Development of Casting Investment Preventing Blackening of Noble Metal Alloys Part 3. Effect of Reducing Agent Addition on the Strength and Expansion of the Investments

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Different reducing agents (B, Al, Si and Ti) were individually added to two gypsum-bonded investments to prepare investments preventing surface blackening of some noble cast alloys. The effect of different additive contents on green-body and burnout compressive strength, setting and thermal expansion of the investments were evaluated. The strength and expansion of the investments were changed by the additives. The compressive strength of Al-, Si- and Ti-added investments decreased with the increase of additive contents. The burnout strength of B-added investments significantly increased while green-body strength remained unchanged. The setting expansion of the B-added investments increased while those of the Al-, Si- and Ti-added investments decreased with the increase of additive contents. The thermal expansion of the Si- and Ti-added investments decreased, and that of the Al- and B-added investments remained unchanged. Further study is necessary to evaluate the effects of these additives on the accuracy of dental castings.

Key words: Casting investment, Compressive strength, Linear expansion

INTRODUCTION

Some noble alloys, especially 12% Au-20% Pd silver-based alloys frequently show blackening of their surfaces after the casting process using gypsum-bonded investments. In our previous study\(^1\), investments that can prevent surface blackening of these alloys were developed by adding reducing agents such as boron, aluminum, silicon and titanium particles to a commercially available gypsum-bonded investment. Color analysis of the surface showed that either aluminum or boron particle was effective in preventing surface blackening of cast 12% Au-20% Pd silver-based alloy. The same effect was also found on Type 4 gold alloys in another study\(^2\). However, the inclusion of these additives in the investments may influence the strength of the investments. Moreover, these additives can react with oxygen during the burnout heating procedures, which may cause excessive expansion of the casting molds and subsequently compromise the precision of the resulted castings. Thus, the objectives of the present study were to investigate the effects of the additives and their different contents on the compressive strength, and the setting and thermal expansion of the gypsum-bonded investments.

MATERIALS AND METHODS

Preparation of the experimental investments

The reducing agents and the commercially available gypsum-bonded investments used in this study are listed in Table 1. The experimental investments were prepared by individually adding these reducing agents to the commercial investments. The contents of B particles in the investment powder were 0.125, 0.25, 0.50 and 1.00 mass%, and those of Si, Al and Ti particles were 5, 10 and 15 mass%. The experimental investment powder was prepared from blending the reducing agent and the commercially available investment powder by hand. A totally of 26 experimental investments were prepared. The original investments without any reducing additive were also evaluated as controls.

<table>
<thead>
<tr>
<th>Products</th>
<th>Code</th>
<th>Purity</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron amorphous*</td>
<td>B</td>
<td>96.45%</td>
<td>Average 0.91 (\mu m)</td>
</tr>
<tr>
<td>Al (Al)-100**</td>
<td>Al</td>
<td>&gt;99.70%</td>
<td>75–150 (\mu m)</td>
</tr>
<tr>
<td>Silicon*</td>
<td>Si</td>
<td>99.999%</td>
<td>&lt;74 (\mu m)</td>
</tr>
<tr>
<td>Titanium powder++</td>
<td>Ti</td>
<td>&gt;99.10%</td>
<td>&lt;45 (\mu m)</td>
</tr>
<tr>
<td>Cristobalite Micro II(^1)</td>
<td>CB</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Newrivers(^2)</td>
<td>NC</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*H.C. Starck GmbH & Co., KG, Goslar, Germany
**Minalco Co., Ltd., Osaka, Japan
+ Hirano Seizaemon Shoten Co., Tokyo, Japan
++ Sumitomo Sitix of Amagasaki, Inc., Amagasaki, Japan
\(^1\)GC Corp., Tokyo, Japan
\(^2\)Mutsumi plaster industries, Mie, Japan

Measurement of the compressive strength

The experimental investment was manually mixed for
15 sec, followed by vacuum mixing for 45 sec using a vacuum mixing machine (J. Morita Tokyo MFG Corp., Tokyo, Japan) at a water/powder ratio of 0.33. For the compressive testing, 10 cylindrical specimens (diameter: 30 mm, height: 40 mm) were made for each of the 26 investments (test conditions) using a stainless steel mold (B-004-2, Japan Mecc Co. Ltd., Tokyo, Japan). The specimens were removed from the molds 30 min after the start of the mixing.

The green-body compressive strength of the investment was measured two hours after the start of the mixing using a universal testing machine (Shimadzu Seisakusho Ltd., Kyoto, Japan) at a crosshead speed of 2 mm/min, and five specimens were tested for each of the 26 test conditions. The effects of reducing agents on the compressive strength of the investments were statistically analyzed using ANOVA and Tukey's multiple comparison.

Measurement of the linear setting expansion and thermal expansion
The investments were mixed as described in the aforementioned compressive test. The setting expansion of the investment was measured at two hours after the mixing using a setting expansion tester (B-005-3, Japan Mecc Co. Ltd., Tokyo, Japan) designed for ISO74903. Cylindrical specimens (diameter: 20 mm, height: 50 mm) were prepared using a silicone rubber mold. Two hours after mixing, the linear thermal expansion was measured using a thermal dilatometer for dental investments (A-010, Japan Mecc Co. Ltd., Tokyo, Japan) at 700°C at a heating rate of 5°C/min, with 15 min holding period at 700°C. Three specimens were tested for both setting and thermal expansion for each of the 26 test conditions. The effects of reducing agents on the linear setting and thermal expansion of the investments were statistically analyzed using ANOVA and Tukey's multiple comparison.

TGA and DTA of the experimental investments
Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a thermal analyzer (Thermo plus 2, Rigaku Corp., Tokyo, Japan). A small amount of experimental investment (15-20 mg) was heated under static air from room temperature to 700°C at a heating rate of 5°C/min, with 15 min holding time at 700°C. The weight change and heat flow were measured for each investment.

RESULTS

Green-body and burnout compressive strength
The green-body and burnout compressive strength of CB and NC investments with different contents of additives were listed in Table 2. The effects of the reducing agents on the green-body and burnout compressive strength of CB investment were shown in Fig. 1 and 2, respectively. For both of the NC and CB investments, the green-body compressive strength of the B-added investments remained unchanged (P>0.05) (Fig.1-a), while the burnout strength increased significantly (P<0.01) with the increase in B contents (Fig.2-a). Both the green-body and burnout compressive strength of the Al-, Si- and Ti-added investments decreased (P<0.01) with the increase of...
Fig. 1 The green-body compressive strength of CB investments with different contents of (a) B, (b) Al, Si and Ti additives.

Fig. 2 The burnout compressive strength of CB investments with different contents of (a) B, (b) Al, Si and Ti additives.

the additive contents (Fig. 1-b and Fig. 2-b).

Linear setting expansion and thermal expansion
The setting and thermal expansion of CB and NC investments with different contents of additives were also listed in Table 2. The setting and thermal expansion curves of CB investments with different additives were shown in Fig. 3. Only the curves of investments with the highest content of each additive were shown. The patterns of the setting expansion curve are similar for all the investments, while the thermal expansion curves of Al-added investment shows some difference mainly in the segment after 500°C, with a steep increase in the expansion compared to those of the other investments. The effects of different contents of reducing additives on the linear expansion of the experimental investments for the CB investment are shown in Fig. 4. The experimental investments for the NC investment also showed similar results.

With the increase of the additive contents, the setting expansion of the B-added investments increased (P<0.01) (Fig. 4-a), while those of the Al-, Si-, and Ti-added investments decreased (P<0.01)
Fig. 3  Setting (a) and thermal (b) expansion curves of CB investment with different additives. Only the curves of investments with the highest content of each additive were shown.

Fig. 4  The linear expansion of CB investments with different contents of (a) B, (b) Al, (c) Si and (d) Ti additives. (SE: setting expansion, TE: thermal expansion. Vertical bars indicate 95% confidence intervals.)
Fig. 5 TG and DTA analysis of CB investments (a) without reducing additive, with (b) 1 mass% B, (c) 15 mass% Al, (d) 15 mass% Si, and (e) 15 mass% Ti additives.

(Fig. 4-b, c, d). The thermal expansion of the Si- and Ti-added investments decreased \((P<0.05)\), and those of the Al- and B-added investments remained unchanged \((P>0.05)\).

The total expansion of the B-added investment showed increasing tendency, while those of Al-, Si- and Ti-added investments showed decreasing tendency with the increase of the additive contents.

**TGA and DTA of the experimental investments**

The TGA and DTA curves of CB investments with different reducing additives are shown in Fig. 5. Those of NC investments also showed similar patterns. Three endothermic peaks occurred at about 55 \(^\circ\)C, 130 \(^\circ\)C, and 250 \(^\circ\)C on the DTA curves for the investments without an additive and investments with Si and Ti additive. The DTA curve of the Al-added investment showed an extra endothermic peak at 657 \(^\circ\)C. The weight gain rates of the experimental investments with B and Ti additives were observed to rise from approximately 550 \(^\circ\)C and 600 \(^\circ\)C, respectively, and continued up to the end of the heating cycles, while no obvious weight gain was observed for the investments with Al or Si additive.

**DISCUSSION**

The previous studies\(^{2,4}\) showed that CuO formation on the casting surface accounted for the blackening of the cast Ag-Pd-Cu-Au alloys and Type 4 gold alloys. B and Al additives in the gypsum-bonded investment were effective in restraining the formation of CuO which is black\(^5\). Cu2O, which is red\(^5\), was formed instead of CuO, and thus the surface blackening of the cast alloys was prevented. The oxidation of the reducing agent consumes the oxygen in the mold cavity and leaves a comparatively inert casting atmosphere. These reducing agents can also compete with Cu to react with oxygen since they have a higher potential to form oxidants than Cu, and thus the oxidation of Cu was reduced. For the B-added investments, it is very likely that the acidic boric oxide produced during burnout heating procedure can still react with metal oxides and serve as a reducing agent to prevent the blackening of the alloys.

In the present study, the addition of Al, Si or Ti resulted in the decrease of both the green-body and burnout compressive strength of the investments. This can be explained by the fact that the content of gypsum binder in the investments decreased with considerable amount (5 to 15 mass%) of Al, Si or Ti particles added to the original investments. Since the amounts of B additive was only 1 mass% at the highest content in the present study, its influence on the green-body strength of the investments was not as significant as the other additives. On the other hand, the burnout compressive strength of the B-added investments increased significantly. Though the reasons remained unknown, it may be that the reaction of B with oxygen at more than 300 \(^\circ\)C during the burnout heating procedure resulted in the formation of B2O3, which melts at about 450 \(^\circ\)C\(^6\). B2O3 could have possibly served as a kind of sintering agent for the investments. The formation of a boric glass phase with some components in the investments could also serve as a sintering agent, which would result in an increase of the compressive strength of the burnt-out investments. The increased burnout strength will make the divesting of a casting difficult. On the other hand, the investments with more than 0.5 mass% B additives could possibly be used for ringless casting molds. Further study is necessary to investigate their validity for ringless techniques.

The setting expansion of the Al-, Si- and Ti-added investments decreased with the increase of the additives. Since the setting expansion of the investments is based on the setting expansion of the gypsum component in the investment, the decrease can be explained by the fact that the content of gypsum in the investments decreased with the addition of the additives. B was found to increase the setting
The addition of the reducing agents resulted in a decrease of the cristobalite concentration in the investments and subsequently the thermal expansion of the investments should have decreased. On the other hand, reaction of the additives with oxygen during the burnout procedure could also cause some expansion of the investments. The thermal expansion of the investments with reducing agent additive is the result of the interaction of the two facts above. Though B has the lowest standard free energy change for the formation of oxide among all the reducing agents used in this study, its fine particle size may have contributed to its higher reactivity with oxygen under the heating cycle of the investments. TGA also showed the weight gain of the investments with B additive. On the other hand, the thermal expansion of the investments with B additive remained unchanged, possibly due to its small amount. The comparatively larger particle size of Al and Si could have contributed to their relatively inert properties under the heating cycle for the investments, although they have higher standard free energy change for the formation of oxide than B.

The reason for the selection of 75–150 μm particle size for Al was that a smaller size than this could easily explode by contact with oxygen in the air. To make the results of the study comparable, Si and Ti with similar particle sizes were also selected. Further study is necessary to determine the effects of the particle size on the reactivity of the reducing additives. In the present study, the TGA failed to show significant weight gains for the Al- or Si-added investments, while weight gains of pure Al and Si additives were observed under the heating cycle of the investments\(^1\). A different degree of oxidation of these additives due to their mixing with the investments may account for the different amount of thermal expansion of the investments. As a result, the addition of Si or Ti particles in the investments resulted in the decrease of the thermal expansion of the investments, while thermal expansion of Al-added investments showed an increasing tendency though the differences from investment without additive were not significant.

Three endothermic peaks were observed at 55°C, 130°C, and 250°C from the DTA curves of investments without additive and investments with Si and Ti additives. These peaks correspond to the temperature of moisture evaporation from the mixed investments, the dehydration temperature of gypsum which begins from about 120°C and the transformation point of cristobalite at about 250°C, respectively. The DTA curve of the Al-added investment showed an extra endothermic peak at 657°C, which corresponds to the melting point of Al (660.37°C)\(^2\).

It should be noted that the oxidation of the additive particles distributed in the surface area of the mold cavity could also change the surface properties of the casting mold, which might subsequently make the casting surfaces rough. The present study also showed that the total expansion of the investments changed after the addition of the reducing agents, which may compromise the fitness of the resulting dental castings. Further study should be carried out to evaluate the effect of the reducing agent addition on the surface properties and precision of the resulting dental castings.

CONCLUSIONS

The objective of this study was to investigate the effect of the addition of different reducing agents (B, Al, Si and Ti) and their contents on the compressive strength and the setting and thermal expansion of the gypsum-bonded investments that can prevent the surface blackening of some noble cast alloys. The green-body and burnout compressive strengths of the Al-, Si- and Ti-added investments decreased with the increase of the additive contents. The burnout compressive strength of B-added investment significantly increased, while the green-body strength remained unchanged with the increase of B contents. The linear expansion of the investments was also changed by the addition of the reducing agents. The total expansion of the B-added investment showed an increasing tendency, and those with Al, Si and Ti additives showed decreasing tendency with the increase of the additive contents. Further study is necessary to evaluate the effect of these reducing additives on the accuracy of dental castings.

REFERENCES


