Phosphate-bonded ZrSiO_4 Investments Added with ZrC and ZrN for Casting Titanium

Junzo TAKAHASHI¹, Kazuyoshi KITAHARA¹ and Fuminobu KUBO²

¹Division of Biomaterials Science, Graduate School of Dentistry, Osaka University, 1-8 Yamadaoka, Suita, Osaka 565-0871, Japan

²Taisei Dental Mfg. Co. Ltd., 4-38-7 Hosida-Kita, Katano, Osaka 576-0017, Japan

Corresponding author, E-mail: j-takaha@dent.osaka-u.ac.jp

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In this study, new investments for titanium were developed by adding ZrC or ZrN as chemical additive for thermal expansion to a phosphate-bonded zircon (ZrSiO_4) investment. The following effects were then examined: setting expansion, residual thermal expansion, and compressive strength of these experimental investments; surface roughness of cast plate; and casting accuracy of titanium crown. For residual thermal expansion, it occurred even while investments were cooled to room temperature after firing in air atmosphere. This was due to the additives' oxidation to ZrO_2 – suggesting that residual thermal expansion increased with increased amount of these additives. As for casting accuracy of full-crown cast into molds at room temperature, it correlated with the ZrN content. Hence by adding the right amount of ZrN, cast titanium crowns with low surface roughness and good adaptability could be obtained.

Key words: Investment, Thermal expansion, Titanium

INTRODUCTION

Recently, many new concepts on dental investments have evolved: ammonia-free phosphate-bonded investments¹⁾, investments preventing blackening of noble alloys^{2,3)}, rapid heating investments^{4,5)}, and a resin-bonded calcia investment⁶⁾. Though new, all these recently-evolved concepts adopt a common, established principle: that is, to make use of the setting and thermal expansions of investment materials to compensate the casting shrinkage of dental alloy. However, when patterns exist, large setting expansion is known to be heterogeneous, thus leading to distortion of patterns in casting investments^{7–13)}. This is a problem that remains to be solved, especially when investing hard resin patterns for superstructures on implant bodies.

It is necessary to develop an investment which compensates the casting shrinkage of titanium (about 1.8%) by thermal expansion only. To date, the thermal expansion of investment materials for titanium has been supported by various methods. They are namely, α - β transformation of silica (cristobalite and quartz), transformation of spinel (such as $\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4$)¹⁴⁾, and oxidation of metallic zirconium (Zr) powder¹⁵⁾ and titanium (Ti) powder¹⁶⁾. Silica has high reactivity with molten titanium, thus causing titanium to deteriorate due to formation of oxide and silicide. Though this reaction can be suppressed by low mold temperature, thermal expansion decreases due to the reversible α - β transformation of silica. Since transformation of spinel is irreversible, it seems like the reaction

between mold and molten titanium can be circumvented by casting titanium into mold at a lower temperature. However, spinel transformation requires a special furnace that is able to heat above 1,000°C. Like spinel transformation, thermal expansion due to oxidization of zirconium is also irreversible. However, metallic zirconium powder is too expensive.

In a previous study¹⁷⁾ we developed thermal expansion-type investments by adding ZrC and ZrN powders to a magnesia (MgO) cement. Like metallic zirconium, ZrC and ZrN are able to oxidize and expand by heating in the atmosphere. Commercial magnesia cement had been selected as a base investment, since it has low thermal expansion and magnesia (MgO) has lower reactivity with molten titanium than silica (SiO_2)^{18–21)}. However, MgO cement as a base investment has two glaring disadvantages: high cost and a long setting time of about two hours.

The purpose of the present study was to develop a cheap, easy-to-operate, and precise casting investment for titanium. Therefore, we selected phosphate as a binder material (which is established in commercial investments for casting of high melting point metals) and zircon (ZrSiO_4) as a refractory material (which has intermediate reactivity between ZrO_2 and SiO_2 with molten titanium). Next, the characteristics of phosphate-bonded ZrSiO_4 investments with varying contents of ZrC and ZrN were examined, as well as the casting accuracy of titanium crown.

MATERIALS AND METHODS

Two kinds of ZrSiO_4 powder were selected as

Table 1 Fluidity of experimental investments

Composition (wt%) NH ₄ H ₂ PO ₄ /MgO/Zircon sand/Zircon flour	Fluidity (mm)
4/6/ 0/90	36.1±0.4
4/6/10/80	36.7±0.3
4/6/20/70	36.2±0.2
5/5/ 0/90	36.5±0.6
5/5/10/80	40.1±0.4
5/5/20/70	68.9±0.9
6/4/ 0/90	98.5±1.3
6/4/10/80	112.7±0.7
6/4/20/70	136.5±1.6

refractory materials: zircon sand (EB, mean particle size: 105 μ m, Iwatsuki Chemical Mining Co., Toyonaka, Japan) and zircon flour (#350, mean particle size: 14.5 μ m, Iwatsuki Chemical Mining Co., Toyonaka, Japan). Nine types of experimental investment were prepared by mixing binder and refractory materials in differing proportions, as shown in Table 1. A low total amount of binder materials (10%) was selected to ensure low setting expansion.

Two kinds of zirconium compounds were selected as chemical additives for thermal expansion: ZrC powder (ZrC-F, mean particle size: 2.25 μ m, Japan New Metals Co., Osaka, Japan) and ZrN powder (ZrN-01, particle size: 1.52 μ m, Japan New Metals Co., Osaka, Japan). These chemical additives (ZrC and ZrN) were then added into the base investment powder at a range of 3-10 wt%. The experimental investment powders were mechanically mixed for 30 seconds with a 10% colloidal-silica solution (dilute solution of Silicadol 30, Nippon Chemical Industrial Co., Tokyo, Japan) at liquid/powder ratio of 0.18. The colloidal-silica solution was used as a mixing liquid to strengthen investment molds.

Fluidity of investment slurry was then measured in the following manner. A casting ring (38-mm internal diameter $\times$ 50-mm height), placed on a glass plate, was filled with the slurry at 2 minutes after mixing. Next, the casting ring was lifted slowly. Fluidity (mm) was calculated from the mean value between maximum and minimum diameters of slurry measured at 1 minute after lifting.

Setting expansion was measured in a longitudinal direction in the following manner. A casting ring (38-mm internal diameter $\times$ 50-mm height), placed on a glass plate, was filled with the investment slurry (a mixture of 200 g of powder and 36 mL of water). A thin plastic square plate (10mm on each side) was placed on the investment slurry, and its displacements measured — longitudinally along the height of the casting ring — by a laser displacement sensor (LB-1000, Keyence Co., Osaka, Japan). Five measurements for each investment were performed at room temperature. The casting liner — a

single layer of Kaowool liner (Casting Liner No. 11, 1.0 mm in thickness, GC Co. Ltd., Tokyo, Japan) — was lined end-to-end, and paraffin was used to seal the gap between the ring and the glass plate to prevent water release.

Thermal gravity (TG) of the 30-mg triturate of each investment concretion was measured with a thermal analysis instrument (DTG-60H, Shimadzu Co., Kyoto, Japan) at a heating rate of 10°C/min from room temperature to 900°C.

For residual thermal expansion tests, the specimens were produced by injecting the investment slurry (a mixture of 50 g of powder and 8 ml of water) into silicone-rubber mold (5-mm internal diameter $\times$ 20-mm height). Two hours after mixing, the tests were performed using a thermal analysis instrument (DTG-60H, Shimadzu Co., Kyoto, Japan) at a heating rate of 10°C/min from room temperature to 800°C (in the case of ZrC) or 900°C (in the case of ZrN) with a load of 1 gf under air atmosphere for each investment. After holding at the firing temperature for two hours, the specimens were cooled to room temperature by the same appliance and at nearly equal conditions.

For compressive strength tests, the specimens were made by injecting the investment paste (a mixture of 200 g of powder and 36 mL of water) into six silicone-rubber molds (16-mm internal diameter $\times$ 24-mm height), and both ends covered with a greased slide glass each. Compressive strength was then evaluated, six times per investment, using a universal testing machine (Autograph AGS-500D, Shimadzu Co., Kyoto, Japan) at room temperature and at a cross-head speed of 1 mm/min. The green compressive strength was measured at 2 hours after setting. The fired compressive strength measurements were obtained from specimens heated to 800°C (in the case of ZrC) or 900°C (in the case of ZrN) in a burnout oven, held at the firing temperature for 60 minutes, and finally cooled down to room temperature in furnace.

Wax patterns for cast crowns were made of an inlay wax (Inlay Wax Soft, GC Co., Tokyo, Japan) by a softened-pressed method, using a special tapered (taper: 6°) metal die, as shown in Fig. 1. A sprue (2.5-mm diameter $\times$ 8-mm length) was vertically attached to the edge of the occlusal surface of crown pattern. The pattern was removed from the metal die and invested by a mixture of 200 g of powder and 36 mL of water in the casting rings (29-mm internal diameter $\times$ 35-mm height), which were lined end-to-end with a single layer of Kaowool liner (Casting Liner No. 11, GC Co., Tokyo, Japan). Two hours after mixing, the invested patterns were heated in a burnout oven to 800°C (in the case of ZrC) or 900°C (in the case of ZrN), heat-soaked for 2 hours, and finally cooled in the oven. Pure titanium (Titan100, 10 gf, Ti>99.5%, Shofu Co., Kyoto, Japan) was cast

Fig. 1 Relationship between the degree of accuracy of crown and the marginal-gap. In an oversized crown, the marginal-gap is calculated from L_2 measured after moving both a spacer (its height= L) and an apical part.

into mold at room temperature in an argon-arc melting and pressurized casting machine (Castmatic CM-230, Iwatani Industry Co., Osaka, Japan) with a copper crucible at a gas pressure of 0.2 MPa. Five castings were made for each condition, and treated by sandblasting (mean grain size: $54\mu\text{m}$) for 5 seconds at a gas pressure of 0.4 MPa. The degree of accuracy of cast crown was examined on the metal die, which was permitted to measure quantitatively crown-type marginal-gap separations.

Casting accuracy (CA) was calculated from this equation:

$$\text{CA (\%)} = 100(D_1 - D) / D$$

where D was the marginal diameter of the metal die (9.35 mm) and D_1 the internal diameter of cast crown. D_1 , on the other hand, was calculated from both the marginal-gap separations and the taper (6°) of the metal die. When cast crown was larger than wax pattern, its negative value was measured by removing the spacer of 7 mm in height and the apical part (Fig. 1) from the metal die. Its casting accuracy was then calculated by using an equation like the one above.

Wax patterns (1.6 mm $\times$ 18 mm $\times$ 18 mm) for measuring surface roughness and cross-section hardness were cut from a paraffin wax (Paraffin Wax, GC Co., Tokyo, Japan), and a sprue (4.0-mm diameter $\times$ 8-mm length) was attached to each pattern. As in the case of cast crown — investing and casting

of this wax pattern, and ultrasonic cleaning of castings were carried out too. The surface roughness (R_a : arithmetic mean deviation of the roughness profile) in three parts of two cast plates was measured using a surface roughness tester (Surftest 201, Mitutoyo Co., Tokyo, Japan) at a cut-off length of 0.8 mm and a traverse length of 2.5 mm. On the other hand, cast plates were cut in half using a diamond disc (Isomet Lowspeed Saw, Buehler) for cross-section hardness measurements. The exposed cross-section was mounted in cold-cured acrylic resin, polished with Emery papers and followed by $0.5\mu\text{m}$ alumina particles on a cloth polishing wheel. The micro-hardness of these specimens was measured through the cross-section at 25 or $50\mu\text{m}$ intervals with a micro Vickers hardness tester at a load of 500 gf (three times per cast plate from each investment mold).

Statistical analysis was done using one-factor analysis of variance (ANOVA). Scheffe's test was used for all post-hoc pair wise comparisons at the 95% confidence level. Scheffe's critical value shown in the results is an indicator of significant difference. If the obtained difference exceeds the critical value for a given comparison, then that comparison is significant.

RESULTS

Table 1 shows the fluidity results of the experimental

Fig. 2 Setting expansion curves of three kinds of phosphate bonded ZrSiO_4 investment with same binder ratio (6/4) and different refractory ratio.

Fig. 3 TG curves of a base phosphate bonded ZrSiO_4 investment (6/4/ 0/90) and those added with 5%ZrC and 7%ZrN.

Fig. 4 Typical residual thermal expansion curves of investments added with varying contents of ZrC and ZrN powders; a) the case of ZrC, and b) the case of ZrN. The addition of ZrC brought about sharper and higher thermal expansion than that of ZrN.

investments. Investments with 6/4 binders ratio had sufficient fluidity. In terms of setting expansion, Fig. 2 shows that investments of 6/4 binders ratio had very low setting expansion.

Fig. 3 shows the TG curves of 6/4/ 0/90 base investments added with 0%, 5% ZrC, or 7% ZrN. A base investment added with 5% ZrC increased the gravity by heating above 580°C, while a base investment added with 7% ZrN increased the gravity by heating above 620°C.

Figs. 4(a) and (b) show the thermal expansion curves of investments added with varying contents of ZrC and ZrN respectively. ZrC-added investments expanded abruptly at 550-750°C (temperature range is about 200°C), and kept its expansion at 750-800°C. This investment then contracted slightly when cooling to room temperature. On the other hand, ZrN-added investments expanded abruptly at 600-900°C (temperature range is about 300°C), continued to

expand gradually during holding at 900°C, and finally contracting slightly when cooling to room temperature. The residual thermal expansion values increased with the content of ZrC and ZrN.

Fig. 5 shows the compressive strengths of ZrC-added and ZrN-added investments. Though the compressive strength of 6/4/ 0/90, which was a base investment, held after firing at 800°C and 900°C, the compressive strengths of most ZrC-added and ZrN-added investments decreased dramatically after firing at 800°C and 900°C respectively.

Fig. 6 shows the surface roughness values of cast titanium plates by different investments. The firing temperatures of ZrC-added and ZrN-added investments were 800°C and 900°C respectively. The burn-in phenomenon due to reaction between molten titanium and investment material was not observed in all cast plates.

Fig. 7 shows the hardness distribution in cross-

Fig. 5 Compressive strength of the investments added with ZrC and ZrN. Scheffe's critical value is an indicator of significant difference.

Fig. 6 Surface roughness of cast titanium plates in different investments and fired temperatures. Molten titanium was cast into molds at room temperature after firing at different temperature (800°C in the case of ZrC and 900 °C in the case of ZrN). Scheffe's critical value is an indicator of significant difference.

Fig. 7 The change of micro-hardness in cast titanium crowns with the distance from the surface toward the inner part.

Fig. 8 The relationship between the casting accuracy of titanium crowns and the content of ZrN. Molten titanium was cast into molds at room temperature after firing at different temperature.

section. Each value is the mean value with standard deviation of three measurements. A commercial phosphate-bonded silica investment mold (CeraVest Quick, GC Co., Tokyo, Japan) was also used for comparison. The hardness at 25 μm from the surface in 6/4/ 0/90 investments added with 0% and 7% ZrN was lower than that of the commercial phosphate-bonded silica investment.

Fig. 8 shows the relationship between the casting accuracy of titanium crowns and the ZrN content of investments. Titanium crowns cast into 6/4/ 0/90 investments added with 4.5% and 5.0% ZrC had some flashes in inner surface of crown. Otherwise, the casting accuracy correlated highly with the quadratic function of the ZrN content. Good casting accuracy stood at about 7.0% ZrN content.

DISCUSSION

Binder content affects setting time, fluidity, setting expansion, and compressive strength of phosphate-bonded investments. Most commercial phosphate-bonded investments contain 20% of binders. Also in our previous study, the setting expansion of phosphate-bonded investments decreased when the amount of binders was reduced from 20% to 5%²²⁾. In the present study, we selected 10% for binders content to suppress setting expansion. It was found that the ratio of binders ($\text{NH}_4\text{H}_2\text{PO}_4/\text{MgO}$) and the particle-size distribution of refractory materials (zircon) had effects on the fluidity of investments, as shown in Table 1. Based on the fluidity results, a 6/4/ 0/90 base investment was selected from these experimental investments.

Thermal expansion of ZrC- and ZrN-added investments could be due to ZrC and ZrN being oxidized to ZrO_2 by atmospheric oxygen. This is because when heated at the same temperature range,

an abrupt mass increase in TG of ZrC- and ZrN-added investments was observed. This result seems like a parallel with the thermal expansion in ZrC- and ZrN-added MgO cements in our previous study¹⁷⁾.

It is very difficult to get a sound casting of pure titanium due to severe reactivity of molten titanium with molds and atmospheric oxygen. Therefore in the present study, we selected low mold temperature (room temperature), argon atmosphere, and ZrSiO₄ refractory material (which has lower reactivity than SiO₂). Zircon (ZrSiO₄: zirconium silicate) (specific gravity of 4.5, melting point of 2,430°C, and thermal expansion coefficient of $4.43 \times 10^{-6}/^{\circ}\text{C}$) is a mineral which can be used as refractory material and white emulsifier for tiles, tableware, and sanitary ceramics. Though ZrSiO₄ has low thermal expansion, the thermal expansion of new investment can be increased by the oxidation of ZrC and ZrN additives. Furthermore, ZrO₂ (which is derived from the oxidation of ZrC and ZrN) is thermodynamically more stable than TiO₂²³⁾. In terms of surface roughness, no burned-in investment was attached on any casting surface. Moreover, this study yielded low surface roughness results – the same as those in the previous studies on investments for titanium^{24,25)}.

To compensate casting shrinkage of pure titanium even at low mold temperature, large residual expansion is necessary. In the present study, residual thermal expansion was examined when investments were cooling down after heating at 800°C and 900°C, as shown respectively in Figs. 3(a) and (b). As the content of ZrC or ZrN increased, the residual expansion increased because more ZrO₂ was formed. Based on these results, it is feasible to cast titanium into mold at room temperature. This study showed that a content of about 7% ZrN brought about good accuracy in casting pure titanium crowns. However, when ZrC was added above 4.5%, some flashes (thin, planar remnants) developed in inner surface of crown. This phenomenon may well be related with mold cracks that occurred due to low compressive strength and high thermal expansion in investments with ZrC content above 4.5%.

Casting accuracy has a non-linear correlation with residual expansion. A high compressive strength of investment restricts the casting shrinkage of molten metal. On this note, compressive strength is also an important factor that influences casting accuracy¹³⁾. In this study, the casting accuracy correlated highly with the quadratic function of ZrN content, as shown in Fig. 8. Furthermore this quadratic relation was also observed in MgO-base investments of previous study¹⁷⁾. These observations may thus suggest that casting shrinkage can be compensated not only by thermal expansion, but also by compressive strength. However, MgO-base investments with lower strength and residual expansion

(than ZrSiO₄-base investments) brought about high adaptability. As to how this matter will be resolved will depend on future studies that focus on the thermal expansion and compressive strength of mold which is in contact with molten titanium.

CONCLUSION

To develop thermal expansion-type investments for casting titanium, ZrC and ZrN powders were added to a phosphate-bonded ZrSiO₄ investment with low setting expansion (0.02%) and thermal shrinkage (0.80%). The residual thermal expansion at room temperature after firing increased with the content of ZrC and ZrN. The casting accuracy of cast titanium crowns into low temperature molds improved with the content of ZrN. The addition of ZrC above 4.5% decreased the compressive strength of fired investments and brought about flashes to cast titanium crowns. Eventually, cast titanium crowns with excellent fit were achieved from a phosphate-bonded ZrSiO₄ investment with 7% ZrN.

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