Effects of Sn, Ga, and In Additives on Properties of Ag-Pd-Au-Cu Alloy for Ultra-low Fusing Ceramics

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Nine 35%Ag-30%Pd-20%Au-15%Cu alloys containing 2, 4 and 6 mass% of Sn, Ga or In as an additive metal were experimentally prepared to investigate the effects of different additives and their content on the physical and mechanical properties as well as the bond with a ultra-low fusing ceramic. Both the different additives and their content or either of these two factors significantly influenced most of the evaluated properties except for the area fraction of the retained ceramic. Based on the evaluated properties three experimental alloys (2%Sn-added alloy, 4%Ga-added alloy and 2%In-added alloy) can be recommended as a suitable alloy for ceramic-metal restorations using ultra-low fusing ceramics.

Key words: Silver alloy, Physical property, Mechanical property

INTRODUCTION

Recently ultra-low fusing dental ceramics have been introduced into dental practice and are presently frequently used by some practitioners. The advantage of these ceramics is their ultra-low fusing temperature. Some marketed products can be fused at 780°C, which allows the alloys to be cast at a temperature lower than 1,000°C using both gas-air torch and gypsum-bonded investment. The alloys for these ceramics, however, are gold alloys which have lower strength than palladium-based alloys for conventional low-fusing dental ceramics.

To improve the mechanical properties of these gold alloys, another alloy system consisting mainly of Ag, Pd, Au and Cu (Ag-Pd-Au-Cu alloy) was developed and the efficacy of this alloy system was reported by Goto et al. In these studies, however, the content of the additive metal elements such as tin and gallium was fixed at 5% and the effect of their content on the alloy properties was not determined. In addition, indium which is well known as an additive element to gold alloys for conventional dental ceramics was not involved in these studies and its effect on the properties should be further investigated.

The purpose of the present study was to investigate the effects of different additive metals such as Sn, Ga and In and their contents on the properties of the Ag-Pd-Au-Cu alloy for the ultra-low fusing dental ceramics, and to explore a suitable Ag-Pd-Au-Cu alloy for ceramic-metal restorations using ultra-low fusing ceramics. The evaluated properties were the liquidus point, solidus point, coefficient of thermal...
expansion, bonding with ultra-low fusing ceramic, tensile strength, 0.2% off-set proof stress, elongation, elastic modulus and hardness.

MATERIALS AND METHODS

Alloy preparation
Based on the previous findings by Goto et al., a 35%Ag-30%Pd-20%Au-15%Cu alloy with the addition of 0.05%Ir was chosen as a mother composition in the present study. Sn, Ga or In was added to this composition varying their content to either of 2, 4 or 6 mass%. Thus, three Sn-added alloys, three Ga-added alloys and three In-added alloys were experimentally prepared in a silica tube (inside diameter: 16 mm) under an argon gas atmosphere using an induction melting unit (High Frequency Induction Heating Unit - 10 kW SCR, Tokyo Koshuha-Denkiro Co. Ltd., Tokyo, Japan). A total of nine alloys (315 g per alloy) were experimentally prepared and subjected to the following evaluations.

Measurements of the solidus and liquidus points, and coefficient of thermal expansion
The liquidus point and solidus point were measured for each prepared alloy using a differential thermal analyzer (DT-1500-H, Shinku-Riko, Yokohama, Japan). Approximately 0.5 g of each alloy and α-alumina particles as control were heated to 1,300 °C at a heating rate of 10°C/min. The thermal change was recorded on a chart. The solidus point and liquidus point were determined from the start point and the end point of the endothermic change on the recorded chart, respectively. The measurement was made for three samples for each alloy.

A rod shape specimen (diameter: 6 mm, length: 20 mm) for the measurement of the coefficient of thermal expansion was prepared using a dental casting procedure. A rod shape pattern was made from inlay wax (Inlay Wax Medium, GC Corporation, Tokyo, Japan) using a stainless steel die and a casting mold was made from a gypsum-bonded investment (Cristobalite Micro GC Corporation Tokyo, Japan) which was mixed following the manufacturer's instructions. After the casting mold was burned out at 650°C, an alloy was cast into the mold using a centrifugal casting machine (Caster VC500, The Daiei Dental MFG. Co. Ltd. Osaka, Japan). A gas-air torch was used to melt the alloy. The mold was bench-cooled to room temperature and then a cast specimen was taken from the mold. The surface of the specimen was cleaned using an ultrasonic cleaner. Three specimens were prepared for each of the prepared nine alloys. The thermal expansion of each specimen was measured from 50°C to 550°C and was recorded on a chart using a thermal dilatometric apparatus (TMA120, Seiko Instruments Inc., Tokyo, Japan). The coefficient of thermal expansion between 50°C and 500°C was determined from the recorded chart.

Evaluation of bond with ultra-low fusing ceramic
The evaluation of the bond with an ultra-low fusing ceramic was carried out
following ISO 9693:1991 "Dental ceramic fused to metal restorative materials"[6]. A plate shape specimen (thickness: 0.5 mm, width: 5 mm, length: 20 mm) as specified in ISO9693 was prepared for each alloy using a dental casting procedure. The materials and casting procedure were as used for the preparation of the specimen for coefficient of thermal expansion. Six cast specimens were prepared for each of the prepared alloys. The surface of each cast specimen was sandblasted (Micro Blaster II A, The Daiei Dental MFG. Co. Ltd. Osaka, Japan) with alumina particles (particle size range: 53-63μm). In addition to the nine experimental alloys, the mother alloy (35%Ag-30%Pd-20%Au-15%Cu alloy) and two commercially available gold alloys (DN: Degnom, Degussa AG, Germany and DV: DG.V08, Duceram, Germany) for ultra-low fusing ceramics were involved in this evaluation.

An ultra-low fusing ceramic (Deguceram Gold, Degussa AG, Germany, Lot No.01) was applied to one surface of the cast specimen. The bond powder, opaque and dentin ceramics, which were the basic components of this ceramic system, were sequentially applied to the surface of a cast specimen, and fired at 800°C, 780°C and 785°C, respectively, under vacuum (50 hPa) following the manufacturer’s instructions. A ceramic-fused alloy specimen was bent on a 10 mm stainless rod, with the ceramic located at the opposite side of the contacting area, to a 90° angle of the specimen ends, and then straightened. After this procedure, the surface was examined by scanning to a computer and the area fraction of the retained ceramic in the middle third of the specimen was measured using an area computing system (NIH Image Ver. 1.47, National Institute of Health., Bethesda, Maryland, USA).

Evaluation of mechanical properties
Using the nine experimental alloys and two commercially available gold alloys (DN and DV), tensile test specimens (diameter: 3 mm, gauge length: 15 mm) and hardness test specimens (width: 10 mm, length: 10 mm, thickness: 1 mm) were prepared following a dental casting procedure. A gypsum-bonded investment (Cristobalite micro, GC Corporation, Tokyo, Japan) was used to prepare the casting mold. The investment was mixed following the manufacturer’s instructions and the mold was burned out at 650°C. Each alloy was melted using a gas-air torch, and cast into the mold using a centrifugal casting machine (Caster VC500, The Daiei Dental MFG. Co. Ltd. Osaka, Japan). The mold was bench-cooled to room temperature and then a cast specimen was removed from the mold. The surfaces of the specimen were cleaned using an ultrasonic cleaner. Following the firing cycle of an ultra-low fusing ceramic (Deguceram Gold, Degussa AG, Germany), all specimens were heated under vacuum (50 hPa) at 800°C, 780°C and 785°C in turn. These were the recommended firing temperatures for the bond powder, opaque and dentine ceramics of the ultra low-fusing ceramic, respectively. Both for the tensile test and hardness test, four specimens were prepared for each alloy. After the heat-treatment, one surface of each hardness test specimen was polished using SiC papers (#240-1200, Microcut disk 12", Buehler, Lake Bluff, IL., USA) and finished using a diamond paste (average particle size: 3μm, METADI aerosol spray, Buehler, Lake Bluff, IL., USA) and alumina
particles (average particle size: 0.05 μm, Micropolish B, Buehler, Lake Bluff, IL, USA).

Tensile strength, 0.2% off-set proof stress, elongation, elastic modulus and hardness were measured for each of the nine experimental alloys and the two gold alloys. Four of the five properties excluding hardness were determined from a tensile test using a universal testing machine (Shimazu Autograph DSS-5000, Shimazu Seisakusho, Kyoto, Japan). The hardness was measured using a Vickers hardness testing machine (Autovic AAV, Akashi Seisakusho, Tokyo, Japan).

The tensile test including the specimen preparation was carried out following ISO9693 “Dental ceramic fused to metal restorative materials”\(^6\). The tensile test was conducted at a cross-head speed of 2 mm/min. A load-elongation curve was recorded on a chart for each specimen, and the tensile strength, 0.2% off-set proof stress, elongation and elastic modulus were determined from the recorded chart. The Vickers hardness test was carried out under 1 kgf load for 15 sec.

Data analysis
For each of the measured items, that were the liquidus point, solidus point, the area fraction of the retained ceramic, tensile strength, 0.2% off-set proof stress, elongation, elastic modulus and hardness, a two-way ANOVA was used to statistically analyze the effects of different additive metals and their different contents. A statistical difference between average values was examined using Tukey's multiple comparison test at the 0.05 level of significance. For the area fraction of the retained ceramic and the mechanical properties, one-way ANOVA and Tukey's multiple comparison test were also used to compare the average values between experimental alloys and commercially available gold alloys at the 0.05 level of significance. When homogeneous variation of the data among the groups could not be assumed, post-hoc comparisons were made using a Dunnett's T3 test also at the 0.05 level of significance.

RESULTS
Solidus point, liquidus point and coefficient of thermal expansion
Table 1 shows the mean values and standard deviations for the liquidus point, the solidus point and the coefficient of thermal expansion for each of the nine experimental alloys. The result of a two-way ANOVA for each property is shown in Table 2. The solidus point and liquidus point were significantly influenced by all three factors that were different additives, the content of the additives and their interaction. Figs. 1 and 2 show the changes in the solidus point and liquidus points, respectively, for three additive systems at different contents. As shown in Fig.1, the increase in the additive content resulted in the significant decrease in the solidus point except for one condition which was the decrease in the Ga content from 2% to 4%. At each additive content, the In-added alloy had a significantly higher solidus point than the Ga- and Sn-added alloys. At 4% and 6% additive contents, the Ga-added alloy showed a significantly lower solidus point than In- and Sn-added alloys.
Table 1 Liquidus point, solidus point and coefficient of thermal expansion (C.T.E.)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Content of additive (%)</th>
<th>Solidus point (°C)</th>
<th>Liquidus point (°C)</th>
<th>C.T.E. (×10⁻⁵/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-added alloy</td>
<td>2</td>
<td>940(13.8)</td>
<td>1050(12.5)</td>
<td>15.6(0.1)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>925(9.9)</td>
<td>1036(15.0)</td>
<td>15.6(0.1)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>859(4.7)</td>
<td>975(6.0)</td>
<td>15.7(0.1)</td>
</tr>
<tr>
<td>Ga-added alloy</td>
<td>2</td>
<td>951(4.0)</td>
<td>1045(3.5)</td>
<td>15.3(0.2)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>896(7.5)</td>
<td>1007(3.1)</td>
<td>15.5(0.1)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>820(3.2)</td>
<td>1009(2.1)</td>
<td>15.6(0.1)</td>
</tr>
<tr>
<td>In-added alloy</td>
<td>2</td>
<td>975(3.1)</td>
<td>1084(1.7)</td>
<td>15.7(0.2)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>955(2.1)</td>
<td>1068(4.6)</td>
<td>15.8(0.1)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>925(5.6)</td>
<td>1044(6.1)</td>
<td>15.7(0.1)</td>
</tr>
</tbody>
</table>

Standard deviations in parenthesis

Table 2 Results of two-way ANOVA for the solidus point, liquidus point and coefficient of thermal expansion (C.T.E.)

<table>
<thead>
<tr>
<th>Factor</th>
<th>Solidus point</th>
<th>Liquidus point</th>
<th>C.T.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different additives</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Additive content</td>
<td>**</td>
<td>**</td>
<td>-</td>
</tr>
<tr>
<td>Interaction</td>
<td>**</td>
<td>**</td>
<td>-</td>
</tr>
</tbody>
</table>

**significant (p<0.01), - not significant (p>0.05)

Fig. 1 Solidus point.
Significant difference (p<0.05) by Dunnett's T3 test
For Sn-added alloy: 2% vs. 6%, 4% vs. 6%, and 2% vs. 6% additive contents,
For Ga-added alloy: 4% vs. 6% and 2% vs. 6% additive contents, For In-added alloy: 2% vs. 6%, 4% vs. 6%, and 2% vs. 6% additive contents
At 2% additive content: Ga- vs. In-added alloys, At 4% additive content: Ga- vs. In-added alloys, At 6% additive content: Sn- vs. Ga-added alloys, Sn- vs. In-added alloys, Ga- vs. In-added alloys
(A vertical line at each average point is the interval of the 95% confidence level.)

Fig. 2 Liquidus point.
Significant difference (p<0.05) by Dunnett's T3 test
For Ga-added alloy: 2% vs. 4%, and 2% vs. 6% additive content, For Sn-added alloy: 2% vs. 6% additive content, For In-added alloy: 2% vs. 6% additive content.
At 2% additive content: between Ga- vs. In-added alloys, At 4% additive content: Ga- vs. In-added alloys, At 6% additive content: Sn- vs. In-added alloys
(A vertical line at each average point is the interval of the 95% confidence level.)
The liquidus points of the In-added alloy and the Sn-added alloy significantly decreased with the increase in its content from 2% to 6%. That of the Ga-added alloy significantly decreased with the increase in the additive content from 2% to 4% and from 2% and 6%. The liquidus point of the In-added alloy was significantly higher than those of the Ga-added alloy at 2% and 4% additive contents, and that of the Sn-added alloy at 6% additive content. No significant difference was found among the other additive systems at each content.

The mean coefficient of thermal expansion of the nine alloys ranged from \(15.3 \times 10^{-6}/\text{°C}\) to \(15.8 \times 10^{-6}/\text{°C}\). Although this range was relatively narrow, a two way ANOVA showed that the effect of different additives was significant, whereas the effect of the other factors were not significant. Fig. 3 shows the coefficient of thermal expansion for three additive systems. The coefficient of thermal expansion of the Ga-added alloy was significantly lower than those of the Sn- and In-added alloys.

Bond with ultra-low fusing ceramic - Area fraction of the retained ceramic after bending

Table 3 shows the area fraction of the retained ceramic after bending. As shown in

![Fig. 3 Coefficient of thermal expansion.](image)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Content of additive (%)</th>
<th>Area of retained ceramic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-added alloy</td>
<td>2</td>
<td>95.6(8.1)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>99.0(2.5)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>100.0(0.0)</td>
</tr>
<tr>
<td>Ga-added alloy</td>
<td>2</td>
<td>97.1(4.5)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>99.8(0.4)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>99.8(0.4)</td>
</tr>
<tr>
<td>In-added alloy</td>
<td>2</td>
<td>99.7(0.3)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>99.9(0.1)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>98.5(2.1)</td>
</tr>
<tr>
<td>Gold-based alloy, DN</td>
<td>–</td>
<td>98.7(1.5)</td>
</tr>
<tr>
<td>Gold-based alloy, DV</td>
<td>–</td>
<td>97.1(1.4)</td>
</tr>
</tbody>
</table>

Standard deviations in parenthesis
Table 3, all experimental alloys showed a high area fraction of the retained ceramic (95.6-100.0%) as well as those of the commercially available gold alloys (DN: 98.7%, DV: 97.1%). The results of one-way ANOVA and Dunnet's T3 test showed that no significant difference in the area fraction existed between the nine experimental alloys and the gold alloys. A two-way ANOVA showed that the effects of all factors were not significant and no significant difference was found among the nine experimental alloys.

Mechanical properties of experimental alloys and gold alloys
The results of the measurements and the statistical comparisons between the experimental alloys and the mother alloy as well as the two gold alloys are listed in Table 4. A two-way ANOVA was used to analyze the effects of the different additives and their content. The results of a two-way ANOVA for each of the measured properties are shown in Table 5.

The tensile strength of the nine experimental alloys ranged from 851.0 to 956.8 MPa for Sn-added alloys, from 680.0 to 782.5 MPa for Ga-added alloys, and from 730.0 to 973.8 MPa for In-added alloys. That of the mother alloy and the two gold

| Table 4 Tensile strength, 0.2% off-set proof stress, elongation, elastic modulus and hardness |
|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Alloy                              | Additive content (%) | Tensile strength (MPa) | Proof stress (MPa) | Elongation (%) | Elastic modulus (GPa) | Hardness (HV1)   |
| Sn-added alloy 2                   |                  | 872.9(34.4)           | 833.4(60.7)       | 5.4(2.90)     | 111.8(1.8)           | 270.0(23.3)*       |
| Sn-added alloy 4                   |                  | 956.8(35.4)           | 886.9(7.64)       | 2.9(1.57)     | 110.8(6.1)           | 280.8(5.7)*        |
| Sn-added alloy 6                   |                  | 851.0(23.4)           | 781.4(34.1)       | 1.6(0.89)     | 119.0(2.9)           | 251.5(6.0)*        |
| Ga-added alloy 2                   |                  | 782.5(23.9)           | 574.1(43.1)       | 9.3(2.26)     | 115.1(7.3)           | 226.8(21.1)         |
| Ga-added alloy 4                   |                  | 715.6(17.7)           | 472.2(25.4)       | 10.2(1.65)    | 113.0(3.3)           | 192.3(3.8)          |
| Ga-added alloy 6                   |                  | 680.0(25.5)           | 422.7(40.5)       | 12.3(1.30)    | 124.6(10.7)          | 178.3(4.0)          |
| In-added alloy 2                   |                  | 730.0(13.9)           | 605.3(48.9)       | 5.9(2.26)     | 113.0(4.3)           | 258.5(21.0)*        |
| In-added alloy 4                   |                  | 909.4(13.9)           | 873.8(13.1)       | 1.8(0.68)     | 118.3(10.3)          | 283.0(14.1)         |
| In-added alloy 6                   |                  | 973.8(15.7)           | 896.8(11.9)       | 1.8(1.01)     | 124.3(8.7)           | 265.3(1.7)          |
| Mother alloy                      |                  | 432.6(35.7)           | 326.8(18.6)       | 12.3(2.10)    | 86.9(9.2)            | 174.5(11.4)         |
| Gold alloy, DN                    |                  | 692.6(10.6)           | 510.5(3.3)        | 9.2(1.57)     | 103.3(1.8)           | 200.8(1.3)          |
| Gold alloy, DV                    |                  | 638.8(13.0)           | 480.1(6.9)        | 6.3(0.37)     | 112.0(4.5)           | 191.3(1.0)          |

*significantly higher than mother alloy, †significantly lower than mother alloy
>>significantly higher than two gold alloys, DN and DV
>significantly higher than DV, "significantly lower than DN

Table 5 Results of two-way ANOVA for Tensile strength (T. strength), 0.2% off-set proof stress, elongation, elastic modulus (E. modulus) and hardness

<table>
<thead>
<tr>
<th>Factor</th>
<th>T. strength</th>
<th>P. stress</th>
<th>Elongation</th>
<th>E. modulus</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different additives</td>
<td>**</td>
<td>**</td>
<td></td>
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<tr>
<td>Additive content</td>
<td>**</td>
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<tr>
<td>Interaction</td>
<td>**</td>
<td>**</td>
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<td></td>
<td>**</td>
</tr>
</tbody>
</table>

**significant (p<0.01), *significant (p<0.05), - not significant (p>0.05)
alloys, DN and DV was 432.6 MPa, 692.6 MPa and 638.8 MPa, respectively. As shown in Table 4, the tensile strength of all experimental alloys was significantly higher than that of the mother alloy. Six of the nine experimental alloys had significantly higher strength than both of the two gold alloys. Although no significant difference in the tensile strength was found between the other three experimental alloys and one gold alloy, DN, two of these three alloys had significantly higher tensile strength than another gold alloy, DV.

The result of a two-way ANOVA showed that all factors including the interaction significantly influenced the tensile strength (Table 5). The effect of the additive content on the tensile strength varied among the three different additive systems. Fig. 4 shows the change in the tensile strength for the three additive systems at different contents. The tensile strength of the Ga-added alloy significantly decreased with the increase in the Ga content from 2% to 4%, whereas that of the In-added alloy increased with the increase in the In content throughout the whole range of its content. On the other hand, the tensile strength of the Sn-added alloy significantly increased with the increase in the Sn content from 2% to 4%, and then significantly decreased with the increase in the Sn content from 4% to 6%. As a result, the highest tensile strength for each additive system was obtained at different additive contents, 2% for Ga-added alloy, 4% for Sn-added alloy and 6% for In-added alloy.

The differences in the tensile strength among the three different alloy systems varied at different additive contents. At 2% content of the additives, Sn-added alloy had significantly higher tensile strength than the other two alloys. At 4% additive content, Sn- and In-added alloys had higher tensile strength than the Ga-added alloy. Finally, at 6% additive content, a significant difference in the tensile strength was found among all three alloys. At this content, the highest was the In-added alloy followed by the Sn-added alloy and the lowest was the Ga-added alloy.

As shown in Table 4, the 0.2% off-set proof stress of the experimental alloys ranged from 781.4 to 886.9 MPa for Sn-added alloys, from 422.7 to 574.1 MPa for Ga-added alloys, and from 605.3 to 896.8 MPa for the In-added alloys. That of the mother alloy and two gold alloys, DN and DV was 326.8 MPa, 510.5 MPa and 480.1 MPa, respectively. Eight of the nine experimental alloys excluding the 6%Ga-added
AG-PD-AU-CU ALLOY FOR MULTIPLE APPLICATIONS

![Graph showing the 0.2% off-set proof stress.](image)

Fig. 5 The 0.2% off-set proof stress.

alloy had significantly higher proof stress than the mother alloy. Five of the nine experimental alloys (all Sn-added alloys, 4% and 6% In-added alloys) had significantly higher proof stress than both of the two gold alloys, but no significant difference was found between the other four experimental alloys (all Ga-added alloys and 2% In-added alloy) and the two gold alloys.

The result of a two-way ANOVA showed that all factors including the interaction significantly influenced the 0.2% off-set proof stress (Table 5). The effect of the additive content on the proof stress varied among three different additive systems and the change in the proof stress with the additive content was very similar to that in the tensile strength. Fig. 5 shows the change in the proof stress for three additive systems at different contents. The mode of the change in proof stress was similar to that in the tensile strength. The mean proof stress of the Ga-added alloy decreased with the Ga content while that of the In-added alloy increased with the In content. For the Ga-added alloy the decrease in the proof stress was significant when the Ga content increased from 2% to 4% and from 2% to 6%. For the In-added alloy the increase in the proof stress was significant when the In content increased from 2% to 6%. Although no significant change was found with the increase in the Sn content for the Sn-added alloy, the mode of the change in the mean proof stress was similar to that in the tensile strength.

Significant differences in the proof stress were found at three additive contents among three different alloy systems. These differences were the similar to those in tensile strength. At 2% content of the additives, the Sn-added alloy had significantly higher proof stress than the other two alloys. At 4% additive content, the Sn- and In-added alloys had higher proof stress than the Ga-added alloy. Finally, at 6% additive content, a significant difference in the proof stress was found among all three alloys. At this content, the highest was the In-added alloy followed by the Sn-added alloy and the lowest was the Ga-added alloy.

The elongation of the experimental alloys ranged from 1.6 to 5.4% for Sn-added alloys, from 9.3 to 12.3% for Ga-added alloys and from 1.8 to 5.9% for In-added alloys as shown in Table 4. That of the mother alloy and the two gold alloys, DN and DV was 12.3%, 9.2% and 6.3%, respectively. Four of the nine experimental alloys
had significantly lower elongation than the mother alloy. Three of the nine experimental alloys (6\%Sn-added alloy, 4\% and 6\%In-added alloy) had significantly lower elongation than both of the two gold alloys. One experimental alloy (4\%Sn-added alloy) had significantly lower elongation than one of the two gold-added alloys, DN but no significant difference was found between this experimental alloy and the other gold alloy, DV. In contrast to these alloys that showed low elongation, the 6\%Ga-added alloy had significantly higher elongation than one of the two gold alloys, DV, but no significant difference was found between this alloy and the other gold alloy, DN.

The result of a two-way ANOVA showed that two factors, different additives and the interaction of different additives and their content, significantly influenced the elongation (Table 5). Fig. 6 shows the change in the elongation for three additive systems at different contents. The effect of the additive content on the elongation was different between the Ga-added alloy and the other two alloys. For the In- and Sn-added alloys, the elongation significantly decreased with the increase in the content of these additives from 2\% to 6\%, whereas no significant change was found for the Ga-added alloy with the increase in the Ga content. Among three additive systems, the elongation of the Ga-added alloy was significantly higher than those of the Sn- and In-added alloys at 4\% and 6\% content.

The elastic modulus of the experimental alloys ranged from 110.8 to 119.0 GPa for the Sn-added alloys, from 113.0 to 124.6 GPa for the Ga-added alloys and from 113.0 to 124.3 GPa for the In-added alloys as shown in Table 4. That of the mother alloy and two gold alloys, DN and DV was 86.9 GPa, 103.3 GPa and 112.2 GPa, respectively. Although the average elastic moduli of the nine experimental alloys were higher than that of the mother alloy, a significant difference was found only between the mother alloy and two experimental alloys (6\%Sn-added alloy and 6\%In-added alloy). Two Sn-added alloys (2\% and 4\%Sn) had significantly higher elastic modulus than one of the two gold alloys, DN, but no significant difference was found between the other seven experimental alloys and the two gold alloys.

The result of a two-way ANOVA showed that the effect of the additive content on the elastic modulus was significant, but the effects of the other factors were not
Fig. 7  Elastic modulus.
Significant difference (p<0.05) by 
Dunnett's T3 test 
2% vs. 6% additive contents for all 
three additive systems 
(A vertical line at the value is the 
internal 95% confidence level.)

significant (Table 5). Fig. 7 shows the average elastic modulus of three additive sys-
tems at different contents. The elastic modulus of all alloy systems significantly in-
creased as the additive content increased from 4% to 6%.

The Vickers hardness of the experimental alloys ranged from 251.5 to 280.8 for 
the Sn-added alloys, from 178.3 to 226.8 for the Ga-added alloy, and 258.5 to 283.0 
for the In-added alloy, as shown in Table 4. That of the mother alloy and two gold 
alloys, DN and DV was 174.5, 200.8 and 191.3, respectively. All of the Sn- and 
In-added alloys had significantly higher hardness than the mother alloy, whereas no sig-
ificant difference was found between the mother alloy and the Ga-added alloys. 
Four of the nine experimental alloys (4% and 6% Sn-added alloys and 4% and 6% 
In-added alloys) had significantly higher hardness than both of the two gold-added 
alloys, whereas one Ga-added alloy (6%Ga) had significantly lower hardness than 
one of the two gold alloys. No significant difference was found between the other 
four experimental alloys and the gold alloys.

The result of a two-way ANOVA showed that the Vickers hardness of the experi-
mental alloy was significantly influenced by all three factors as shown in Table 5. 
Fig. 8 shows the Vickers hardness for three additive systems at three different con-
tents of the additives. Dunnett's T3 test indicated that the Vickers hardness of the 
Sn-added alloy and the In-added alloy was significantly higher than that of the Ga-
added alloy at every content of the additives. Although the average hardness value 
of the Ga-added alloy decreased as the additive content increases, this decrease was 
not significant.
DISCUSSION

Alloy Composition
In the previous studies by Goto et al.\textsuperscript{1,2)} 5\%Sn- and 5\%Ga-added Ag-Pd-Au-Cu alloys were investigated. Among these alloys 35\%Ag-30\%Pd-20\%Au-15\%Cu and 30\%Ag-30\%Pd-20\%Au-20\%Cu alloy compositions were suitable both with Sn and Ga additions for the application of ultra-low fusing ceramics. The evaluated properties were similar between these two compositions when they were combined with either Sn or Ga. Therefore, both of these alloys were a candidate for the mother composition of the present study. In addition, the central composition in those previous studies was 35\%Ag-30\%Pd-20\%Au-15\%Cu which could represent a series of the evaluated alloys, and thus this composition was chosen for the present study.

It was also reported by Goto et al.\textsuperscript{1,2)} that Pd and Cu contents influence the properties of Ag-Pd-Au-Cu alloys consisting of 20-40\%Ag, 20-40\%Pd, 10-20\%Cu and 20\%Au and several alloys in this Ag-Pd-Au-Cu composition range were recommended as suitable alloys for the application of ultra-low fusing ceramics. Different contents of Sn and Ga additives may provide different effects on the properties of these alloys. A further investigation should be carried out for the other recommended alloy compositions at different contents of the additives.

The content of the Sn and Ga additives was fixed at 5\% in the previous studies\textsuperscript{1,2)}, and the effects of their different contents were not investigated. The properties of Ag-Pd-Au-Cu alloys are very likely to change with varying the content of the additives. Although some experimental Ag-Pd-Au-Cu alloys in previous studies\textsuperscript{1,2)} had suitable properties for the application of ultra-low fusing ceramics, these properties could be further improved with different contents of the additives. Based on this point of view, the contents of Sn and Ga were varied from 2\% to 6\% with a 2\% interval. In addition to these additives, In was used or included in the present study because this metal is well known as an additive to gold alloys for conventional dental ceramics.

Effects of different additives and their content on physical properties and bonding with ultra-low fusing ceramic
The effects of different additives and their contents, both or either of them, significantly influenced the physical properties evaluated in the present study. The solidus and liquidus points, in general, decreased with the increase in the content of the additives. This result was apparently due to the addition of Sn, Ga and In which have very low melting points. Goto et al.\textsuperscript{1)} reported that the solidus and liquidus points of the 35\%Ag-30\%Pd-20\%Au-15\%Cu alloy containing no additives (mother alloy) were 1,019\degree C and 1,097\degree C, respectively. In comparison with the mother alloy, the experimental alloys had lower solidus and liquidus points even at 2\% content of the additives. This suggests that the additives used in this study had a marked effect to decrease the solidus and liquidus points of the Ag-Pd-Au-Cu alloy.

The Ga-added alloy had a significantly lower coefficient of thermal expansion
than the Sn- and In-added alloys. This may be mainly due to the higher coefficient of thermal expansion of the Sn and In than Ga\(^2\). Goto et al.\(^1\) reported the coefficient of thermal expansion of the 5%Sn- and 5%Ga-added alloys as well as that of the mother alloy, but no significant difference was found between the Sn- and Ga-added alloys. In their study, different compositions in Pd and Cu contents were involved and thus the variation of the findings appears to be greater than the present study. In addition, the difference between the average values was very small. A wide variation in the findings and a small difference between the average values may be the reason for no significant difference between the Ga- and Sn-added alloys in their study. The content of the additives did not significantly influence the coefficient of thermal expansion. This may be also due to a slight change in the coefficient of thermal expansion between different contents.

All experimental alloys as well as two gold alloys had high area fraction of retained ceramic (95.6-100\%) and no significant difference in the area fraction between the nine experimental alloys and the two gold alloys in the present study. These results suggest that the Sn, Ga and In additives are effective for producing a good bond with an ultra-low fusing ceramic even at a low content such as 2%. It has been well known that the coefficient of thermal expansion and the suitable oxides on the alloy surface are the key factors for a good bond with ceramics. As listed in Table 1, the coefficient of thermal expansion of the experimental alloy was in the range of 15.3-15.8×10\(^{-6}\)/\(^\circ\)C. According to the disclosed information by the manufacturer, that of the ultra-low fusing ceramic used in this study (Deguceram Gold) is 15.8×10\(^{-6}\)/\(^\circ\)C. Although the coefficient of the 2%Ga-added alloy (15.3×10\(^{-6}\)/\(^\circ\)C) was much lower than that of the ultra-low fusing ceramic, the area fraction of this alloy was competitive with those of the two gold alloys and the other experimental alloys. This suggests that a suitable oxide is formed on the surface of this alloy with the addition of Ga even at 2% content. Un addition to Ga, Sn and In would also be good additives to form a suitable oxide. The Sn- and In-added alloys also showed a high area fraction, which may be attributed by compatible coefficients and oxides with the ultra-low fusing ceramic.

**Effects of different additives and their content on mechanical**

As shown in Table 4, the tensile strength, 0.2% proof stress, elastic modulus and Vickers hardness of all nine experimental alloys containing any of the additives were significantly higher than those of the mother alloy. On the other hand, the elongation of these nine alloys was significantly lower than that of the mother alloy. These results suggest that three additive metals, Sn, Ga and In work as a hardening additive for the Ag-Pd-Au-Cu alloy in the range of 2-6% content. It has been reported by several studies\(^8\)\(^-\)\(^12\) that the Ag-Pd-Au-Cu alloy system produces an ordered Pd-Cu phase which is responsible for the increase in strength. Although the Ag-Pd-Au-Cu alloy compositions of the present study are slightly different from those of those previous studies, the Pd and Cu are likely to be related to the hardening of the
alloys in the present study. The experimental alloys in the present study, however, contain either Sn, Ga or In which was not added in the aforementioned previous studies. The coauthors of the present study have been investigating their microstructures and a part of their findings was reported previously at some meetings\textsuperscript{11,12}. According to those findings, the experimental alloys consist of two or three different phases. Among these phases, the Pd-rich phase containing these additives appears similar to a precipitate and would be responsible for the hardening of the Ag-Pd-Au-Cu alloy. Figs 9-11 show a backscattered electron image and images of element distribution for Ag, Pd, Au, Cu and the respective additive metal in the three alloy systems at 6% additive content. These pictures were taken using an electron probe microanalyzer (JXA-8900, JEOL, Tokyo, Japan). As shown in these figures, Pd-Sn-, Pd-Ga- or Pd-In-rich phase are clearly formed in each respective alloy system. A further study is currently being carried out and the detailed results will be reported in the near future.

The results of a two-way ANOVA (Table 5) for the mechanical properties showed that the effects of different additives, additive content and their interaction
Fig. 10 Element distribution images for Ag, Pd, Au, Cu and Ga in 6% Ga-added alloys (CP: Backscattered electron image).

were all significant for the tensile strength, proof stress, elongation and hardness, indicating that these properties of the three experimental alloy systems are differently affected by the additive content. As shown in Fig. 4, the tensile strength of the In-added alloy increased with the increase in the In content throughout the whole content range and that of the Sn-added alloy increased with the increase in the Sn content from 2% to 4% and then decreased with the increase in the Sn-content from 4% to 6%. On the other hand, the tensile strength of the Ga-added alloy decreased with the increase in the Ga content throughout the whole content range. A similar mode of these changes was observed on the proof stress and Vickers hardness. It appears that these properties of the In-added alloy may further increase at greater than 6% content, or come close to the maximum value at 6% content, while that of the Sn-added alloy may reach the maximum value at 4% content. For the Ga-added alloy, the maximum value may be obtained at less than 2% content. Thus, each additive may have its maximum effect at a different specific content. These changes are very likely to be related to the microstructure of each additive system. As aforementioned, a Pd-additive-rich phase is formed in each additive system at 6% additive...
The solidus point of an alloy for metal-ceramic restorations has to be higher than the firing temperature of the ceramics. According to the manufacturer's instruction, the firing temperature of the ultra-low fusing ceramic (Deguceram Gold) is a maximum 800°C. The solidus point of the experimental alloys with additives ranged from 820°C to 975°C. Although the solidus point of all experimental alloys with additives was higher than the firing temperature of the ultra-low fusing ceramic, that of the 6%Ga-added alloy was only 20°C higher than the firing temperature of the ultra-low ceramic. This suggests that the 6%Ga-added alloy may not be applicable for the tested ultra-low fusing ceramic. The solidus point of the other eight alloys was at least 59°C higher than the firing temperature and thus these alloys may withstand the firing of the ultra-low fusing ceramic.
AG-PD-AU-CU ALLOY FOR MULTIPLE APPLICATIONS

The liquidus point of an alloy is one of the essential properties to choose a melting procedure. A gas-air torch could not be used to melt most of the alloys for conventional ceramic application due to their high liquidus point. In the previous studies by Goto et al.\(^1\), a gas-air torch was used to melt the Ag-Pd-Au-Cu alloys among which the highest liquidus point was 1,223°C. They reported that this alloy could be melted with a little difficulty. In the present study, the liquidus point of the nine experimental alloys ranged from 975 to 1,084°C and thus no difficulty was recognized for all nine experimental alloys.

The area fraction of the retained ceramic on the experimental alloys was in the range of 95.6 to 100%. This range of the area fraction highly exceeded the 50% requirement in ISO 9693:1991 “Dental ceramic fused to metal restorative materials”\(^6\), indicating that all nine experimental alloys have a very good bond with the ultra-low fusing ceramic and are suitable for the ultra-low fusing ceramic. Although the area fraction of the retained ceramic is a practical measure to actually evaluate the bond between the alloy and ceramic, the coefficient of thermal expansion is regarded as another measure to access the bond. It has been claimed that the coefficient of thermal expansion of a metal-ceramic alloy should be slightly higher than that of a ceramic to induce compressive stress in the ceramic resulting in its reinforcement\(^13-15\). A previous study\(^15\) claimed that a fracture is unlikely to occur at a coefficient difference of \(0.5 \times 10^{-6}/°C\) or less, and many metal-ceramic restorations which have a 0.5-1.0\(\times 10^{-6}/°C\) difference in the coefficient are known to survive for many years. It appears that the difference in the coefficient would be acceptable up to \(1.0 \times 10^{-6}/°C\). For the safety of the restorations, however, a difference of \(0.5 \times 10^{-6}/°C\) should be chosen as the criterion for the maximum coefficient difference. According to the information disclosed by the manufacturers, the coefficient of ultra-low ceramics is 15.3\(\times 10^{-6}/°C\) for Duceragold and Duceram Gold, and 15.3-15.9\(\times 10^{-6}/°C\) for Carrara. In comparison with these values, the coefficient of 2%Ga-added alloy was 15.3\(\times 10^{-6}/°C\) which is \(0.5 \times 10^{-6}/°C\) less than the ultra-low fusing ceramic. From the above criterion, it may be safe to exclude this alloy from the use with ultra-low fusing ceramics.

The tensile strength of the nine experimental alloys containing the additive ranged from 680.0 to 973.8 MPa. As shown in Table 4, most of these experimental alloys had higher strength than the two gold alloys. Eight of the nine experimental alloys excluding the 6%Ga-added alloy showed a high tensile strength of greater than 700 MPa which is comparative with those of Pd-Cu alloys (690-1,300 MPa) and Pd-Co alloy (793 MPa)\(^13\). These eight alloys, therefore, are expected to show a high resistance at a stress bearing area as well as the Pd-Cu and Pd-Co alloys.

Goto et al.\(^2\) advocated minimum criteria for the mechanical properties of the alloys used for ceramic application, based on the reported values of these alloys and the reported hardness of tooth enamel. These criteria are as follows:

- **Proof stress:** Greater than 400 MPa
- **Elastic modulus:** Greater than 90 GPa
- **Elongation:** Greater than 3%
Vickers hardness: Less than 300 HV1

All nine experimental alloys containing the additive met the above criteria except for one criterion which was greater than 3% elongation. Four alloys, however, failed the elongation criterion and five alloys (2%Sn-added alloy, 2%, 4% and 6%Ga-added alloys, and 2%In-added alloys) passed. Among these five alloys, the 2%Ga-added alloy and the 6%Ga-added alloy have been excluded from the recommendation due to the low coefficient of thermal expansion and the low solidus point, respectively. Finally, three alloys; 2%Sn-added alloy, 4%Ga-added alloy and 2%In-added alloy can be recommended as a suitable alloy for the ceramic-metal restorations using ultra-low fusing ceramics.

The 4% Sn-added alloys as well as the 4% and 6% In-added alloys failed the above qualification due to their low elongation. These three alloys, however, have high tensile strength and proof stress as well as a suitable coefficient of thermal expansion. The 2%Ga-added alloy is excluded from the recommendation due to its low coefficient of thermal expansion, although the elongation of this alloy is very high (9.3%). It is very probable that the shortcomings of these additives can be compensated if they are added together in the mother composition. The combination of these additives may further improve the property of the Ag-Pd-Au-Cu alloy.

CONCLUSION

Nine 35%Ag-30%Pd-20%Au-15%Cu alloys containing 2, 4 and 6 mass% of an additive metal that was Sn, Ga or In were experimentally prepared to investigate the effects of different additives and their content on the physical and mechanical properties as well as in bonding with an ultra-low fusing ceramic. Based on the findings of the evaluation, a suitable Ag-Pd-Au-Cu alloy for ceramic-metal restorations using ultra-low fusing ceramics was explored.

Both the different additives and their content or either of these two factors significantly influenced most of the evaluated properties except the bonding with an ultra-low ceramic. The solidus and liquidus points were significantly decreased with the increase in the content of all additives. The coefficient of thermal expansion of the Ga-added alloy was significantly lower than those of the Sn- and In-added alloys regardless of their content. The area fraction of the retained ceramic was not significantly influenced by the two factors and a high area fraction (95.6-100%) was observed for all experimental alloys.

The tensile strength and 0.2% proof stress of the nine experimental alloys were significantly higher than those of the mother alloy containing no additives (35%Ag-30%Pd-20%Au-15%Cu alloy), which suggests that all additives are effective to increase these properties. These properties were significantly influenced by the different additives and their content, but the effect of the additive content significantly varied among different additive systems. The elastic modulus of all three additive systems significantly increased as the additive content increased from 4% to 6%, but no significant difference was observed between these alloys and the mother.
AG-PD-AU-CU ALLOY FOR MULTIPLE APPLICATIONS

alloy. The Vickers hardness of the Sn- and In-added alloys was significantly higher than that of the mother alloy, whereas no significant difference was found between the mother alloy and the Ga-added alloy which had significantly lower hardness than the other two additive systems.

Three of the nine experimental alloys (2%Sn-added alloy, 4%Ga-added alloy and 2%In-added alloy) can be recommended as a suitable alloy for ceramic-metal restorations using ultra-low fusing ceramics, based on their physical and mechanical properties as well as in the bonding with the ultra-low fusing ceramic.

REFERENCES