New dental precious metal alloys for resin bonding without alloy surface modification were developed by adding base metals (In, Zn, or Sn). Before this, binary alloys of Au, Ag, Cu, or Pd containing In, Zn, or Sn were studied for water durability and bonding strength with 4-META resin. The adhesion ability of the binary alloys was improved by adding In equivalent to 15% of Au content, Zn equivalent to 20% of Ag content, and In, Zn, or Sn equivalent to 5% of Cu content. There was no addition effect of the base metals on Pd, however 15% of In addition improved adhesion with Pd-based alloys containing equi-atomic % of Cu and Pd. The alloy surfaces were analyzed by XPS and showed that oxides such as In$_2$O$_3$, ZnO, or SnO play an important role in improving the adhesive ability of the alloys.

Key words: Adhesion, 4-META, Precious metal alloy

INTRODUCTION

Dental adhesive resins do not adhere strongly to dental precious metal alloys without surface modification. Different methods of surface modification for alloys have been developed to improve their adhesive ability, but these require special equipment, have short shelf agent life, and suffer from complicated handling procedures. If dental adhesive resins could be made to bond strongly to dental precious metal alloys without surface modification, the adhesion procedures would be simplified.

In the present study, a base metal was added to a dental precious metal alloy in an attempt to develop alloys which adhere strongly to dental adhesive resins without surface modification of the alloy. The idea for the present study was derived from the experimental finding that 4-META/MMA-TBB resin (4-META resin) bonds strongly to as-polished surfaces of silver based alloys such as Ag-Sn-Zn and Ag-In-Zn with excellent water durability at the adhesion interface$^1)$. This excellent adhesive ability may be caused by the effect of the base metals (In, Zn, and Sn) because the
4-META resin does not adhere strongly to pure silver. Nor does 4-META resin adhere strongly to pure gold. It was assumed that alloying base metals (In, Zn, and Sn) with precious metal alloys having poor adhesive ability to adhesive resins could improve the adhesive ability of the dental precious metal alloys without the need for surface modification.

First, binary Au, Pd, Ag, or Cu based alloys containing In, Zn, or Sn were made to determine what base metals were effective in improving adhesion. The efficacy of the added elements was evaluated from the water durability of the adhesion interface and the bonding strength. As oxides on the alloy surface play a very important role in the adhesion with 4-META, the alloys were analyzed by X-ray Photoelectron Spectroscopy (XPS). Next, new dental precious metal alloys for resin bonding were developed on the basis of the results of the binary alloy experiments, and the adhesive ability of these alloys was evaluated by their water durability.

**EXPERIMENTAL METHODS**

**Materials**

Binary Au, Ag, Cu, or Pd based alloys containing In, Zn, or Sn up to 35 mass% were made to study the effects of added base metals on adhesive ability. To make these alloys, metals of purity higher than 99.9% were melted in an alumina crucible covered with graphite using a high frequency induction furnace in an argon gas atmosphere. Weight loss by the melting was less than 0.02%.

The dental adhesive, 4-META resin (Super-Bond C&B, SUN MEDICAL CO. LTD., Kyoto, Japan) was used in the present study.

**Evaluation of adhesive ability**

1) Water durability at the adhesion interface

Evaluation of water durability at the adhesion interface was performed with a peeling test after thermal shocks using liquid nitrogen as follows: A 18 × 18 × 1.5 mm³ precious metal alloy plate formed by cold working or casting was polished metallographically to eliminate mechanical factors in the bonding. A 0.2 mm thick polymethylmethacrylate (PMMA) film was bonded with 4-META resin to the metal plate. Immediately after applying 4-META resin to the metal surface with the PMMA film, the specimen was pressed with a 20-kgf load for five minutes to maintain a constant 50-μm thick 4-META resin layer, and then kept in a dry chamber at 37°C for one day. Subsequently, the specimen was subjected to 20 thermal cycles from-196°C liquid nitrogen to 40°C water for 60 sec each. The water durability was evaluated from the peeled area traced by a profile projector. Measurements were made on 10 specimens.

2) Bonding strength

With alloys melting above 700°C, the tensile test piece was soldered to a 11 mm² × 6 mm circular block of stainless steel. Alloys melting below 700°C were cast in the same size as the stainless steel block. The adhesion surfaces were metallographically
polished to eliminate possible mechanical factors affecting the bond strength. An adhesion apparatus with a micrometer was used for two purposes: to attach the 5 mm stainless rod vertically to the alloy surface and also to maintain a constant 50-μm thick 4-META resin layer. The effect of excess resin at the adhesion area on the bond strength was eliminated by attaching Scotch Tape with a 5 mm diameter hole to the precious metal alloy surface. The tensile test of the bond strength measurement was carried out after keeping the specimen at 37°C for 24 hr. Before the tensile test, the specimens were subjected to the thermal cycling described above. The test was performed on a testing machine (Shimadzu Auto-Graph, Shimadzu Co. Ltd., Kyoto, Japan) with a cross head speed of 2 mm/min. Measurements were made individually on 5 specimens at each condition.

Surface analysis of alloys by XPS
Binary alloys of Au with 20% (mass%) In, 20% Zn, or 20% Sn were made. Alloy specimens for XPS were 4 mm in diameter with the surfaces metallographically polished to a mirror-like finish with sandpaper and buffed with a wet abrasive of aluminum oxide powder.

The XPS measurements were performed with an electron spectrometer (ESCA-850, Shimadzu Co. Ltd., Kyoto, Japan) with Al Kα radiation (1486.6 eV) under a pressure of $2 \times 10^{-6}$ Pa evacuated with a turbo-molecular pump. The binding energy of the measured photoelectron peaks was calibrated by the C 1s peak of hydrocarbon contamination at a binding energy of 285.0 eV.

RESULTS

Adhesive ability to binary alloys
Fig. 1 shows the mean values of peeled area (%) as the results of the water durability tests at the adhesion interface, obtained from Au-based binary alloys containing In, Zn, or Sn. Larger peeling areas (%) indicate lower water durability. Addition of In was the most effective method to improve the adhesive ability of gold, resulting in water durability improvements with more than 15% In.

Fig. 2 shows the relationship between bonding strength and added In amounts with the Au-In alloys showing the most excellent adhesive ability. No fracture appeared at the interface between the stainless rod and 4-META resin. The marks indicate the fracture appearance after the tensile test: ○ indicates total interface failure; ● indicates failure in the resin (cohesive failure), and □ shows a cohesive failure with interface failure at the periphery of the adhesion area. The figure shows that the adhesive ability decreases in the order ● > □ > ○. The mean values of bonding strengths increased and the interface failure at the periphery decreased with higher amounts of In. The failures with 20% In were only cohesive failures. The results of bonding strength measurements coincided with the water durability at the interface.

Fig. 3 shows the peeled areas (%) obtained from the Ag-based binary alloys containing In, Zn, or Sn. The water durability was improved with more than 20% Zn.
Bonding strength increased with increasing Zn content as shown in Fig. 4, finally exhibiting only cohesive failure with 20% Zn added.

Fig. 5 shows the peeled areas (%) obtained from the Cu-based binary alloys containing In, Zn, or Sn, showing that the water durability was remarkably improved by small amounts of base metal. Fig. 6 shows that the Cu-based alloy was involved only in cohesive failures. Although the tensile tests of pure copper also showed only cohesive failure, the peeled area (%) here was about 50%. The adhesive ability of 4-
Fig. 5 Peeled area (%) of Cu-based binary alloys containing In, Zn, or Sn.

Fig. 6 Bonding strength versus In amounts with Cu-In alloys.

Fig. 7 Peeled area (%) of PdCu based alloy containing In.

Fig. 8 In 3d spectra obtained from (a) as-polished Au-In alloy surface before argon ion etching, (b) In$_2$O$_3$, and (c) Au-In alloy surface after argon ion etching.
Fig. 9 Zn LMM auger spectra obtained from (a) as-polished Au-Zn alloy surface before argon ion etching, (b) ZnO, and (c) Au-Zn alloy surface after argon ion etching.

Fig. 10 Sn 3d spectra obtained from (a) as-polished Au-Sn alloy surface before argon ion etching, (b) SnO$_2$, (c) SnO, and (d) Au-Sn alloy surface after argon ion etching.

META resin to pure copper is poor in humid environments, indicating low water durability at the interface.

There was no effect of base metal addition with Pd which displayed 100% peeling. The characteristics of Pd were improved by adding In in the equi-atomic alloy PdCu as shown in Fig. 7.

**Oxides on the alloy surface**
The XPS spectra obtained from the Au-In, Au-Zn, and Au-Sn alloys before and after argon ion etching with standard spectra are shown in Figs. 8 to 10. Fig.8 shows In 3d spectra obtained from (a) the as-polished Au-In alloy surface before argon ion etching, (b) In$_2$O$_3$, and (c) the Au-In alloy surface after argon ion etching indicating the metallic state. The structure of the oxide on the adhesion surface in (a) was a mixture of In and In$_2$O$_3$.

Fig. 9 shows Zn LMM auger spectra obtained from (a) the as-polished Au-Zn alloy surface before argon ion etching, (b) ZnO, and (c) the Au-Zn alloy surface after argon ion etching. The structure of the oxide on the adhesion surface (a) was a mixture of Zn and ZnO. Fig. 10 shows Sn 3d spectra obtained from (a) the as-polished Au-Sn alloy surface before argon ion etching, (b) SnO$_2$ and (c) SnO as standards, and
Table 1 Compositions (mass%) of Experimental Alloys for Resin Bonding and Water Durability at Adhesion Interface (Peeled Area (%))

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Au</th>
<th>Pd</th>
<th>Ag</th>
<th>Cu</th>
<th>In</th>
<th>Zn</th>
<th>Sn</th>
<th>Peeled Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>58.0</td>
<td>-</td>
<td>10.0</td>
<td>12.0</td>
<td>20.0</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>No. 2</td>
<td>61.4</td>
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<td>7.2</td>
<td>13.3</td>
<td>16.1</td>
<td>2.0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>No. 3</td>
<td>65.8</td>
<td>-</td>
<td>7.7</td>
<td>14.2</td>
<td>10.6</td>
<td>1.7</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>No. 4</td>
<td>65.0</td>
<td>-</td>
<td>8.0</td>
<td>15.0</td>
<td>5.0</td>
<td>2.0</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>No. 5</td>
<td>70.0</td>
<td>-</td>
<td>8.0</td>
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<td>-</td>
<td>2.0</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>No. 7</td>
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<td>-</td>
<td>5.0</td>
<td>15.0</td>
<td>3.0</td>
<td>-</td>
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<td>No. 8</td>
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<td>16.3</td>
<td>44.7</td>
<td>8.1</td>
<td>7.7</td>
<td>13.0</td>
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<td>No. 9</td>
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<td>47.3</td>
<td>11.2</td>
<td>4.6</td>
<td>9.4</td>
<td>-</td>
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</tr>
<tr>
<td>No. 10</td>
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<td>15.0</td>
<td>40.0</td>
<td>8.0</td>
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<td>-</td>
<td>0</td>
</tr>
<tr>
<td>No. 11</td>
<td>12.0</td>
<td>20.0</td>
<td>55.0</td>
<td>13.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>No. 12</td>
<td>12.0</td>
<td>20.0</td>
<td>40.0</td>
<td>8.0</td>
<td>-</td>
<td>20.0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>No. 13</td>
<td>12.0</td>
<td>20.0</td>
<td>45.0</td>
<td>15.0</td>
<td>-</td>
<td>8.0</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>No. 14</td>
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<td>20.0</td>
<td>40.0</td>
<td>18.0</td>
<td>3.0</td>
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<tr>
<td>No. 15</td>
<td>12.0</td>
<td>20.0</td>
<td>45.0</td>
<td>18.0</td>
<td>3.0</td>
<td>2.0</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>No. 16</td>
<td>20.0</td>
<td>20.0</td>
<td>40.0</td>
<td>18.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>57</td>
</tr>
</tbody>
</table>

also (d) the Au-Sn alloy surface after argon ion etching. The oxide on the adhesion surface (a) was a mixture of Sn and SnO rather than SnO₂ because the Sn 3d₅/₂ spectrum in (a) could be separated graphically with two components, SnO and metallic Sn.

**Design of gold alloy**

Table 1 shows the alloy compositions designed on the basis of the results mentioned above. A commercial gold alloy (Alloy No.6) was chosen as the starting alloy. The composition of the experimental 18 K gold alloy (Alloy No.3) was determined as follows; firstly, the amounts of base metals added to 100 g of Alloy No.6 were calculated. Since this alloy contained 75 g Au and 16.2 g Cu, the amount of In added was calculated to be 12.06 g (15% Au + 5% Cu). The amount of Zn was also calculated to be 1.76 g (20% Ag). Then the composition of Alloy No.3 (Au 75 g, Ag 8.8 g, Cu 16.2 g, In 12.06 g, Zn 1.76 g) was calculated and is shown in Table 1. The compositions of Alloys No.1, 2, 4, 5, and 7 were obtained by modifying Alloy No.3.

**Design of Au-Ag-Pd alloy**

The composition of the experimental Ag-Pd-Cu-Au alloy (Alloy No.9) was determined in addition to the experimental 18 K gold alloy. A commercial Ag-Pd-Cu-Au alloy (Alloy No.11) was chosen as the starting alloy. The composition of Alloy No.9 was obtained by adding In equivalent to 15% of Au content, Zn equivalent to 20% of Ag content, In equivalent to 5% of Cu, and In equivalent to 15% of Pd content coexisting
with Cu. The compositions of Alloys No.8, 10, and 12 to 16 were obtained by modifying Alloy No.9.

**Adhesive ability of experimental alloys**

The water durability at the adhesive interface is shown in Table 1. Alloys No.6 and 11 without addition of In, Zn, and Sn, resulted in total peeling, showing no water durability. Adding In, Zn, and Sn effectively improved the adhesive ability of the gold alloys. The water durability for Ag-Pd-Cu-Au alloys was not improved by the addition of small amounts of In, Zn, or Sn. Good water durability of the Ag-Pd-Cu-Au alloys was obtained by adding total amounts of In and Zn above 15% (Nos. 8 and 9) or a large amount of Zn (Nos. 10 and 12).

**DISCUSSION**

**Evaluation of adhesive ability**

The most critical factors influencing the mechanical behavior of adhesive joints are water and humidity. The water durability of adhesive structures exposed to environments like the oral cavity is very important. In general, long immersion times are needed for evaluation of water durability at the adhesive interface. The adhesive ability was evaluated by peeling and tensile tests in the present study. With the peeling test, a thin PMMA film was attached to metal specimens with 4-META resin in order for the water content at the interface to reach equilibrium in a short time. The peeling test is effective as a quick evaluation method for the water durability at the adhesive interface.

Observation of the fracture appearance after the tensile test is also effective for evaluating the adhesive ability because the appearance reflects the characteristics of the metal surface. A weak chemical bond of 4-META to the alloy surface leads to total interface failure. An increased area of interface failure at the periphery indicates a decrease in bonding strength.

**Adhesive ability of designed dental precious metal alloys**

The silver-based alloys, Ag-Zn-Sn and Ag-In-Zn, showed mainly cohesive failures with tensile bond strengths near 40 MPa and excellent water durability by the peeling test, although using silver as the main component in the silver-based alloys gave poor adhesive ability with 4-META. It was considered that the effect of the base metals could be the reason for the excellent adhesive ability, and on this basis dental precious metal alloys for resin bonding without alloy surface modification were developed.

The adhesive ability of Au was improved by adding 15% In, Ag was improved with 20% Zn, Cu was improved with small amounts of In, Zn, or Sn, and Pd was improved with 15% In coexisting Cu equivalent to equi-atomic% of Pd. The compositions of dental precious metal alloys for resin bonding were designed on the basis of these results.
Adhesive ability affected by adding base metals

Oxides on dental precious metal alloys play very important roles in the adhesion with 4-META. The adhesive ability of adhesive resin to alloys depends on both the kinds and amount of oxides on the alloy surface. The XPS study showed formation of In$_2$O$_3$, ZnO, and SnO on the binary gold alloys, the Au-In alloy, the Au-Zn alloy, and the Au-Sn alloy (Figs. 8-10). The thickness of the oxide layers formed on these binary gold alloys was below the escape depth of the photoelectron (1 nm). The same oxides were formed on the silver-based alloys. With precious metal alloys containing two and three base metals, oxides forming preferentially on the alloy surface depend on the activity coefficients of oxygen and base metal, concentration of oxygen and solute metal, and the Gibbs' standard free energy of formation.

The chemical bonds of 4-META with oxides on gold alloys containing In, Zn, Sn, or Si were described on the basis of theoretical considerations of acid-base interactions presented by Bolger et al. Bolger's theory considers electrostatic interaction between acids or bases of polymer and hydroxyl groups on the metal surface at polymer-metal interfaces on the basis of measured values of the isoelectric point of oxides and the acid dissociation constants of adhesive monomers. The chemical interaction of 4-META with In$_2$O$_3$, ZnO, and SnO was considered to be ionic. Hydrogen bonding was assumed with SiO$_2$.

There was no effect of base metal addition with Pd which displayed 100% peeling. This emphasizes that although Pd plays an important role in inhibiting sulfide formation of Ag-based alloys, Pd also hinders resin bonding. This characteristic appears to be due to Pd easily absorbing hydrogen, resulting in an alteration of the characteristics of the hydroxyl groups adsorbed at the top of the metal surface. The characteristics of Pd were improved by adding In to the equi-atomic alloy PdCu as shown in Fig. 7. The reason why the adhesion ability of Pd improved with the coexisting Cu is unknown.

CONCLUSIONS

The present study developed dental precious metal alloys having excellent adhesive ability to 4-META resin without alloy surface modification. This was attempted because Ag-based alloys containing In, Zn, and/or Sn have excellent adhesive ability with 4-META, although pure silver does not adhere strongly to 4-META resin.

The water durability and bonding strength of 4-META resin to binary alloys of Au, Ag, Cu, or Pd containing In, Zn, or Sn were studied to determine the kinds and amounts of base metals that may be added to the dental precious metal alloys. Gold binary alloys containing In, Zn, or Sn were analyzed by XPS, showing that In$_2$O$_3$, ZnO, and SnO formed on the binary gold alloys. The adhesive ability of adhesive resin to alloys depends on the kind of oxide and should be affected with the amount of oxide on the alloy surface.

The adhesion ability of the binary alloy was improved by adding In equivalent to 15% of Au content, Zn equivalent to 20% of Ag content, and also In, Zn, or Sn
equivalent to 5% of Cu content. There was no addition effect of base metals for Pd. However, 15% of In addition was effective with Pd based alloys containing an equal-atomic ratio of Cu and Pd.

Dental precious metal alloys for resin bonding without alloy surface modification were developed on the basis of the results detailed above. Alloy constituents should ultimately be determined on the basis of factors such as corrosion behavior, mechanical properties, aging characteristics, and castability.

REFERENCES


