

Gypsum-bonded Alumina Dental Investment for High-fusing Casting

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In this study, we developed a new gypsum-bonded investment for high-fusing alloys. The investment was composed of gypsum as a binder and alumina as a refractory. Effects of type of alumina powder and gypsum content on characteristics of the gypsum-bonded alumina investment were investigated. Obtained characteristics of this experimental investment were as follows: fluidities ranged from 48.8 to 88.9 mm; setting times ranged from 21.2 to more than 120 minutes; setting expansions ranged from 0.4 to 1.3%; green strengths showed 0.5 to 4.5 MPa; fired strengths ranged from 0.2 to 1.7 MPa; thermal expansions after firing were -1.60 to 2.16%. Thermal expansion occurred because of the chemical reaction between Al_2O_3 and CaO decomposed from gypsum. These results suggest that this gypsum-bonded alumina investment with 20 or 25 mass% gypsum content possessed the fundamental properties for high-fusing alloy casting.

Key words : Gypsum-bonded investment, Investment for high-fusing alloy, Alumina

INTRODUCTION

The gypsum-bonded investment was used approximately a hundred years ago by Taggart¹⁾. This type of investment has advantages such as easy operation, relatively large setting expansion and adequate green and fired strength. Therefore, it is now being widely used for low and medium-fusing dental casting alloys²⁾.

However, it is generally believed that the gypsum-bonded investment is not suitable for high-fusing casting alloys because of its gypsum decomposition at around 1000°C; moreover, the gypsum begins to decompose into calcia at 700°C in presence of carbon^{3–5)}. As a result, phosphate-bonded investments and ethylsilicate-bonded investments have been used for high-fusing casting alloys instead of gypsum-bonded investments²⁾.

In recent years titanium casting for dental applications has become a large concern. Unfortunately, fabrication of sound titanium castings using the phosphate-bonded and ethylsilicate-bonded investments is very difficult because of the strong chemical reaction between melting titanium and silica used for the refractory in these investments⁶⁾. Therefore, non-silica investments have been developed utilizing more stable refractories such as MgO ^{7,8)}, Al_2O_3 ^{9,10)}, ZrO_2 ¹¹⁾, CaO ^{12,13)} and Y_2O_3 ¹⁴⁾.

In 1991, thermal behaviors of gypsum mixed with various refractories were investigated¹⁵⁾. This investigation suggested that gypsum with alumina showed a large

expansion at 1200–1400°C because of the reaction between alumina and calcia. If the gypsum mixed with alumina shows adequate compressive strength and thermal expansion heated at a temperature equal to or higher than that of the decomposition of gypsum, the mixing is thought to be a potentially suitable investment for high fusion casting.

In this study, the effects of the type of alumina powder and gypsum content on the characteristics of a gypsum-bonded alumina investment were investigated, and the thermal behaviors of this experimental investment were analyzed.

MATERIALS AND METHODS

Experimental Investment

A calcium sulfate hemihydrate without an additive, essentially identical to a dental stone used for a commercial gypsum-bonded investment (Cristobalite Micro, GC, Tokyo, Japan), was selected as a binder. Gypsum was added in 10, 15, 20 and 25 mass% to the alumina powder.

Two types of alumina powder, #220 (Fuji-random wa-220, Fujiseisaku, Tokyo, Japan) and #700 (Aluminum B powder, Panaheraeus Dental, Osaka, Japan), were selected as a refractory. Their chemical compositions and particle sizes are listed in Table 1. The particle size distributions were analyzed by a laser diffraction particle analyzer (Sald-2000J, Shimadzu, Kyoto, Japan).

The water/powder ratio was 0.31 according to a previous study¹⁵⁾. This investment was mixed by hand for 30 seconds and another for 30 seconds with a vacuum mixing machine (Vac-U-Mixer, Whip-Mix, Fort Wayns, IN, USA).

Fluidity

Fluidity was measured using the slump test JIS T6601¹⁶⁾ for gypsum-bonded investment. The freshly mixed investment was poured into a brass ring (28 mm in diameter and 50 mm in length) on a glass slab, then the brass ring was pulled up 2 minutes after the start of mixing. Fluidity was determined as the mean of the maximum and the minimum slurry diameter 3 minutes after the start of mixing. Three measurements were performed for each investment.

Table 1 Chemical composition and particle size of alumina powder used in this study

Code	Composition mass%						Mode diameter μm	Median diameter μm
	Al_2O_3	TiO_2	SiO_2	Fe_2O_3	Na_2O	CaO		
#220	99.72	0.007	0.025	0.029	0.18	0.026	89.9	84.7
#700	99.0	—	0.3	0.1	0.5	—	23.6	25.3

Setting time

The Vicat needle penetration test was employed to measure the setting time; the diameter of the Vicat needle was 2 mm and its load was 3 N. The freshly mixed investment was poured into a brass ring (30 mm in diameter and 30 mm in length); the needle was allowed to penetrate the mix at 15-second intervals until it no longer penetrated the mass. The setting time was recorded as the total time from the start of mixing to the time when the needle failed to make a perceptible circular indentation on the surface of the specimen. Three repetitions were done for each investment.

Dimensional changes during setting

Dimensional changes during setting were continuously measured up to 120 minutes after the start of mixing. The freshly mixed investment was put into a steel ring (35 mm in diameter and 45 mm in length) with two folds of a 0.7 mm ceramic liner (New Casting Liner No.3, GC, Tokyo, Japan). A 17 mm diameter circular acrylic plate was placed on top of the investment. Movement of the acrylic plate was monitored by a dial gauge (Peacock 107, Ozakiseisaku, Tokyo, Japan); the measuring load was approximately 0.16 g/mm². The dimensional change of the investment was calculated as the percentage expansion based on the smallest reading of the dial gauge during setting and the final length of the measured specimen¹⁷⁾. Three measurements were performed for each investment.

Compressive strength

The freshly mixed investment was poured into a brass mold (10 mm in diameter and 15 mm height). The set specimen was removed from the mold 55 minutes after the start of mixing and kept in a container with a 100% relative humidity. Green strengths were obtained by a compressive test using a universal test machine (1123, Instron, Canton, MA, USA) with a crosshead speed of 0.5 mm/min at 2 hours after the start of mixing. Fired strengths of the specimens were also obtained in the above-mentioned manner. The specimens were heated to 1200°C at a rate of 10°C/min from 24 hours after the start of mixing and to 1400°C at a rate of 5°C/min using a SiC furnace (FG41, Yamato, Tokyo, Japan), then cooled to room temperature. Six specimens of each investment were tested.

Thermal analysis

Thermal expansion was measured with a dilatometer (Dilatometer 5020, Mac Science, Tokyo, Japan). A cylindrical set investment (6 mm in diameter and 12 mm height) was heated in air from 2 hours after the start of mixing in the above-mentioned manner.

Weight and endothermal/exothermal changes during heating and cooling of the set investment were analyzed using a TG-DTA (TG-DTA 2000, Mac Science, Tokyo, Japan). A piece of set investment was milled to powder using a mortar and a pestle, then the powder was kept in a desiccator for removing physical water from the investment at least 24 hours. Alumina powder was used as a standard; the examined

mass of powder was 10.0 mg; the powder was heated to 1400°C at a 10°C/min heating rate and cooled to room temperature at a 10°C/min cooling rate. Thermal analysis was performed three times for each investment.

X-ray diffraction

The mixed investment was poured into a 42 mm in diameter and 55 mm in height alumina ring lined with a sheet of a 2 mm thickness ring liner (Ceramic liner cyclarc, Morita, Tokyo, Japan). The investments removed from the ring before and after firing were crushed into powder for the measurement. The investments were heated to 1000, 1100, 1200, 1300 and 1400°C at a rate of 10°C/min, held at these temperatures for 60 min, and cooled to room temperature in the SiC furnace. Changes of the crystal components before and after firing were detected using an X-ray diffractometer (RAD-II A, Rigaku, Tokyo, Japan) with $\text{CuK}\alpha$ radiation, a fixed divergence slit and a 2°/min scanning speed.

RESULTS

Fluidity

The obtained fluidities are shown in Fig. 1. The error bars in the figure indicate the standard deviations. The fluidities of the #220 alumina investments ranging from 48.8 to 57.4 mm were smaller than those of the #700 alumina investment ranging from 64.8 to 88.9 mm. The increase of gypsum content of the #220 alumina investments had a tendency to decrease the fluidity; whereas that of the #700 alumina investment had a tendency to increase the fluidity. The fluidities of the #220 alumina investments except the 15 mass% gypsum content failed the investment standard re-

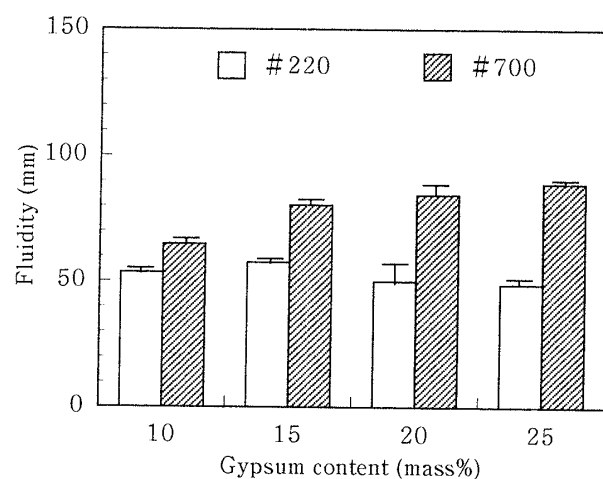


Fig. 1 Effect of alumina type and gypsum content on fluidity.

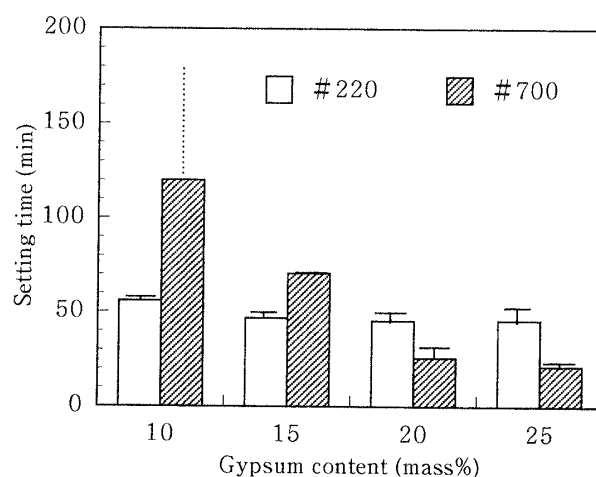


Fig. 2 Effect of alumina type and gypsum content on setting time.

The #700 alumina investment with 10 mass% gypsum content did not set until 120 minutes.

quirement of 55 mm¹⁶⁾.

Setting time

The obtained setting times are indicated in Fig. 2. The setting times of the #220 alumina investments ranged from 45.5 to 55.7 minutes; the gypsum content did not change the setting time of the #220 alumina investments. The #700 alumina investment with 10 mass% gypsum content did not set until 120 minutes after the start of mixing, but the setting time of the #700 alumina investments dramatically decreased when the gypsum content increased. The setting times of the #700 with 15, 20 and 25 mass% gypsum content were 70.3, 25.7 and 21.2 minutes, respectively.

Dimensional change during setting

The dimensional changes at 120 minutes after the start of mixing are illustrated in Fig. 3. The #220 alumina investments showed expansion until 120 minutes after the start of mixing; the linear expansion values at 120 minutes after the start of mixing ranged from 0.47 to 0.66%. The #700 alumina investments exhibited a larger and faster expansion than the #220 alumina investments did; the linear expansion values at 120 minutes after the start of mixing were 1.02 to 1.34%. With these investments, the setting expansion tended to increase with an increase of gypsum content.

Compressive strength

Fig. 4 shows the green and fired strengths of each investment. The green strengths of the #220 alumina investments were larger than those of the #700 alumina investments when the gypsum content was identical; the increase of gypsum content increased the green strength. The green strengths of these investments except the #700 alumina investment with 10 mass% gypsum content fulfilled the requirement of the

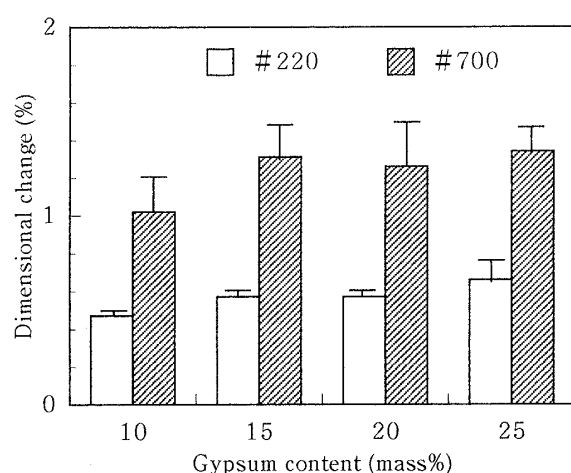


Fig. 3 Effect of alumina type and gypsum content on dimensional change at 120 minutes after the start of mixing.

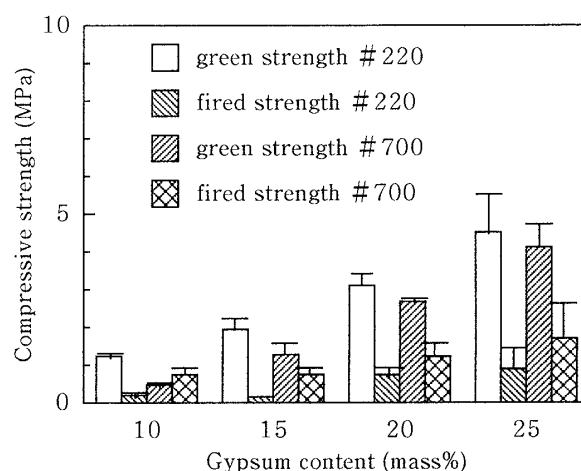


Fig. 4 Effect of alumina type and gypsum content on green strength and fired strength.

standards¹⁶⁾ which is 1 MPa.

The fired strength of the #700 alumina investments was larger than that of the #220 alumina investments when the gypsum content was identical. The fired strength of the investments with a higher gypsum content showed a large value.

Thermal analysis

Figs. 5 A-B show typical thermal dimensional changes of the investments. Thermal contractions occurred between 300–350°C and between 900–1150°C, while thermal expansion occurred between 1200–1400°C. Thermal linear contractions were observed during cooling to room temperature. Changes of thermal contraction and expansion increased with an increase of gypsum content. The thermal expansions after firing of the #220 alumina investments were 0.14 to 2.16%; those of the #700 alumina investments were –1.60 to 0.51 % (Fig. 6). Thermal contraction of the #700 alumina investments was larger than that of the #220 alumina investments; however, the absolute degree of thermal expansion of both investments were similar.

A typical TG-DTA diagram of the #220 alumina investment is illustrated in Fig. 7. The thermal behaviors monitored by the TG-DTA of the #700 alumina investments were similar to those of the #220 alumina investments.

An endothermic peak with weight loss was observed between 100 and 130°C; a small exothermic peak without weight loss was observed approximately 350°C; a broad endothermic peak with weight loss began from approximately 900°C; an endothermic peak without obvious weight loss was recognized at 1200°C; a gradient weight loss and endothermic peak were observed until 1400°C; there were no obvious endo/exothermic peaks and weight loss during cooling to room temperature. The changes of weight loss increased with increasing gypsum content of investments; means $\pm$ standard deviations of amounts of weight loss before firing to 200°C with 10, 15, 20, 25 mass% gypsum content were $2.3 \pm 0.0\%$, $3.4 \pm 0.0\%$, $4.5 \pm 0.0\%$ and $5.6 \pm 0.0\%$, respectively; means $\pm$ standard deviations of amounts of weight loss before firing to

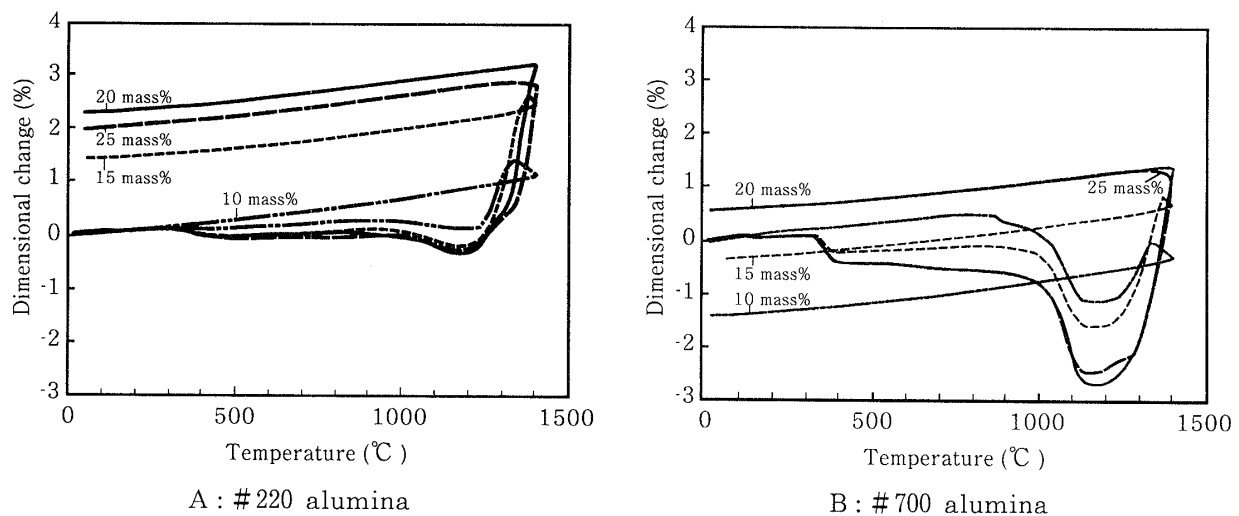


Fig. 5 Typical thermal expansion curves.

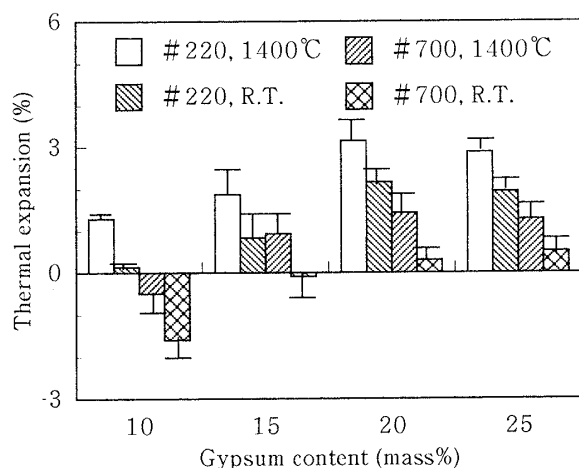


Fig. 6 Effect of alumina type and gypsum content on thermal expansion at 1400 °C and residual expansion after cooling to room temperature (R.T.).

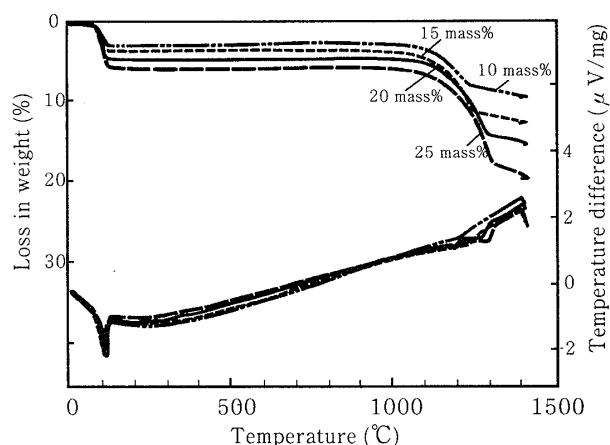


Fig. 7 Typical TG-DTA curves (#220 alumina investment).

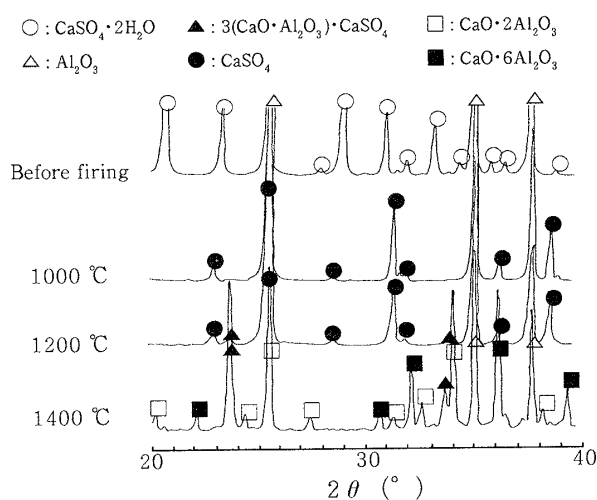


Fig. 8 X-ray diffraction patterns of the investment before and after firing (#700, 20 mass% gypsum).

1400°C with 10, 15, 20, 25 mass% gypsum content were $8.5 \pm 0.1\%$, $12.0 \pm 0.0\%$, $15.3 \pm 0.1\%$ and $18.7 \pm 0.1\%$, respectively.

X-ray diffractometer

The X-ray diffraction patterns are shown in Fig. 8. Strong diffraction lines of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Al_2O_3 were observed from the powder before firing; diffraction lines of CaSO_4 instead of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were found from the powder after 1000°C firing; diffraction lines of $3(\text{CaO} \cdot \text{Al}_2\text{O}_3) \cdot \text{CaSO}_4$ appeared from the powder after 1200°C firing; diffraction lines of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ were also observed from the powder

after 1400°C firing. Final crystal components after 1400°C firing were considered to be Al_2O_3 , $3(\text{CaO} \cdot \text{Al}_2\text{O}_3) \cdot \text{CaSO}_4$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, and $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$.

DISCUSSION

Setting and thermal behaviors of gypsum are easily affected by additives. Therefore, a dental stone without an additive was selected as a binder based on the previous report¹⁵⁾. Several studies^{9,10,15)} have examined the advantage of alumina as a refractory material because alumina is a stable oxide at high temperatures. There are several commercially available alumina powders. Sasaki suggested a large thermal expansion of gypsum-bonded alumina at 1300°C¹⁵⁾; however, not all alumina powder bonded with gypsum showed expansion at high temperatures in our pilot study. Therefore, two types of alumina powder, with relatively small and large particles, were used in this study. Alumina contents of the two powders were more than 99.0 mass%; however, their chemical compositions were not identical. Therefore, small amounts of impurities in the alumina powder might have an influence on the characteristics of gypsum-bonded alumina investments.

A dental gypsum-bonded investment contains 25% to 45% gypsum content²⁾. In this study, it is likely that the gypsum in the investment decomposed with the byproduct of SO_3 . Accordingly, a small amount of gypsum in the investment might be desirable. Hence, 10 to 25 mass% gypsum contents to alumina powder were investigated.

For dental casting the investment must possess adequate fluidity for investing, a proper setting and thermal expansion for compensation of casting shrinkage, and sufficient compressive strength to resist deformation during heating and casting.

Fluidity of the #220 alumina investments was nearly at the minimum limit of the JIS¹⁶⁾ requirement. However, it was possible to use these investments because of their relatively long setting time and thixotropicity.

Large amounts of small silica particles in a phosphate-bonded investment was reported to reduce the fluidity as a result of an increase of the surface area of particles¹⁸⁾. In contrast, small alumina particles of an alumina sol-bonded alumina investment was reported to increase its fluidity⁹⁾. These results suggested that viscoelastic behavior of the alumina slurry might not be identical to that of silica slurry. Moreover, the effect of gypsum content on fluidity showed a different behavior regarding the alumina type.

The setting time of the investment must be between 5 and 30 minutes¹⁶⁾. Only the #700 alumina investment with 20 and 25 mass% gypsum content fulfilled this requirement. The setting time of the #700 alumina investments was sensitive for the gypsum content compared with the #220 alumina investments. The differences of chemical composition of the two alumina powders might be responsible.

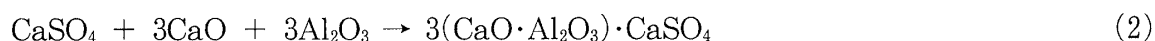
The setting expansion mechanism of this experimental investment might be similar to that of a conventional gypsum-bonded silica investment. In this study the setting expansion of the experimental investments showed a larger value than that of the gypsum used which was 0.4%. Concerning a conventional gypsum-bonded silica

investment, the small particle size of silica produces a higher setting expansion and the hygroscopic expansion of the investment increases with an increase of silica/gypsum ratio¹⁹⁾. The gypsum-bonded alumina investments in this study obeyed a similar principle.

It has been reported that the green strength of gypsum increased with a decrease of setting expansion of gypsum²⁰⁾. Green strengths of the #700 alumina investments showed smaller values than those of the #220 alumina investments; these phenomena were responsible for the larger setting expansion of the #700 alumina investments. However, fired strength of the #700 alumina investments showed larger values compared with those of the #220 alumina investments; this might be caused by the large sintering ability of smaller particles of alumina and the reaction with alumina and calcia decomposed from gypsum because of the large surface area. Fired strengths of recent commercial gypsum-bonded investments were reported to be 0.4 to 1.6 MPa¹⁷⁾. Obtained fired strengths of gypsum-bonded alumina investments were within the range of these values except for the #220 alumina investments with 10 and 15 mass% gypsum content.

The gypsum-bonded alumina investments lost weight by means of dehydration of gypsum at 100–130°C. It was difficult to distinguish dehydration of a hemihydrate from that of a dihydrate. Theoretical amounts of weight loss due to anhydration from dihydrate gypsum with 10, 15, 20 and 25 mass% gypsum content are 2.4, 3.6, 4.8 and 5.9%, respectively; actual amounts of weight loss were almost equal to the theoretical figures. Thermal contraction occurred at 350°C and from 900°C because of transformation of III-CaSO₄ to II-CaSO₄ and decomposition and sintering of CaSO₄, respectively²¹⁾.

There were most likely several chemical reactions within the gypsum-bonded alumina investment from 1200 to 1400°C.



If the gypsum of the 10, 15, 20 and 25 mass% gypsum-bonded alumina investments were completely decomposed at 1400°C (equation (1)), the theoretical amounts of weight loss of these investments before firing to 1400°C would be 7.9, 11.7, 15.4 and 19.1%, respectively. Observed weight loss were similar to these calculated amounts. However, some amount of CaSO₄ was observed as 3(CaO·Al₂O₃)·CaSO₄ after 1400°C firing on the X-ray diffraction pattern. The theoretical volume expansion values of equations (2) and (3) could be calculated to 30.1% and 3.8%, respectively, when the molecular mass and density (g/cm³) of CaO, Al₂O₃, 3(CaO·Al₂O₃)·CaSO₄ and CaO·6Al₂O₃ were 56.08 and 3.37²²⁾, 101.96 and 3.99²²⁾, 610.26 and 2.605²³⁾, and 667.84 and

3.785²⁴⁾, respectively. Unfortunately, the density of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ was not confirmed; the theoretical volume expansion values of equations (4) could not be calculated.

Thermal expansion of dental investments are obtained by means of transformation of silica, oxidation of metal powder, and the chemical reactions among components of investments. The thermal expansion of the gypsum-bonded alumina investment was mainly the reaction of the components of the investment, especially calcia decomposed from gypsum. The above-mentioned chemical reaction might be affected by chemical additives; therefore, all alumina powders did not show a large expansion at a high temperature. To control thermal expansion of the gypsum-bonded alumina investment, the effects of chemical additives must be investigated. Additionally, the amounts of gypsum content in the alumina investment is a significant factor on thermal expansion. However, the investment with a higher than 25 mass% gypsum content might not show a larger expansion than that with the 25 mass% gypsum content because of a large shrinkage due to decomposition and sintering of gypsum.

Characteristics of the gypsum-bonded alumina investments changed according to the type of alumina powder and quantity of gypsum. Both types of alumina powder were considered suitable refractories for casting; however, an interaction between alumina powder type and gypsum content might exist. The casting shrinkage is mainly compensated by the setting expansion when the #700 alumina powder is employed; whereas the casting shrinkage is mainly compensated by the thermal expansion when the #220 alumina powder is employed. With respect to gypsum content, 20 and 25 mass% might fulfill the requirements for the investment. However, the characteristics of these investments could be improved by the use of some chemical additives. Further investigations are necessary from this point of view.

We tried to obtain a titanium casting using this experimental investment to confirm the possibility of usage for high-fusing casting. A trapezoid wax pattern was prepared and invested using #220 alumina powder with 20 mass% gypsum in the alumina ring lined with the ceramic liner mentioned previously. This mold was

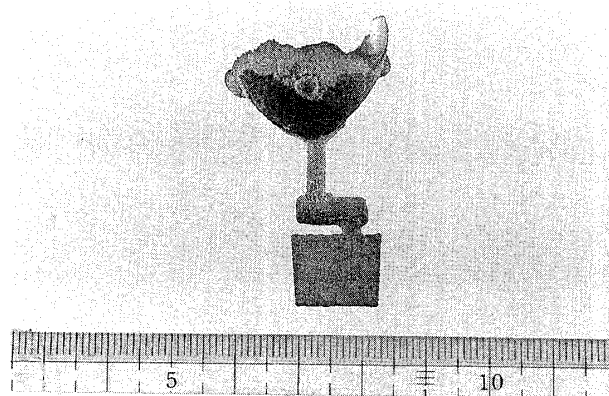


Fig. 9 Casting obtained from investment (#220, 20 mass% gypsum).

heated and cooled to room temperature in the same manner described for the determination of compressive strength. A commercially pure titanium (Dental pure titanium A, Morita, Tokyo, Japan) was cast into the mold using an argon arc melting centrifugal and gas pressure casting machine (Vulcan-T, Shofu, Kyoto, Japan). The obtained casting without sandblasting is shown in Fig. 9. There were no casting fins on the surface of the casting. The investment was easily removed from the casting. This result indicated the possible use of a gypsum-bonded alumina investment for high-fusing castings such as titanium and cobalt-chromium alloy.

CONCLUSION

The effects of type of alumina powder and amount of gypsum content on the characteristics of a gypsum-bonded alumina investment for high-fusing casting were investigated. Gypsum content of 20 or 25 mass% was considered a suitable composition for a gypsum-bonded alumina investment.

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