Adhesive bonding of alumina air-abraded Ag-Pd-Cu-Au alloy with 10-methacryloxyloxydecyl dihydrogen phosphate

Hirotake MIYAHARA1, Hiroshi IKEDA2, Sri Ayu ANGGRAIN1, Yuki FUJIO1, Shinji YOSHII1, Yuki NAGAMATSU1, Chiaki KITAMURA1 and Hiroshi SHIMIZU2

1 Division of Endodontics and Restorative Dentistry, Department of OralFunctions, Kyushu Dental University, Fukuoka 803-8580, Japan
2 Division of Biomaterials, Department of Oral Functions, Kyushu Dental University, Fukuoka 803-8580, Japan
3 Advanced Manufacturing Research Institute (AMRI), National Institute of Advanced Industrial Science and Technology (AIST), Saga 841-0052, Japan

Corresponding author, Hiroshi IKEDA; E-mail: r16ikeda@fa.kyu-dent.ac.jp

The aim of this paper is to study changes in the Ag-Pd-Cu-Au alloy surfaces by alumina air-abrasion process and effect of those changes on the adhesive bonding characteristic. Surface roughness, surface composition and chemical state of the alumina air-abraded alloys were analyzed by a confocal laser scanning microscope, an energy dispersive X-ray spectroscopy and an X-ray photoelectron spectroscopy. The results showed that the alumina air-abrasion changed the alloy surface by mechanical roughening, alumina remain and copper oxidation. Effect of the changes in the alloy surface on the adhesive bonding characteristic was examined by using a methyl methacrylate/tri-n-butylborane derivative (MMA/TBB) resin cement with the 10-methacryloxyloxydecyl dihydrogen phosphate (MDP) contained primer. The shear bond strength test results indicated that the surface oxidation by the abrasion is the main contributor that improved the adhesive bonding rather than other effects such as mechanical roughening or alumina remain.

Keywords: Sandblast, Al2O3, Dental alloy, Copper, Phosphate monomer

INTRODUCTION

Ag-Pd-Cu-Au alloys are widely used for dental cast restorations in Japan as an alternative to ISO type-III or -IV gold alloys, because the Japanese national health insurance covers the use of the alloy for restorative and prosthetic treatments. For improving the adhesive bonding of the alloy, alumina air-abrasion followed by application of a primer agent is considered to be an indispensable step. A combination of the abrasion process and the use of a primer could allow us to ensure a long-term and reliable bond between the alloy and tooth without unintended failure in the oral environment. Hence, a dentist should know the appropriate conditions to use alumina-air abrasion technique and the correct choice of primers which can be different depending on alloy types used for clinical practice.

The Ag-Pd-Cu-Au alloy is categorized as a noble (precious) metal alloy. Therefore, it is believed that suitable primers for noble metal must be used to create a strong chemical bond with the alloy. Commercial primers for noble metals are generally contained functional monomers such as 6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine-2,4-dithione (VTD)1-7 or 6-methacryloxyhexyl 2-thiouracil-5-carboxylate (MTU-6)8-12. On the other hand, commercial primers for base metal alloy include a carboxylic acid monomer or phosphate monomer, e.g. 4-methacryloxyethyl trimellitate anhydride (4-META)13-15, 10-methacryloxyloxydecyl dihydrogen phosphate (MDP)16-18. However, the use of these primers for base metal is normally avoided, since they are often ineffective in promoting adhesive bonding to the Ag-Pd-Cu-Au alloy. This opinion has been overturned by our previous report20, in which we found that the MDP contained primer could enhance the adhesive bonding of the alumina air-abraded Ag-Pd-Cu-Au alloy surface, whereas it failed to do so on a non-abraded surface. The alumina air-abrasion process is known to capable of improving the adhesive bonding characteristic of an alloy, since it could eliminate contaminants from the alloy surface and roughen the alloy surface, leading to increment of the surface area20,21. Thus, it is believed that the improvement in bond strength by the abrasion process is originated from the mechanical interlocking, while no influence from chemical bonding22,23. However, our previous study has revealed that the alumina air-abrasion process not only has mechanically roughened the alloy surface but also affected the chemical alterations of the alloy surface, as suggested by remaining of the abraded alumina and the existence of copper oxide at the surface20. Although the anomalous effect of the MDP monomer to the abraded alloy surface is suspected to correlate with the alterations of the alloy surface after the abrasion, the detail working mechanism remains unclear.

In this study, we aim to reveal how the MDP-contained primer could improve the adhesive bonding characteristic of the alumina abraded Ag-Pd-Cu-Au alloy surface. As reported in our previous study20, synergetic effect of the alumina air-abrasion on the adhesive bonding has been found when using MDP contained primer, but not in the case of VTD contained...
primer. Therefore, we herein focus on the use of MDP contained primer. In order to achieve our goal, we firstly elucidate the effects of the alumina air-abrasion treatment on the alloy surface. Those effects were later investigated with regards to the adhesive bonding characteristic of methyl methacrylate/tri-\textit{n}-butyl borane (MMA/TBB) resin cement with use of the MDP contained primer to the alloy.

**MATERIALS AND METHODS**

**Sample preparation**

Table 1 lists the Ag-Pd-Cu-Au alloy, primer and luting agent used in this study. The alloy ingot was formed into a disc shape with 11 mm in diameter, 3 mm in thickness by a conventional casting method. The alloy disc surface was polished by using a SiC abrasive paper up to #600 with dry condition. The polished surface was subjected to an alumina air-abrasion by using an air-borne particle abrader (Jet Blast II, J. Morita, Suita, Japan) with the use of 50-μm particles (A-220, Akiyama Sangyo, Neyagawa, Japan) at the pressure of 0.6 MPa with the distance of 10 mm for 20 s. These parameters used for abrasion process here is based on our previous study\textsuperscript{20}. The abraded alloy samples were characterized by surface analysis and were subjected to shear bond strength (SBS) tests. The control alloy samples were prepared by heat-treating the polished alloy in a furnace at 400°C for ~5 min to form a copper oxide layer on its surface. This thermal oxidation procedure for the alloy is similar with the one reported by T. Tanaka \textit{et al.}\textsuperscript{24}. For the other control sample, the abraded alloy was immersed in 35% hydrochloric acid (Wako pure chemical Industries, Osaka, Japan) for an hour at room temperature and subsequently cleaned by ultrasonication in distilled water. This HCl treatment is expected to remove the oxide layer that can be formed on the alloy surface\textsuperscript{25}. The summary of the surface preparation processes for the samples is listed in Table 2.

**Surface characterization**

Surface roughness of the alloys was measured by using a confocal laser scanning microscope (CLSM; VKX-100, Keyence, Osaka, Japan). The chemical composition and elemental mapping image of the alloy surfaces were obtained by using an energy dispersive X-ray spectroscopy (EDX; Ametek, PA, USA) equipped with the scanning electron microscope (SEM; S-4300, Hitachi-Technologies, Tokyo, Japan). The chemical states of the alloy surfaces were examined by using an X-ray photoelectron spectroscopy (XPS; ESCA-3400, Shimadzu, Kyoto, Japan).

| Table 1 Materials list |
|------------------------|
| Material/Trade name     | Composition | Lot number | Manufacturer     |
| Ag-Pd-Cu-Au alloy       |             |            |                 |
| Castwell M.C.12         | Ag 46, Pd 20, Cu 20, Au 12, (mass%) | 1609061 | GC              |
| Primer                  |             |            |                 |
| Super-Bond PZ Primer (Liquid A) | MDP, MMA | MW2 | Sun Medical |
| MMA/TBB resin cement    |             |            |                 |
| Polymer: Super-Bond Polymer | PMMA, Titanium oxide | MW1 | Sun Medical |
| Opaque Ivory            |             |            |                 |
| Initiator: Super-Bond Catalyst V | TBB | MT32F | Sun Medical |
| Monomer: MMA            | Regent grade of MMA | DSL5153 | Wako Pure Chemical Ind. |

10-methacryloyloxydecyl dihydrogen phosphate (MDP), methyl methacrylate (MMA), Polymethyl methacrylate (PMMA), tri-\textit{n}-butylborane derivative (TBB).

| Table 2 Surface treatments for Ag-Pd-Cu-Au alloys |
|-----------------------------------------------|
| Sample name                                  | Surface treatment method                           |
| (a) Abraded alloy                            | The alumina air-abrasion                           |
| (b) Abrasion/HCl treated alloy               | The alumina air-abrasion followed by the HCl treatment |
| (c) Thermal oxidized alloy                   | Thermal oxidation in furnace at 400°C for 5 min     |
| (d) HCl treated alloy                        | Immersed in the HCl solution followed by ultrasonication |
SBS test

SBS between the alloy and MMA/TBB resin cement was measured for each sample group (n=10), as listed in Table 3. To prepare the sample, a Teflon tube with inner diameter of 5 mm was firstly attached on each treated alloy surface by using a fixed tape in order to regulate constant adhesive area. The MDP contained primer was then applied on the alloy surface and followed by loading the MMA/TBB resin cement onto the alloy surface through the Teflon tube by means of a conventional brush-dip technique. The cemented samples were aged in an oven at 37°C for 24 h and later immersed in distilled water at 37°C for 24 h. The Teflon tube and fixed tape were removed from the alloy surface. The samples were then subjected to 20,000 cycles of thermocycling process which was conducted by alternating immersion in water baths of 5 and 55°C with a 60-s dwell time for each bath. The SBSs for the samples before and after the thermocycling process were measured by using a universal testing machine (AGS-H, Shimadzu, Kyoto, Japan) at a crosshead speed of 1.0 mm/min. After the measurements, the de-bonded surfaces were observed by an optical microscope (BHSM363NEL, Olympus, Tokyo, Japan) with 50× magnification whether the cement remained on the alloy surface. The failure modes were classified into three categories as follows; (AF) adhesive failure at the cement/alloy interface, (CF) cohesive failure within the cement and (MF) mixed failure of AF with CF.

Statistical analysis

Statistical analyses were carried out to the SBS data using statistical software, SPSS (version 23, SPSS, Chicago, IL, USA) and EZR (Saitama Medical Center, Jichi Medical University, Saitama, Japan). The mean and standard deviation were calculated by using n=10 raw data. First, the Kolmogorov-Smirnov test was used to each data set in order to check their distribution. In the case of the surface roughness, the result shows normal distribution. Then, the one-way analysis of variance (ANOVA) was conducted, subsequently Tukey’s post-hoc test was used for a multiple comparison. Since the SBS data did not show normal distribution, the non-parametric test (the Mann-Whitney U-test) was employed to compare the values between two groups. The significance level was set at 0.05 for all analyses.

RESULTS

Surface characterization of Ag-Pd-Cu-Au alloy

Prior to the SBS tests, mechanical and chemical changes on the Ag-Pd-Cu-Au alloy surface that has been subjected to alumina air-abrasion process were investigated. The abraded alloy surfaces were characterized by its roughness, alumina particles remaining and copper oxide formation. Surface roughness comparison of each treated alloy is shown in Fig. 1. It is evident that the alumina air-abrasion process led to the increase of surface roughness of the alloy, while neither the HCl treatment nor the thermal oxidation affect the roughness of the alloy surface.

Figure 2 shows SEM images, EDX spectra and elemental mapping images for each alloy surface. Results

Table 3 Sample preparation for the SBS test

| Group | Alloy sample                  | MDP application |
|-------|-------------------------------|-----------------|
| A     | HCl treated alloy             | –               |
| B     | Abrasion/HCl treated alloy    | –               |
| C     | Abrasion/HCl treated alloy    | +               |
| D     | Abraded alloy                 | +               |
| E     | HCl treated alloy             | +               |
| F     | Thermal oxidized alloy        | +               |

The surface condition of the alloy in each group is given in Table 5.
Fig. 2  SEM images, EDX spectra and elemental mapping images of each Ag-Pd-Cu-Au alloy surface after receiving (a) abrasion, (b) abrasion/HCl treatment, (c) the thermal oxidation and (d) the HCl treatment.

Fig. 2  SEM images, EDX spectra and elemental mapping images of each Ag-Pd-Cu-Au alloy surface after receiving (a) abrasion, (b) abrasion/HCl treatment, (c) the thermal oxidation and (d) the HCl treatment.

for the abraded alloy denote the considerable amount of alumina components exists on the alloy surface (Fig. 2(a)). These alumina components could not be removed from the surface even after the HCl treatment, as clearly seen in Fig. 2(b). Figure 2(c) shows the higher amount of Cu and O elements compared with other elements, which indicates that the thermal oxidation treatment promotes the formation of copper oxide layer on the alloy surface. Meanwhile the alloy that only received HCl treatment has no oxide layer formed on its surface, as indicated by the absence of O signals in Fig. 2(d).

In order to confirm chemical states of the alloy surfaces, we firstly examined the XPS spectra of Ag 3d, Pd 3d, Cu 2p, Au 4f and O 1s. However, since differences can be found only in the spectra of Cu 2p and O 1s, we therefore focus our explanation herein only regarding the changes in Cu 2p and O 1s spectra from each alloy sample. Figure 3 shows the XPS spectra of Cu 2p for the alloys. The assignments of Cu 2p spectra are referred to the studies27-29. In Fig. 3(a), the peaks are centered at around 932.5 and 952.5 eV which can be attributed to Cu 2p3/2 and Cu 2p1/2, respectively. These binding energies are believed to indicate the presence of Cu(0 or 1+). It is important to note that it is difficult to make a correct interpretation for Cu0 and Cu1+ from the Cu 2p spectra, due to the similar binding energies for Cu0 and Cu1+. Therefore, these binding energies is assigned as Cu(0 or 1+) from herein. Another doublet that was centered at 933.5 and 957 eV can be attributed to Cu2+. In addition, satellite peak at 944 eV further confirm the existence of Cu2+. Based on these results, there is a clear difference in the valence state of copper for the sample that received the abrasion (Fig. 3(a)) and for that received the abraded/HCl treatment (Fig. 3(b)). Figure 3(a) shows the presence of Cu2+ together with Cu(0 or 1+) in sample that received the abrasion. Meanwhile, the Cu 2p spectra for the abraded/HCl treated alloy only show peaks for Cu(0 or 1+) (Fig. 3(b)). Similar results were observed in the Cu 2p spectra of the thermal oxidized alloy (Fig. 3(c)) and the HCl treated alloy (Fig. 3(d)). The
Fig. 3 XPS spectra of Cu 2p for each Ag-Pd-Cu-Au alloy surface after receiving (a) abrasion, (b) the abrasion/HCl treatment, (c) the thermal oxidation and (d) the HCl treatment.

Fig. 4 XPS spectra of O 1s for each Ag-Pd-Cu-Au alloy surface after receiving (a) abrasion, (b) the abrasion/HCl treatment, (c) the thermal oxidation treatment and (d) the HCl treatment.
Table 4 Effects of the surface treatments on Ag-Pd-Cu-Au alloys, which was determined by the surface characterizations of CLSM, SEM-EDX, XPS

| Sample name                      | Changes in the treated alloy surface |
|----------------------------------|--------------------------------------|
| (a) Abraded alloy                | Surface roughening                    |
| (b) Abrasion/HCl treated alloy   | Surface roughening                    |
| (c) Thermal oxidized alloy       | —                                    |
| (d) HCl treated alloy            | —                                    |

Table 5 Surface conditions of the alloy for the samples used in the SBS tests, based on the result for the surface characterization (Table 4)

| Group | Surface condition of the Ag-Pd-Cu-Au alloy |
|-------|-------------------------------------------|
| A     | —                                         |
| B     | Surface roughening                        |
| C     | Surface roughening                        |
| D     | Surface roughening                        |
| E     | —                                         |
| F     | —                                         |

The sample preparation for the groups is given in Table 3.

Table 6 Failure modes for each group sample after the shear bond strength tests

| Group | Before thermocycle | After thermocycle |
|-------|--------------------|-------------------|
|       | AF  | MF  | CF  |      |      |      |
|       |     |     |     |      |      |      |
| A     | 10  | 0   | 0   | 10   | 0   | 0   |
| B     | 10  | 0   | 0   | 10   | 0   | 0   |
| C     | 9   | 1   | 0   | 10   | 0   | 0   |
| D     | 2   | 8   | 0   | 3    | 7   | 0   |
| E     | 10  | 0   | 0   | 10   | 0   | 0   |
| F     | 2   | 8   | 0   | 4    | 6   | 0   |

AF: Adhesive failure at the alloy-cement interface, MF: Mixed failure of adhesive and cohesive, CF: Cohesive failure within the cement.
Influence of the alumina air-abrasion on SBS test results

From the surface characterization results, the samples were divided into six groups for this examination, as listed in Table 5. The SBS value for each group were compared between the appropriate groups as presented in Figs. 5–8. The failure modes for each group after the SBS tests are summarized in Table 6.

Figure 5 shows the evaluation for effect of mechanical roughening on the adhesive bonding which was done by comparing the SBS values for A and B. The sample surfaces in group B was mechanically roughened while that of in group A did not receive similar treatments. In order to elucidate only the mechanical roughing effect without any chemical effects, these groups are not used the MDP contained primer. The SBS before the thermocycling for group B is the mean value of 7.0±2.0 MPa, which is significantly higher than that for group A (2.7±1.5 MPa). After thermocycling, there is no difference between the SBS values for both groups (0 MPa for group A, 0.1±0.3 MPa for group B).

Figure 6 presents the comparison of the SBS values for samples in which MDP contained primer was applied (group C) or not (group B). This comparison allows us to evaluate the effect of alumina remain on the adhesive bonding characteristic when MDP contained primer was used. There is no difference between the SBS values for group B (7.0±2.0 MPa) and group C (6.9±1.9 MPa) before thermocycling. There are also no significant differences in SBS value after thermocycling, since the SBS value decreased to 0.1±0.3 MPa for group B and to 1.2±1.1 MPa for group C.

The comparison between the SBS values for groups C and D is given in Fig. 7. This investigation was done on samples that has (group D) or has no (group C) copper oxide layer on the abraded alloy surface, in order to study the effect of copper oxide layer formed on the abraded alloy surface on adhesive bonding characteristic. The SBS value before the thermocycling for group D is 24.8±2.3 MPa, which is significantly higher than that for group C (6.9±1.9 MPa). After thermocycling, the SBS

![Fig. 5](image1)

**Fig. 5** Comparison of the shear bond strengths between samples in group A and B (a) before and (b) after the thermocycling, in order to evaluate the alumina air-abrasion effect (i) for mechanical roughening. The asterisk * indicates a significant difference between the groups (*p<0.05, Mann-whitney U-test, n=10).

![Fig. 6](image2)

**Fig. 6** Comparison of the shear bond strengths between samples in group B and C (a) before and (b) after the thermocycling, in order to evaluate the alumina air-abrasion effect (ii) on alumina remain (Mann-whitney U-test, n=10).
The asterisk (*) indicates a significant difference between the groups (*p<0.05, Mann-whitney U-test, n=10).

The value for group D is decreased to 13.0±4.5 MPa, which is still significantly higher than that of group C (1.2±1.1 MPa). The effect of copper oxidation (effect (iii)) is further clarified in Fig. 8, which shows results from samples that has (group F) or has no (group E) copper oxide layer formed on the non-abraded alloy surface. The SBS before the thermocycling for group F is 24.0±6.9 MPa, which is significantly higher than that for group E (2.7±1.5 MPa). After thermocycling, the SBS value for group F is still significantly higher than that for group E, as shown by the decrease of SBS value down to 0 MPa for group E while the SBS value for group F is 10.8±3.8 MPa.
DISCUSSION

Based on the present surface characterization results, mechanical and chemical alterations on the Ag-Pd-Cu-Au alloy surface which was induced by the alumina air-abrasion process is schematically described in Fig. 9. The alumina air-abrasion process resulted in three effects on the alloy surface: (i) mechanical roughening, (ii) alumina remain and (iii) copper oxidation. The remained alumina could not be removed from the surface even after the HCl treatment, as clearly seen in Fig. 2(b). This fact suggested that components of the abraded alumina particles tightly attached to the alloy surface. From the results given in Figs. 5–8, the influence of these effects on the adhesive bonding characteristic is elucidated as follows.

The effect of mechanical roughening (effect (i)) on adhesive bonding characteristic is given in Fig. 5 which shows the comparison of the SBS values for the groups A and B. The difference lies on the roughness of the alloy surface. Samples in group B was roughened by the abrasion, while samples in group A did not receive similar treatment. It is important to note that the alumina remain in group B is ineffective to improve the SBS value since the MDP contained primer did not use in this group. Results in Fig. 5 verify the effectiveness of the mechanical roughening on the SBS value, which suggested that the abrasion improved the SBS in both groups before thermocycling, although such an improvement cannot be observed after thermocycling. In addition, the failure modes of the samples (Table 6) support the results of the SBS. Therefore, the mechanical roughening has relatively low effect on the adhesive bonding.

The effect of alumina remain (effect (ii)) was investigated by comparing the SBS values for the groups B and C. The difference between these groups is in the use of MDP contained primer which was applied onto the abraded alloy surface (group C), while samples in group B did not receive similar treatment. Since MDP is known to be quite effective to alumina\(^{30}\), a positive effect on the alumina-remaining-alloy surface. Samples in group B was roughened by the abrasion, while samples in group A did not receive similar treatment. It is important to note that the alumina remain in group B is ineffective to improve the SBS value since the MDP contained primer did not use in this group. Results in Fig. 5 verify the effectiveness of the mechanical roughening on the SBS value, which suggested that the abrasion improved the SBS in both groups before thermocycling, although such an improvement cannot be observed after thermocycling. In addition, the failure modes of the samples (Table 6) support the results of the SBS. Therefore, the mechanical roughening has relatively low effect on the adhesive bonding.

As clearly seen in Fig. 2(b), the remaining alumina only covers the alloy surface locally and not homogenously covered the entire surface. It is speculated that the amount of remaining alumina components on the alloy surface was insufficient, hence unable to improve the bond strength.

The effect of copper oxidation on the surface (effect (iii)) was confirmed by comparing the SBS values between groups C and D, where the main difference is in the presence of copper oxide layer which was formed by the abrasion (group D) or eliminated by the HCl treatment (group C). Based on results in Fig. 7, the presence of copper oxide layer can be confirmed to yield in higher SBS values before and after the thermocycling, compared with those of samples that has no copper oxide layer on its surface. Similar to that, Fig. 8 showed the effect of copper oxide by the thermal treatment on the adhesive bonding by comparing the SBS values for the groups E and F. The SBS value of the thermally oxidized alloy (group F) is significantly higher than that of non-thermally-oxidized alloy (group E). The results in Figs. 7 and 8 showed similar tendency, i.e. samples that have copper oxide layer formed on their surfaces (either by the abrasion or thermal oxidation) gave positive effect on the adhesive bonding characteristic. For the failure modes as listed in Table 6, similar results were obtained in the abraded alloy (group D) and the thermally oxidized alloy (group F). This tendency is corresponding to the SBS results. Hence, it is considered that the copper oxidation by the abrasion has positive effect on the SBS as similar as that by the thermal treatment.

Based on these findings, the contribution of effects from alumina air-abrasion treatment on the adhesive bonding characteristic is considered to be in the following order; alumina remain<mechanical roughening<copper oxidation. Therefore, we can conclude that the presence of copper oxidation on the alloy surface which was induced by the abrasion is the most important effect on the improvement of the adhesive bonding rather than the other examined effects.

CONCLUSION

The alumina air-abrasion to the Ag-Pd-Cu-Au alloy surface generates mechanical and chemical effects such as mechanical roughening, remain of alumina component and the formation of copper oxide layer. Among them, the presence of copper oxide on the alloy surface was found to give the most prominent influence on the SBS between the alloy and the MMA-TBB resin cement using the MDP contained primer.

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