Original paper

Effects of Magnesia and Potassium Sulfate on Gypsum-bonded Alumina Dental Investment for High-fusing Casting

Min YAN and Hidekazu TAKAHASHI

Department of Dental Technology I, Faculty of Dentistry, Tokyo Medical and Dental University 1-5-45 Yushima, Bunkyo-ku, Tokyo 113-8549, Japan

Received July 15, 1998/Accepted October 2, 1998

The purpose of this study was to improve the characteristics of gypsum-bonded alumina investments using magnesia and potassium sulfate as chemical additives. Magnesia content improved fluidity, delayed setting reaction, increased green strength, and decreased setting expansion, when mixed with distilled water. When the investment was mixed with potassium sulfate, the setting time and setting expansion were reduced, and the thermal expansion increased, however, the green strength decreased. Therefore, the investment with a small amount of magnesia mixed with potassium sulfate was considered a suitable composition, having adequate setting behavior, enough green strength and sufficient compensate expansion for casting.

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

INTRODUCTION

Gypsum-bonded investments are considered unsuitable for high-fusing alloy casting because of the decomposition of gypsum at high temperatures¹⁾. However, it has been reported that a mixture of gypsum and alumina shows high expansion because of the reaction of alumina and calcia decomposed from gypsum²⁾. In previous papers³⁾, we developed an experimental gypsum-bonded alumina investment for high-fusing alloys, and its characteristics were investigated; 20 or 25 mass% gypsum content gave the fundamental properties for high-fusing alloy casting. However, a few problems regarding setting time of these investments were found.

It is well known that chemical additives have an influence on the characteristics of a gypsum product. Magnesia is one stable refractory at a high temperature⁴⁾ and forms the oxide compound spinel with alumina at 900-1200°C⁵⁾. Potassium sulfate functions as an accelerator for gypsum and controls the setting expansion^{1,6)}. In this study, magnesia and potassium sulfate were selected as chemical additives for a gypsum-bonded investment. The effects of these additives on the investment were investigated in an effort to improve the characteristics of the investment, and casting of titanium using this investment was evaluated.

MATERIALS AND METHODS

Experimental investment

According to our previous study³⁾ 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 and added at 20 mass% to the refractory material.

Alumina powder (Fuji-random wa-220, Fujiseisaku, Tokyo, Japan) was selected because investments of this powder show relatively small setting expansion and a large thermal expansion. Electrically fused magnesia powder (MgO; RA-F, Tateho Kagaku, Hyogo, Japan) was selected as an additive for the alumina powder. The chemical compositions of the alumina and magnesia powders supplied are listed in Table 1. Five kinds of experimental gypsum-bonded investments were prepared; their magnesia contents were 0.0, 6.1, 11.7, 16.3, and 28.7 mass% (Table 2).

The investment was mixed with distilled water or 2 mass% potassium sulfate $(K_2SO_4; Grade S, Wako Chemical Industries, Osaka, Japan)$ solution at a water/powder ratio of 0.28 by hand for 30 seconds and another 30 seconds with a vacuum mixing machine (Vac-U-Mixer, Whip-Mix, Fort Wayns, IN, USA). As the investments containing more than 16.3 mass% MgO mixed with distilled water did not set until 120 minutes after the start of mixing, the only the fluidity investments were taken.

Fluidity

Fluidity was measured using the slump test JIS T6601⁷⁾ for a 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 diameter of the slurry 3 minutes after the start of mixing. Three measurements were performed for each investment.

Table 1 Chemical composition of alumina and magnesia powder

Refractory material	Composition (mass%)							
	Al_2O_3	MgO	${\rm TiO}_2$	${ m SiO}_2$	$\mathrm{Fe_2O_3}$	Na_2O	CaO	B_2O_3
Alumina	99.7		0.01	0.03	0.03	0.18	0.03	
Magnesia	0.08	99.2		0.26	0.08		0.38	0.03

Table 2 Compositions of experimental investments and water/powder ratio

	MgO content (mass%)	Mol ratio of MgO to Al ₂ O ₃	Gypsum content (mass%)	Water/powder ratio
1	0.0	0:1	20	0.28
2	6.1	1:6	20	0.28
3	11.7	1:3	20	0.28
4	16.3	1:2	20	0.28
5	28.7	1:1	20	0.28

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 would no longer do so. 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 composition.

Setting expansion

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. The 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 setting expansion 120 minutes after the start of mixing was calculated as the percentage expansion based on the smallest reading of the dial gauge during setting and the final length of the measured specimen. Three measurements were performed for each investment type.

Compressive strength

The freshly mixed investment was poured into a brass mold (10 mm in diameter and 15 mm height). The set specimens were removed from the mold 55 minutes after the start of mixing except for the specimens of 11.7 mass% MgO investment mixed with distilled water which were removed 115 minutes after the start of mixing. These specimens were kept in a container with a 100% relative humidity. Green strengths 2 hours after the start of mixing were obtained by the compressive test using a universal test machine (1123, Instron, Canton, MA, USA) with a crosshead speed of 0.5 mm/min. The fired strengths of the specimens were also obtained in the abovementioned manner after firing. The specimens were heated from 24 hours after the start of mixing to 1200°C at a rate of 10°C/min and to 1400°C at a rate of 5°C/min using a SiC furnace (FG41, Yamato Engineering, Tokyo, Japan), then cooled to room temperature. Six specimens of each investment were tested.

X-ray diffraction

Cylindrical specimens of the investment with 11.7 mass% MgO content mixed with K_2SO_4 fired at 1000, 1200 and 1400°C as described previously³⁾ were crushed into powder for the measurement. Changes of crystal component before and after firing were measured by an X-ray diffraction analyzer (XRD; RAD-II A, Rigaku, Tokyo, Japan) with CuK α radiation, a fixed divergence slit and a 2°/min scanning speed.

304

GYPSUM-BONDED ALUMINA-MAGNESIA INVESTMENT

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 at a similar heating rate as that described for fired strength. 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 each set investment was milled to a powder using a mortar and a pestle, then the powder was kept in a desiccator for at least 24 hours to remove physical water from the investment. Alumina powder was used as a standard; the examined mass of powder was 10.0 mg; the powder was heated to 1400°C at 10°C/min and then cooled to room temperature at 10°C/min. Thermal analysis was performed three times for each investment.

Casting

An invar-steel mold was employed for fabrication of a trapezoidal wax pattern⁸⁾ (Fig. 1); the wax pattern was prepared using the mold with inserters. The dimensions of the wax patterns were 12.7 mm in the upper length, 14.0 mm in the lower length, 11.0 mm in height and 2.0 mm in thickness. Distances between the upper line of the wax pattern and the mold without the smaller inserter at three locations were measured using a profile projector (Model 6C, Nikon, Tokyo, Japan) and recorded as DW. A wax sprue (2.5 mm in diameter) and a running bar (4.0 mm in diameter and 10 mm in length) were attached to the wax pattern, the wax pattern was held at the center of a ceramic ring (42 mm in diameter and 55 mm in height) lined with one fold of a 2.0 mm ceramic liner (Ceramic liner Cyclarc, Morita, Kyoto, Japan). The alumina investment with 6.1 and 11.7 mass% MgO content mixed with the 2 mass% K₂SO₄ solution was employed. The mold was heated at the same heating rate described for the fired strength, commencing 24 hours after the start of mixing. A titanium ingot



Fig. 1 Mold and wax pattern; the upper and lower lines of the wax pattern were 12.7 and 14.0 mm, respectively; the height and thickness were 11.0 and 2.0 mm, respectively.

(Dental pure titanium A, 10 g, Morita, Kyoto, Japan) was cast into the mold using an argon arc melting, gas pressure and centrifugal casting machine (Vulcan-T, Shofu, Kyoto, Japan). The dimensions of the casting after sandblasting using alumina powder (Pencil jet SM, Yoshida, Tokyo, Japan) were also measured by the same procedure as for the wax pattern, and recorded as DC. Dimensional accuracy of the casting (D) was calculated by the following formula based on the dimensions of the invar-steel mold:

$$D = \Delta d \times [(14.0 - 12.7)/(11.0 \times 12.7)] \times 100$$

where $\Delta\,d$ was the amount of dimensional discrepancy between DW (mm) and DC (mm).

The surfaces of the casting obtained from the 11.7 mass% MgO content investment after sandblasting were analyzed using a electron probe micro analyser (EDX; Delta V, Kevex, Foster, CA, USA) for determining the contamination of the investment elements by the casting. The centers of the sprue, the running bar and the casting were measured three times.

RESULTS

Fluidity magnesia

The fluidity measurements are shown in Fig. 2. The error bars in the figure indicate the standard deviations. The fluidities of the investments ranged from 31.0 to 55.8 mm. The fluidity of the investment without magnesia mixed with K_2SO_4 could be not measured because of the short setting time; however, that mixed with distilled water could be measured (31.3 mm). The fluidities of the investment increased with increasing of magnesia content. Fluidity of almost all investments showed a smaller value compared to the minimum limit of the JIS requirement⁷⁾ of 55 mm; however, it was possible to use them as investment using a vibrator because of their thixotropicity.





Fig. 2 Effect of magnesia content and potassium sulfate on fluidity.

Fig. 3 Effect of magnesia content and potassium sulfate on setting time.

NII-Electronic Library Service

GYPSUM-BONDED ALUMINA-MAGNESIA INVESTMENT



Fig. 4 Effect of magnesia content and potassium sulfate on setting expansion 2 hours after the start of mixing.



Fig. 5 Effect of magnesia content and potassium sulfate on green strength 2 hours after the start of mixing, and fired strength.

Setting time

306

The obtained setting times are indicated in Fig. 3. Increased MgO content of the investments had a tendency to delay the setting time. The investments with more than 11.7 mass% MgO content did not set until 120 min when mixed with distilled water. The setting times significantly decreased when the investments were mixed with K_2SO_4 .

Setting expansion

The setting expansion of the investments 120 minutes after the start of mixing is illustrated in Fig. 4. The setting expansions mixed with K_2SO_4 were significantly smaller than those mixed with distilled water. Increased magnesia content of the investments mixed with K_2SO_4 caused only a slight change of the setting expansion; however, when mixed with distilled water, a small amount of magnesia content decreased the setting expansion.

Compressive strength

Fig. 5 shows the green strengths 2 hours after the start of mixing, and the fired strengths of each investment. When mixed with distilled water, the green strength of 6.1 mass% MgO content was larger than that without MgO; however, the green strength of 11.7 mass% MgO content decreased because the investment was not completely set when measured.

The fired strengths of the investments with K_2SO_4 showed a larger value than those mixed with distilled water. The 6.1 mass% MgO content investment showed the largest fired strength, 1.61 MPa.

X-ray diffractometer

The X-ray diffraction patterns are shown in Fig. 6. Strong diffraction lines of



Fig. 6 X-ray diffraction pattern of the investment before and after firing Investment with 11.7 mass% MgO content mixed with K₂SO₄.

CaSO₄ · 2H₂O, MgO, Mg(OH)₂ and Al₂O₃ were observed from the powder before firing; diffraction lines of CaSO₄ instead of CaSO₄ · 2H₂O and MgAl₂O₄ 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 CaO · 2Al₂O₃ and CaO · 6Al₂O₃ were also observed from the powder after 1400°C firing. The final crystal components after 1400°C firing were considered to be MgAl₂O₄, Al₂O₃, $3(\text{CaO} \cdot \text{Al}_2\text{O}_3) \cdot \text{CaSO}_4$, CaO · 2Al₂O₃ and CaO · 6Al₂O₃.

Thermal analysis

Figs. 7A-B show the typical thermal dimensional changes of the investments. Thermal contractions between 350-450 °C were detected in all investments; those between 900-1150 °C were also observed in almost all investments; thermal expansion between 1200-1400 °C and thermal linear contractions during cooling were observed in all investments. These behaviors are consistent with the previous report³⁰. When the investments were mixed with K₂SO₄, the thermal contraction at 900-1150 °C was smaller and the thermal expansion at 1200-1400 °C was more rapid and larger. When the MgO content increased, the thermal contraction at 900-1150 °C increased, however, the thermal contraction between 900-1150 °C of the investment with 11.7 mass% MgO content was the smallest (0.00%); the thermal expansion at 1200-1400 °C also increased, especially when the MgO content was 11.7 mass%; the residual expansions of magnesia content at 0.0, 6.1, 11,7, 16.3 and 28.7 mass% were 1.81%, 2.36%, 2.48%, 1.54% and 0.77%,

307

308

GYPSUM-BONDED ALUMINA-MAGNESIA INVESTMENT







Fig. 8 Effect of magnesia content and potassium sulfate on thermal expansion at 1400 ℃ and residual expansion after cooling to room temperature.



Fig. 9 Typical TG-DTA curves.

respectively (Fig. 8).

Typical TG-DTA diagrams of the investments are illustrated in Fig. 9. When the MgO content was identical, there was no obvious difference except for weight loss at 400°C between the TG-DTA diagrams of the investments mixed with distilled water and those mixed with K_2SO_4 . An endothermic peak with weight loss due to dehydration of $CaSO_4 \cdot 2H_2O_4$ was observed between 100-130°C; a small exothermic peak without weight loss due to transformation from II CaSO₄ to II CaSO₄ was observed at approximately 350°C; an endothermic peak with weight loss at 400°C because of $Mg(OH)_2$ dehydration⁹⁾ was observed when the investment contained MgO mixed with K_2SO_4 ; a broad endothermic peak with weight lost due to decomposition of CaSO₄ was seen from approximately 900°C; an small endothermic peak without obvious weight





loss was recognized at 1220°C; and 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 amount of weight loss of the investment mixed with K_2SO_4 before firing to 200°C and that before firing from 600°C to 1400°C were 4.4-4.7 and 9.7-11.4%, respectively, regardless of the amount of MgO content; however, the amount of weight loss of the investment mixed with K_2SO_4 at 400°C increased with increasing MgO content: the means and standard deviations of weight loss before firing 200 to 600°C at 0.0, 6.1, 11.7, 16.3 and 28.7 mass% magnesia content were $0.0\pm0.0\%$, $0.5\pm0.1\%$, $1.8\pm0.3\%$, $2.1\pm0.2\%$ and $2.2\pm0.1\%$, respectively.

Casting

The obtained casting is shown in Fig. 10. Almost all investments were easily removed from the casting without sandblasting. After sandblasting, a metallic surface was easily obtained. Small casting fins were observed on the upper line of one half of the castings. The EDX analysis revealed contamination of Al, Mg, S, Ca and K on the titanium casting (Table 3). The amount of contamination was the largest at the running bar; however, contamination was the smallest at the center of the casting. The obtained castings were larger than their wax patterns. Dimensional accuracy of castings obtained from 6.1 and 11.7 mass% magnesia content were $0.01\pm0.09\%$ and $0.23\pm0.10\%$, respectively.

DISCUSSION

The water/powder ratio used in this study (0.28) was smaller than that in the previous report³⁾ (0.31) in an effort to reduce setting time; as a result, the setting time

309

GYPSUM-BONDED ALUMINA-MAGNESIA INVESTMENT

Sampling part	Element (mass%)						
	Mg	Al	S	K	Ca	Ti	
Running bar	0.9 (0.1)	8.5 (0.7)	0.3 (0.2)	0.1 (0.0)	0.3 (0.1)	90.1 (0.8)	
Sprue	0.7(0.4)	4.3(0.5)	0.2(0.1)	$0.1 \ (0.0)$	0.4(0.2)	94.3 (0.6)	
Center	0.4(0.1)	4.5(0.5)	0.2 (0.1)	$0.1 \ (0.0)$	0.3 (0.1)	94.5 (0.5)	
						():SD	

 Table 3 Results of elemental analysis of the surface of the titanium casting after sandblasting

and the fluidity decreased, and the setting expansion increased compared with the investments of identical composition in the previous report. Potassium sulfate accelerates the setting of gypsum; however, the effect of magnesia on gypsum setting have not been clearly confirmed. XRD and TG-DTA analysis revealed that some amount of magnesia in the investment hydrated to magnesium dihydrate after setting. Magnesium dihydrate is reported to be an accelerator⁶⁾, however, magnesia acted as a retarder of setting with respect to fluidity and setting time in this study.

Potassium sulfate and magnesia are also known to reduce the setting expansion and green strength of gypsum^{6,10}. The experimental investment used in this study consisted of gypsum and alumina: the alumina powder increased the setting expansion and decreased green strength of the gypsum³⁾. When mixed with distilled water, the green strength of 6.1 mass% MgO content was larger than that without MgO; however, that of 11.7 mass% MgO content decreased because, the investment was not completely set 2 hours after the start of mixing. The means and standard deviations of green strength 4 hours after the start of mixing of 0, 6.1 and 11.7 mass% MgO content investments mixed with distilled water were 2.64 ± 0.43 MPa, 3.06 ± 0.18 MPa, and 3.23 ± 0.27 MPa, respectively. After setting, the investments with MgO mixed with distilled water slightly increased and did not change with respect to MgO content. Mixing with potassium sulfate decreased the green strengths of the investments, while magnesia increased the green strengths of the investments; nevertheless the green strengths of the investments were lower than that of gypsum. Fig. 11 shows SEM images of the experimental investment structures after setting. The calcium sulfate dihydrate crystals of the MgO content investment mixed with distilled water (Fig. 11b) were larger than those in the investment without MgO (Fig. 11a), while those of the investment without MgO mixed with K_2SO_4 (Fig. 11c) were smaller than those of the investment mixed with distilled water (Fig. 11a). Such variation in crystal size had an influence on the setting behavior of the investment. However, it was advantageous that the green strength of the investment mixed with potassium sulfate increased when the investment contained magnesia.

In this study, the experimental investment were fired at 1400°C. As a result, the fired strengths of the investment were similar to those of recent commercial gypsumbonded investments because of sintering of some components.

The thermal behavior of the investment was consistent with the previous report³⁾ except for the dehydration of $Mg(OH)_2$ and the formation of alumina-

310



Fig. 11 SEM images of experimental investments structure after setting.
a: 0 mass% MgO content investment mixed with distilled water
b: 6.1 mass% MgO content investment mixed with distilled water
c: 0 mass% MgO content investment mixed with K₂SO₄
d: 6.1 mass% MgO content investment mixed with K₂SO₄

magnesia spinel (MgAl₂O₄). When all magnesia in the investment was hydrated, the theoretical weight losses of Mg(OH)₂ to MgO for the investments with 6.1, 11.7, 16.3 and 28.7 mass% MgO content were 0.0%, 2.2%, 4.2%, 5.9% and 10.1%, respectively. The observed weight losses due to Mg(OH)₂ dehydration were almost one third to one fifth of the theoretical values. These results suggested that not all magnesia hydrated after setting. This hydration ratio was smaller when the investment was mixed with distilled water. We conclude that potassium sulfate acted as an accelerator for magnesia hydration in this study.

The thermal expansion at 1200-1400 °C depended on the formation of $3(\text{CaO} \cdot \text{Al}_2\text{O}_3) \cdot \text{CaSO}_4$, $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and MgAl_2O_4 . The theoretical expansions due to formation of $3(\text{CaO} \cdot \text{Al}_2\text{O}_3) \cdot \text{CaSO}_4$, $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ and MgAl_2O_4 were 35.9%, 3.8% and 8.1%, respectively. Addition of a small amount of MgO content to the gypsum-bonded alumina investment was effective in increasing the thermal expansion because of MgAl_2O_4 formation, however, large amounts of MgO were not so effective. This might be due to the reduction of alumina content in the investment. When the investment was mixed with K_2SO_4, its investment showed a small setting expansion;

312

GYPSUM-BONDED ALUMINA-MAGNESIA INVESTMENT

therefore, the refractory particle (MgO and Al_2O_3) packed tightly by the gypsum and had a large contact surface area to the gypsum. These phenomena might be responsible for reducing the thermal contraction at 900-1150°C and increasing the thermal expansion 1200-1400°C.

The following effects of potassium sulfate and magnesia on the gypsum-bonded alumina investment became clear after examining the experimental results. Mixing the investment with potassium sulfate solution accelerated the setting reaction but decreased setting expansion and green strength. Magnesia content of the investment improved fluidity and retarded the setting reaction, but increased the green strength. Especially when mixed with K_2SO_4 , the investments with small amounts of magnesia content showed suitable setting times, small setting expansion, and sufficient green strength. It was possible to control the amount of thermal expansion by adjusting the magnesia content of the investment. Therefore, the investments with 6.1 and 11.7 mass% MgO content mixed with K_2SO_4 were employed for evaluating the titanium casting.

It was possible to fabricate a titanium casting using this experimental investment. The investment was completely removed from the casting surface with sandblasting. Small casting fins were found on the upper line of some castings. The green and fired strengths of the investments used for titanium casting were smaller than phosphate-bonded investments¹¹⁾ or special investments for titanium casting¹²⁾. The casting pressure of the casting machine used was relatively large, which may have been the cause of the casting fins. The EDX revealed contamination by Al, Mg, S, Ca and K from the casting, however, the amount of the contamination was small. The surface of the titanium casting was rough, and it would be necessary to modify the particle distribution of the refractory to obtain a smooth cast surface.

The setting expansion and residual thermal expansion values of the investments with 6.1 and 11.7 mass% MgO content investment were 0.03 and 2.36% and 0.06 and 2.48%, respectively. The total expansion of these investments was estimated to be 2.39 and 2.54%; therefore, the casting shrinkage of a titanium was calculated 2.38 and 2.31%. This casting shrinkage of titanium was larger than the previous report of $1.8-2.0\%^{13,14}$. These discrepancies were considered to be due to differences in the casting conditions.

CONCLUSION

In this study, the effects of magnesia and potassium sulfate on the gypsum-bonded alumina investment were investigated. Magnesia content improved the fluidity, delayed the setting reaction, and increased the green strength, and decreased the setting expansion of the investment mixed with distilled water. When the investment was mixed with potassium sulfate, the setting time and setting expansion were reduced, and the thermal expansion increased, however, the green strength decreased. Therefore, the investment with small amount of magnesia content mixed with potassium sulfate was considered a suitable composition, having adequate setting behavior,

enough green strength and sufficient compensate expansion for casting. A titanium casting was obtained using the investment and contamination by investment components of the casting surface was minimal.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to professor Fumio Nishimura of the Department of Dental Technology I at Tokyo Medical and Dental University for his valuable guidance and help throughout his research. We also thank Dr. Hideo Nakamura, Dr. Kazuo Motomura and Mr. Naohiko Iwasaki of the same department for preparing the manuscript.

We would like to extend our gratitude to GC Corp., Japan, for providing the gypsum.

REFERENCES

- 1) Anusavice, K.J.: Phillips' science of dental materials, 10th ed., W. B. Saunders. Co., Philadelphia, 1996, pp.69-490.
- 2) Sasaki, T.: Study on refractory materials of gypsum-bonded investments, J J Dent Mater 10(2): 219-240, 1991. (in Japanese)
- 3) Yan, M. and Takahashi, H.: Gypsum-bonded alumina dental investment for high-fusing casting, *Dent Mater J* 17(3): 174-185, 1998.
- 4) Tokunaga, K.: Application of magnesia clinker to dental casting investments, J Japan Res Soc Dent Mat Appl 34(3): 205-220, 1977. (in Japanese)
- 5) Oda, Y.: Some feature of titanium casting systems, DE 111:11-20, 1994. (in Japanese)
- 6) Sekitani, M.: Gypsum, Kasai Press, Tokyo, 1964, pp.208-237. (in Japanese)
- 7) JIS T 6601-1989 Gypsum-bonded dental investments for casting.
- Habu, N.: study of reduction of dental casting time using quick heating gypsum-bonded investment mixed with accelerator solution, J J Dent Mater 17(1): 76-88, 1998. (in Japanese)
- 9) Hayashi, T.: Basic refractory, Casting techniques editorial board: Nenryo taikabutsu (Fuel and refractory), Nikkan Kougyou Shinbunsya, Tokyo, 1969, pp.219-225. (in Japanese)
- Hiyama, S. and Fukui, H.: Expansion of gypsum by adding material, *Gypsum* 2:27-37, 1951. (in Japanese)
- Yan, M., Takahashi, H., Nishimura, F., Habu, N., Nakamura, H. and Motomura, K.: Comparison of properties of phosphate-bonded investments for quick heating, J J Dent Mater 16(5): 405-414, 1997. (in Japanese)
- 12) Ohtani, T., Nakano, F., Habu, N., Yan, M., Iwasaki, N., Motomura, K., Nakamura, H., Takahashi, H., Nishimura, F. and Ishiwata, M.: Studies of short-time cast for titanium (Part 1) properties of dental investments for titanium with quick heating, Society for titanium alloys in dentistry 10th : 68-69, 1997. (in Japanese)
- 13) Takahashi, H., Miyazaki, T. and Kawawa, T.: Accuracy of titanium casting crowns obtained from calcia base mold, *Clinical Materials* 16:155-160, 1994.
- 14) Nishimura, F., Watari, F., Nakamura, H., Fukumoto, R. and Morita, N.: Casting accuracy and shrinkage of titanium castings made with zirconia investment, J J Dent Mater 9(6): 850-857, 1990. (in Japanese)