequency in the particle size distribution by weight were detected, particularly for investment B.

The range of solid densities of CS hemihydrate, dihydrate, and anhydrate were 2.69–2.79 g/cm³, 2.32–2.37 g/cm³, and 2.88–2.97 g/cm³, respectively. Considering the additives and other reference data^{3,5}, densities of 2.75 g/cm³, 2.32 g/cm³, and 2.90 g/cm³, respectively, were used for the following calculation data. Table 3 shows the solid densities of six different types of quartz and cristobalite powders used in a commercial dental investment. Here, the silica powders measured in this study were not the refractory powders used in investments A and B.

Table 4 shows the measured solid densities and porosities of the compacts. Here, time is the duration from the start of mixing with water, and has an error of

Table 1 Specifications provided by the manufactures

Investment	Water/powder ratio recommended value	Linear setting expansion after 2 h	Thermal expansion at 700°C
A	0.33	0.5%	1.45%
B	0.35	0.9%	1.10%

Here, expansion values are tested data according to JIS T 6601¹³⁾ (ISO 7490¹⁴⁾) by the manufactures.

Table 2 Solid densities and particle sizes of as-received powder

Investment	Density g/cm ³	Average particle size (SD) μ m	Detected relatively high frequency peak range, μ m
A	2.474	11.63 (0.58)	5–10; 20–30; 50–70
B	2.549	11.56 (0.57)	1–2; 10–20; 50–60

within 10 min, because a gas pycnometer requires more than 10 min before it can be used for wet specimen measurements. The designations “Dry” and “Fired” are the data for the compacts after one day of setting and for compacts once fired at 700°C, respectively.

DISCUSSION

Estimation of composition of investments

The as-received powders were composed of hemihydrate CS and refractory silica. The solid density of the as-received powder ρ_0 was estimated using the following equations:

$$\rho_0 = \rho_H V_H + \rho_X V_X$$

$$V_H + V_X = 1 \quad (3)$$

Here, the subscripts H and X refer to CS hemihydrate and refractory silica, respectively. After setting, the solid density of the set dry compact ρ_1 is determined using following equations.

$$\rho_1 (V_D + V_X) = \rho_D V_D + \rho_X V_X \quad (4)$$

Here, the subscript D refers to CS dihydrate. The relationship between V_H and V_D is

$$V_D = k V_H \quad \text{here, } k = \frac{M_D \rho_H}{M_H \rho_D} \quad (5)$$

Here, M is the molecular mass. From (3)–(5), ρ_X and V_X

can be calculated as follows:

$$\rho_X = \frac{(\rho_H - \rho_0)\rho_1 + k(\rho_1 - \rho_D)\rho_0}{(\rho_H - \rho_0) + k(\rho_1 - \rho_D)} \quad (6)$$

$$V_X = \frac{\rho_0 - \rho_H}{\rho_X - \rho_H} \quad (7)$$

The density of silica ρ_X is the solid density of a mixture of cristobalite and quartz with solid densities of ρ_C and ρ_Q and volume fractions of V_C and V_Q , respectively.

$$\rho_X V_X = \rho_C V_C + \rho_Q V_Q \quad (8)$$

$$V_X = V_C + V_Q \quad (9)$$

Then,

$$V_C = \frac{\rho_X - \rho_Q}{\rho_C - \rho_Q} V_X \quad (10)$$

$$V_Q = 1 - V_C \quad (11)$$

Table 5 shows the computed results for the compositions of investments A and B compared with the data obtained by chemical and quantitative X-ray analyses¹⁵. Because the solid density of quartz is higher than that of cristobalite, a high W/P ratio should be used if the same porosity should be attained for a high content of quartz as that for refractory silica.

Porosity and water content of set investment

The equivalent volumes of the hemihydrate, water,

Table 3 Solid densities and particle sizes of silica

Cristobalite		Quartz	
Density g/cm ³	Average particle size (SD) μm	Density g/cm ³	Average particle size (SD) μm
2.337	20.80 (0.58)	2.647	269.32 (0.10)
2.339	11.11 (0.57)	2.655	195.67 (0.14)
2.349	11.01 (0.47)	2.655	43.20 (0.51)
2.378	5.98 (0.52)	2.661	28.34 (0.61)
2.356	4.76 (0.48)	2.638	26.09 (0.69)
2.355	2.56 (0.33)	2.651	15.58 (0.39)

Table 4 Solid densities and porosity of set and heated investment compacts

Investment	A		B	
	Solid density g/cm ³	Porosity %	Solid density g/cm ³	Porosity %
Time				
Min				
60	1.922	11.2	1.903	11.2
120	1.962	14.6	1.967	16.0
180	2.069	22.7	2.039	21.5
240	2.160	29.4	2.173	31.0
Dry	2.341	39.2	2.409	43.0
Fired	2.489	47.0	2.571	51.5

refractory silica, and the reaction product are as follows:

Weight: W_H W_W W_E W_X

Volume: V_H V_W V_E V_X

Weight: W_D W_E W_X

Volume: V_D V_E V_X

The volume of excess water V_E can be calculated from the W/P ratio and the volume of water necessary for the setting reaction of the CS hemihydrate. Then, the porosity and solid density of the set investment with the full excess water and dry compact can be calculated using the following equations:

For the fully wet set investment

$$P_1 = 1 - \frac{V_D + V_X + V_E}{(V_H + V_X + V_W + V_E)} \quad (12)$$

$$\rho_1 = \frac{W_D + W_X + W_E}{V_D + V_X + V_E} \quad (13)$$

For the dry set investment

$$P_2 = 1 - \frac{V_D + V_X}{(V_H + V_X + V_W + V_E)(1 + 3a)} \quad (14)$$

$$\rho_2 = \frac{W_D + W_X}{V_D + V_X} \quad (15)$$

Here, a is the setting linear expansion of the investment. Under the wet condition, most of the pores were filled with the excess water and these pores were not included in the calculation of porosity. The calculated porosities and solid densities are shown in Table 6 for comparison with the experimental measured data. The set compact

is a mixture of the solid investment excess water and pores. Then, the volume of excess water can be calculated from the solid density of the set investment. Figure 1 shows the volume of excess water in the set investment. Because the thermal diffusivity of water vapor is high, excess water helps prevent the thermal fracture of the investment. That is why the rapid-heating type investment, which was kept in ambient air for a few days after mixing with water (dry compact), had cracks in the furnace when kept in the furnace at 700°C¹⁶⁻¹⁸. It is a technical matter to form a uniform distribution of pores in the set compact by controlling the crystal structures of refractory and CS dihydrate.

Porosity of heated investment

The porosity and solid density of the heated investment can be calculated using the following equations.

$$P_3 = 1 - \frac{V_{An} + V_X}{(V_H + V_X + V_W + V_E)(1 + 3a)} \quad (16)$$

$$\rho_3 = \frac{W_{An} + W_X}{V_{An} + V_X} \quad (17)$$

Here, the subscript An refers to CS anhydrate. Porosity and solid density were not measured at 700°C but at room temperature after heating. The transformation of cristobalite and quartz is rapid type, *i.e.*, reversible¹⁹. Thus, at 700°C (burnout temperature), porosity is not the same as the calculated porosities shown in Table 6.

Figure 2 shows the summarized porosity related to the setting and heating processes of the investments. Porosity increased with time owing to the dehydration of slurry. The W/P ratio is an effective factor for determining the porosity of the dry set investment, because the initial volume is the sum of the volume of as-received powder and that of mixing water. During heating, porosity

Table 5 Compositions of as-received investment powders A and B

Investment	CS hemihydrate	Cristobalite	Quartz
Calculated results in this study			
A	34.1%	65.2%	0.7%
B	33.0%	40.0%	27.0%
Data from Hirose <i>et al.</i> ¹⁵⁾			
A	28.5%	66.8%	4.8%
B	27.4%	38.2%	33.5%

Table 6 Computed solid densities and porosities of set and fired investment compacts

Investment	Solid density g/cm ³		Porosity %	
	A	B	A	B
Set fully wet compact	1.842	1.847	3.2	4.2
Set dry compact	2.341	2.409	39.2	42.3
	(Input data)	(Input data)	(39.2)	(43.0)
Fired compact	2.506	2.583	47.6	50.3
	(2.489)	(2.571)	(47.0)	(51.5)

The values within the parentheses are experimentally measured data

Fig. 1 Volume of excess water in set investments in relation to elapsed time after mixing the powder with water. The values in the figure are the porosities for dry compacts calculated by theoretical estimation.

Fig. 2 Porosity in relation to setting and heating processes. The values in the figure are the porosities for investments A and B determined by theoretical estimation.

increased owing to the evaporation of water from CS dihydrate and hemihydrate. However, the increase in porosity is about 10% if the thermal/transformation expansion is neglected. The permeability of the investment at casting is affected by not only porosity but also the dimensions, shape, and distribution of pores. However, the morphology of the pores is beyond the scope of this study.

CONCLUSION

The solid volume of the fine investment powders and wetting set compacts are measured using a gas pycnometer. The solid density and porosity of the conventional and rapid-heating type gypsum-bonded investments were calculated in relation to the setting and heating process. The composition of the as-received gypsum investment could be estimated from the measured solid densities of the as-received powders and set investments. Experimentally determined porosity and density were discussed in relation to the theoretical analogy developed in this study. The volume of excess water in the set investment and the porosity of the heated investment compacts well agreed with the theoretical estimations. It is concluded that the numerical computing procedure developed in this study is a powerful tool for designing the composition of gypsum products and the appropriate process for such products.

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