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Effect of metal primers and tarnish treatment on bonding between dental alloys and veneer resin

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PURPOSE. The aim of this study was to evaluate the effect of metal primers on the bonding of dental alloys and veneer resin. Polyvinylpyrrolidone solution's tarnish effect on bonding strength was also investigated.
MATERIALS AND METHODS. Disk-shape metal specimens (diameter 8 mm, thickness 1.5 mm) were made from 3 kinds of alloy (Co-Cr, Ti and Au-Ag-Pd alloy) and divided into 4 groups per each alloy. Half specimens (n=12 per group) in tarnished group were immersed into polyvinylpyrrolidone solution for 24 hours. In Co-Cr and Ti-alloy, Alloy Primer (MDP + VBATDT) and MAC-Bond II (MAC-10) were applied, while Alloy Primer and V-Primer (VBATDT) were applied to Au-Ag-Pd alloys. After surface treatment, veneering composite resin were applied and shear bond strength test were conducted. **RESULTS.** Alloy Primer showed higher shear bond strength than MAC-Bond II in Co-Cr alloys and Au-Ag-Pd alloy (*P*<.05). However, in Ti alloy, there was no significant difference between Alloy Primer and MAC-Bond II. Tarnished Co-Cr and Au-Ag-Pd alloy surfaces presented significantly decreased shear bond strength. **CONCLUSION.** Combined use of MDP and VBATDT were effective in bonding of the resin to Co-Cr and Au-Ag-Pd alloy. Tarnish using polyvinylpyrrolidone solution negatively affected on the bonding of veneer resin to Co-Cr and Au-Ag-Pd alloys. *[J Adv Prosthodont 2015;7:392-9]*

KEY WORDS: Metal primer; Resin; Polyvinylpyrrolidone solution; Shear bond strength; Tarnish

INTRODUCTION

Metal-resin restorations have been used extensively because of convenient handling, favorable aesthetics, and ease of repair.[1] Recently, several studies have shown enhancement in the mechanical properties and wear resistance of metal-resin restorations, which are on a par with properties of natural tooth.[2,3] However, the relatively low bond strength between the veneering composite resin and metal in metal-resin restorations is a major clinical concern.[4]

To overcome this limitation, a number of resin-metal bonding methods, such as macro and micromechanical retention, chemical bonding, or a combination of these have been suggested.[5,6] Limitations of mechanical retention, such as bulky framework and microleakage in the interface, result in decreased retention.[6] The various chemical bonding methods are technique sensitive, time consuming, and require special devices.[7] On the other hand, the application of a metal primer requires only air-borne particle abrasion of the metal surface before bonding.[8,9] Metal primers can be simply applied with a brush and lead to higher bond strength and durability after thermal cycling.[10]

Representative priming agents for base metals contain an acidic monomer, while primers for noble metals include a sulfur-containing monomer.[7] A carboxylic monomer can be effectively bonded to nickel-chromium alloy (Ni-Cr), cobalt-chromium (Co-Cr) alloy, and titanium (Ti) alloy.[11] The bond strength to the base metal alloys has been

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improved with the use of a hydrophobic phosphate monomer.[12-17] The durable bonding of the adhesive resin to nickel-chromium and cobalt-chromium alloys is well-known.[18] For noble metals, the inclusion of sulfur-containing monomers as an adhesive monomer component of the methyl methacrylate-tri-n-butylborane partially oxide (MMA-TBBO) resin has been shown to improve the bonding strength.[19] Studies have also shown the positive effect of metal primers on the bonding of 4-methacryloyloxyethoxy-carbonylphthalic anhydride (4-META)/MMA-TBBO resin to noble metal alloys.[20,21] Studies have shown the addition of various functional monomers does not negatively affect the bond strength to metals,[22,23] and the bond strength significantly improved when a functional monomer was used in combination.[24]

Another point to consider in the adhesion of the metal and resin is the long-term use of contaminated restoration in the oral cavity. When a veneering composite material is fractured, the repair using a primer and composite resin is often hampered because of the tarnished metal surface. Tarnish, which is a surface discoloration or loss of luster, often occurs because of the formation of deposits on the surface of used restoration. Tarnish is regarded as a forerunner of corrosion because the tarnish film accumulates components that can chemically attack the metallic surface. Sulfide, oxide, and chloride ions in saliva and food contribute to the corrosive attack.[25,26] Moreover, various acidic solutions, such as phosphoric, acetic, and lactic acids can

also promote corrosion.[26,27] However, the exact effect of tarnish on the metal-resin bonding strength needs to be investigated.

The purpose of this study was to evaluate 1) the effect of three adhesive primers on the shear bond strengths (SBS) of light polymerized resins to noble and base dental alloys and 2) the tarnish effect of static immersion tests using a polyvinylpyrrolidone solution on the bonding strength.

MATERIALS AND METHODS

The materials used in this study are shown in Table 1 and the experimental design is illustrated in Fig. 1.

Disk-shaped wax patterns (8 mm in diameter and 1.5 mm in thickness) were cast using a Co-Cr alloy (n = 48) and an Au-Ag-Pd alloy (n = 48) according to the manufacturer's instructions. The Ti alloy specimens were machine-milled (n = 48) in the same shape. After casting and milling, the specimens were embedded into an autopolymerzing resin (Jet Tooth Shade, Lang Dental Mfg Co Inc., Wheeling, IL, USA) using molds. The disk surfaces were finished with 600-grit silicon carbide paper (SiC Sand Paper 8", #600 PSA, R&B Inc., Daejon, Korea) under water. The finished surface was subjected to air-borne particle abrasion with 50 μm aluminum oxide. The air-borne particle abrasion was performed for 10 seconds at an air pressure of 0.5 MPa an angle of 45° with the nozzle-metal surface distance set to 5
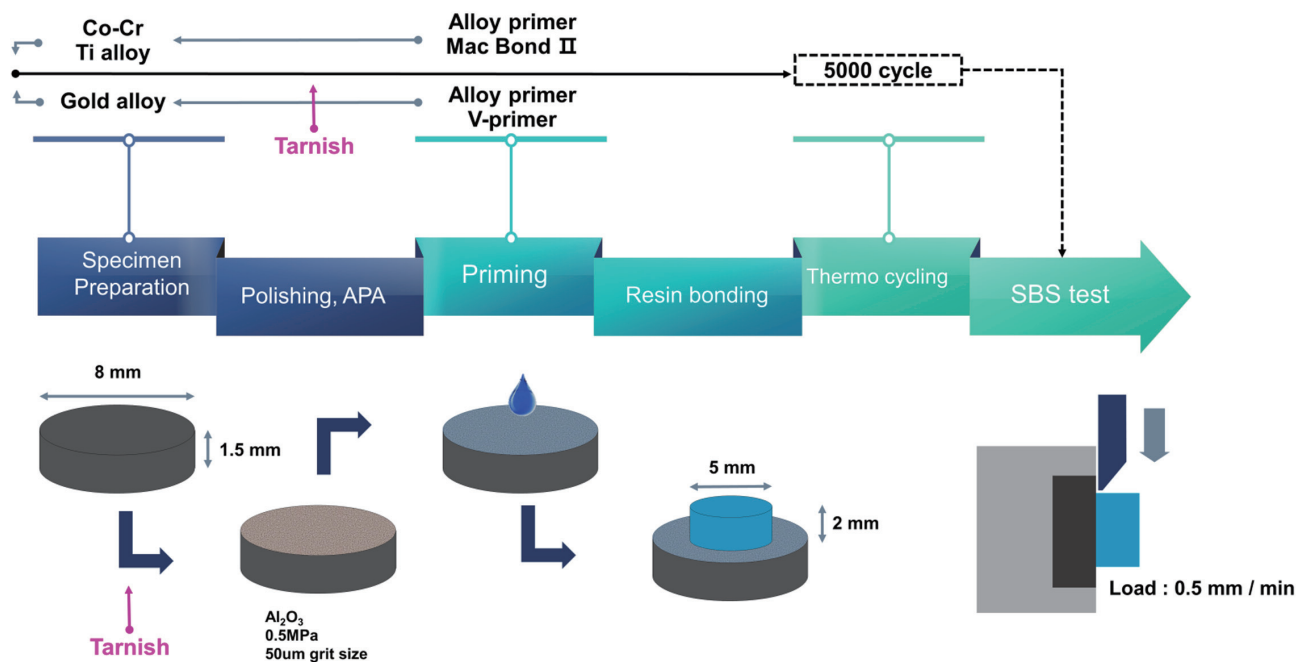

Fig. 1. Experimental protocols.

mm (Basic Master, Renfert GmbH, Hilzingen, Germany). All the specimens were cleaned in an ultrasonic bath for 5 minutes and air dried for 30 seconds.

Half of the specimens were immersed in a 20 mL glass vial containing 15 mL polyvinylpyrrolidone solution at 37°C. After immersion for 24 hours, the specimens were removed from the solution and rinsed with tap water for 15 seconds and air dried for 30 seconds.

Forty-eight specimens per alloy were classified into four subgroups (n = 12 per each group), according to the metal primers and tarnish treatments used (Fig. 1). The following metal primers were applied to the metal surfaces: AP (Alloy Primer), MB (MAC-Bond II), and VP (V-Primer) (Table 1). In the base metal group (Co-Cr and Ti alloys), AP and MB were applied to the tarnished and untarnished subgroup. In the case of the Au-Ag-Pd alloy specimens, AP and VP were applied. All the primers were applied using a disposable brush according to the manufacturer's instructions.

After the surface treatments, a round acrylic mold (inner diameter = 5 mm and height = 2 mm) was placed on the top of the bonding area. Tescera ATL II opaque resin was applied to each specimen with a brush and light-polymerized. Then, the acrylic mold was filled with Tescera ATL II A2 shade resin and light-polymerized for 90 seconds.

To relieve the polymerization stress and increase the conversion rate, the bonded composite resin specimens were stored at room temperature for 30 minutes and then stored in distilled water at 37°C for 24 hours. After water storage, thermal cycling was carried out between 5°C and 55°C for 5,000 cycles with a dwell time of 30 seconds in each bath. The 5,000 cycles were carried out for a period of six months.[28]

The SBS of all the specimens were tested with a universal testing machine (RB 302 ML, R&B Inc., Daejon, Korea) at a crosshead speed of 0.5 mm/min. The shear bond strength values were obtained in kgf and converted into MPa. The fractured surfaces were evaluated with an optical stereomicroscope at ×40 magnification to determine the failure mode (cohesive, adhesive, or mixed). The fracture mode was classified as adhesive failure when the percentage of the veneering material remaining on the metal surface was less than 25%, cohesive when the value was more than 75%, and as mixed when the value ranged between 25% and 75%.

Representative specimens of each experimental group were examined using a scanning electron microscope (SEM) operating at 20 kV (Inspect F50, FEI Co., Hillsboro, OR, USA) four times i.e., after the air-borne particle abrasion, tarnish treatment, primer application, and shear bond test. To observe the features of the fractured surface, each specimen was coated with a gold-palladium alloy at 30 mA for 120 seconds after the SBS test. SEM images were acquired at magnifications of ×1,000 and ×4,000 magnifications to inspect the surface after each procedure and magnifications of ×40 and ×100 were used for confirming the fracture mode after the SBS test.

Two-way ANOVA (IBM SPSS statistic 21.0, IBM corp., New York, NY, USA) was performed to compare the effect of the different metal primers and tarnish treatments. Differences among the mean values were determined by *post-hoc* Tukey test at a preset alpha of 5%. A chi-square test was performed to detect correlation between the primer, metal, tarnish, and failure mode.

Table 1. Materials used in this study

Material	Product Name	Composition	Manufacturer
Co-Cr alloy	Biosil® f	Cobalt 64.8% Chromium 28.5% Molybdenum 5.3% Silicon 0.5% Manganese 0.5%	Degudent GmbH, Bohmte, Germany
Ti alloy	Ti-Al$_6$-V$_4$ ASTM B 348 Grade V	Titanium 89.0% Aluminium 6.0% Vanadium 4.0%	Kobe steel co., New York, USA
Au-Pd-Ag alloy	GOLDENIAN C-55	Gold 55.0% Silver 19.90% Palladium 3.00% Platinum 1.00% Etc 21.10%	Shinhung, Seoul, Korea
Primers	Alloy Primer MAC-Bond II V-Primer	MDP, VBATDT MAC-10 VBATDT	Kuraray Medical Inc., Okayama, Japan Tokuyama Dental Corp., Tokyo, Japan GC Corp., Tokyo, Japan
Composite Resin	Tescera ATL 2		Bisco Inc. Schaumbrug, IL, USA

RESULTS

Two-way ANOVA (Table 2) revealed significant interactions ($P < .05$) among the metal primers and between the tarnish treatments. The mean shear bond strength values (MPa) and standard deviations (SDs) of all the samples are shown in Table 3. In the Co-Cr alloy groups, the specimens treated with AP exhibited significantly higher SBS in comparison to MB treated specimens ($P < .05$). The specimens treated with AP and MB in the Ti alloy group ($P > .05$) was insignificant. Among the Au-Ag-Pd alloy specimens, the group treated with AP exhibited significantly higher SBS in comparison to the group treated with VP. Figure 2 shows the SBS values of the tarnished and untarnished samples. A significant difference was found between the tarnished and untarnished specimens, with the exception of the Ti alloy specimens ($P < .05$).

Figures 3 - 5 show the SEM images of the metal surfaces subjected to surface treatment. The surfaces of the Co-Cr alloy specimens subjected to airborne-particle abrasion (Fig. 3A) showed sharp edges with a honeycomb structure. Such cavities could be observed when the specimens were tarnished (Fig. 4A).

In the Ti alloy specimens, the samples subjected to airborne-particle abrasion and those that were tarnished group did not show any significant differences (Fig. 3B, Fig. 4B). The tarnished surface of the Ti alloy specimens resembled a chemically etched surface.

Table 2. Two-way ANOVA table for overall models

	Sum of squares	df	Mean square	F	P
Metal Primer	287.498	5	57.500	17.081	.000
Tarnish	50.315	1	50.315	14.947	.000
Metal Primers * Tarnish	98.561	5	19.712	5.856	.000
Error	444.359	132	3.366		
Total	880.734	143			

Table 3. Mean (standard deviation) shear bond strength value (MPa)

Metal	Primer	No tarnish	Tarnish
Co-Cr alloys	AP	12.1 (1.6)[a]	10.5 (2.7)[b]
	MB	8.4 (2.2)[c]	7.9 (1.5)[cd]
Ti alloys	AP	11.4 (1.5)[a]	12.3 (1.2)[a]
	MB	10.9 (1.6)[ab]	11.0 (1.5)[ab]
Au-Ag-Pd alloys	AP	11.6 (1.9)[a]	10.7 (1.3)[b]
	VP	9.9 (2.1)[bc]	6.8 (2.3)[d]

AP = Alloy Primer, MB = MAC Bond II, VP = V-Primer
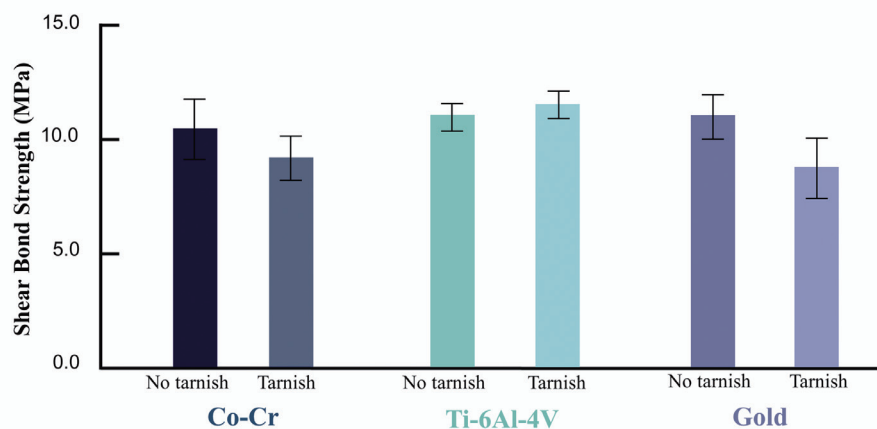※ The different superscript letters indicate values that are significantly different ($P < .05$).

Fig. 2. Mean shear bond strength values. Untarnish vs. Tarnish.

The surface texture of the Au-Ag-Pd alloy specimens subjected to airborne-particle abrasion was clearly different from the tarnished surfaces (Fig. 3C, Fig. 4C). Corrosion attack was observed over the entire exposed surface of the tarnished Au-Ag-Pd alloy. Small crystalline corrosion products of silver iodide (AgI) covered the surface of the tarnished Au-Ag-Pd alloy specimens.

Most debonded surfaces showed complete adhesive failure, which occurred between the metal surface and the opaque resin. Table 4 shows the failure mode of all the experimental groups. SEM images of each representative failure mode can be seen in Figure 5. The chi-square test revealed no significant correlation between the primer, metal, tarnish, and failure mode ($P > .05$).
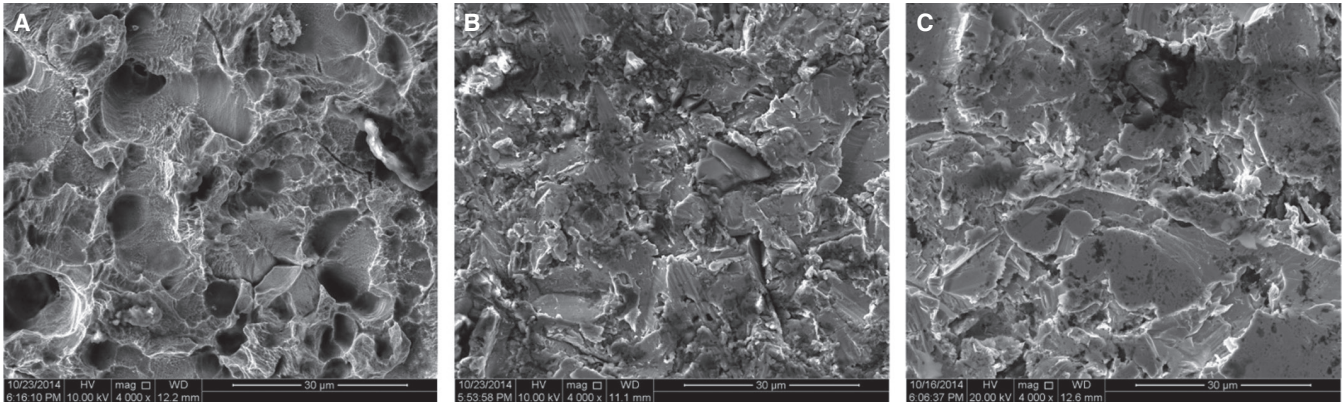

Fig. 3. Airborne-particle abraded specimen with Al_2O_3 (SEM photograph, ×4,000 magnification). (A) Co-Cr alloy, (B) Ti alloy, (C) Au-Ag-Pd alloy.

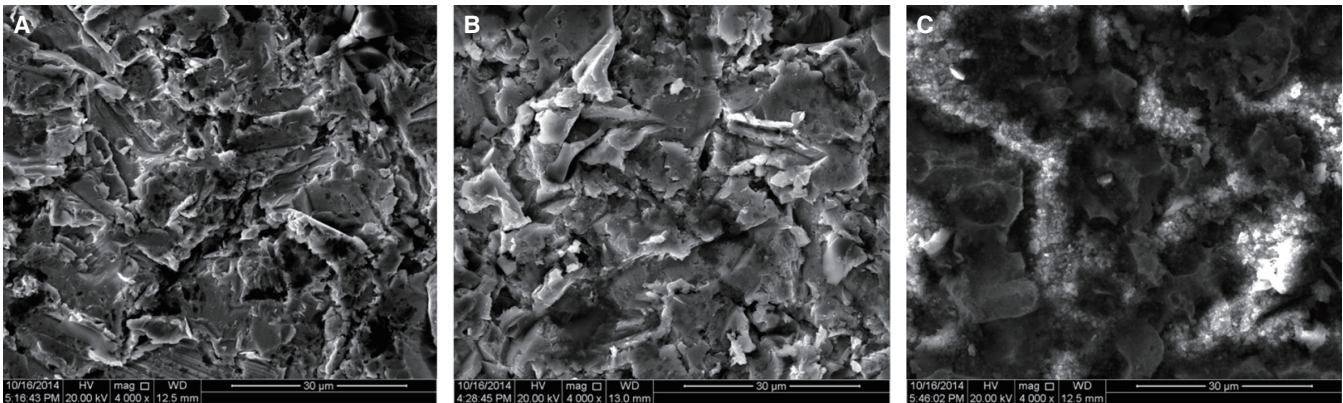**Fig. 4.** Tarnished specimen by polyvinylpyrrolidone solution (SEM photograph, ×4,000 magnification). (A) Co-Cr alloy, (B) Ti alloy, (C) Au-Ag-Pd alloy.
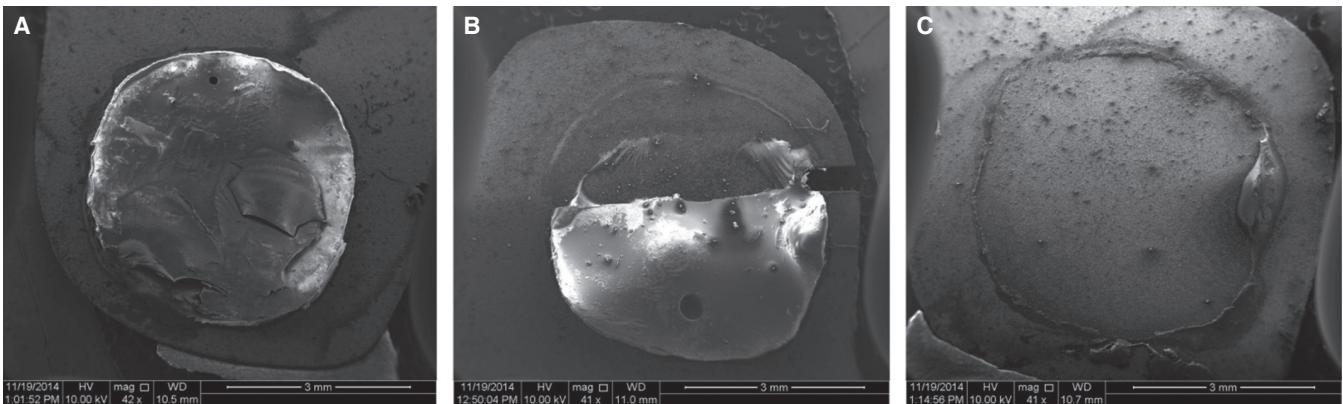

Fig. 5. Representative SEM photograph for failure mode. (A) cohesive failure, (B) mixed failure, (C) adhesive failure.

DISCUSSION

This study evaluated the differences in the bonding characteristics among dental alloys and the effect of static immersion test in a polyvinylpyrrolidone solution on the resin-metal bonding using three metal primers. To verify the positive effect of combining functional monomers, MAC-10 (MB), MDP+VBATDT (AP), and VBATDT (VP) were selected.

AP was a more effective functional monomer than MB or VP for Co-Cr and Au-Ag-Pd alloys. MDP in AP and MAC-10 in MB have been known to play a major role in bonding to Co-Cr alloys.[12] These results contradict previous reports, which indicate MAC-10 as more effective than MDP for bonding in Co-Cr alloys.[12,29] In these previous reports, however, thermal cycling was not carried out and an autopolymerizing acrylic resin was used. In contrast, Koizumi et al.[10] concluded that MDP is more effective than MAC-10 for bonding in the case of Ti alloys after thermal cycling, which is agreement with the results reported in this study. It can be assumed that MDP promoted adhesion more effectively and durably than MAC-10 and improved the adhesion of resins to the Co-Cr alloy during functioning in the oral cavity.

Several studies have found the effectiveness of the VBATDT monomer for bonding in the case of noble metal alloys.[13,19-22] The bonding mechanism between the VBATDT monomer and noble metals is attributed to the chemical interaction between sulfur and the noble metals.[13] Bonding of triazinedithione (a VBATDT) to a noble metal works on the basis of tautomerism, where a stable thione type (-NH-CS-) structure tautomerizes to the reactive thiol structure (-N=C(SH)-) on the noble metal surface.[23] If the thiol groups are in excess, the propagation of the resin polymerization could be inhibited because thiol causes a chain transfer reaction with the resin monomer. In the polymer network, a chain transfer reaction with any amount of the VBATDT could affect the final conversion.[24,29] Therefore, the concentration difference of the VBATDT between AP and VP could be attributed to the significant differences in the SBS of the Au-Ag-Pd alloys. We can only assume this because the concentration of VBATDT included in each primer is unknown.

In this study, the combined use of sulfur-containing monomers and acidic monomer (AP) resulted in a higher SBS than when an acidic monomer (MB) and a sulfur-containing monomer (VP) were used independently. These results are similar to the findings of Minami et al.[24] and Taira et al.[30] who also observed a similar superior bond strength with the combined use of an acidic monomer and a sulfur-containing monomer. MDP and VBATDT did not interfere with each other.[29] Moreover, combining an acidic monomer and a sulfur-containing monomer is advantageous to the bonding durability compared to the use of only one type of monomer.[22,24,30]

Unlike base metals, which are characterized by a thicker oxide layer, pure noble metals contain lesser oxide layers without artificial surface treatment. Thus, an acidic monomer, which adheres to the oxide layer could not be strongly attached to a pure noble metal surface. Unlike pure noble metals, noble metal alloys contain a variety of trace elements. X-ray photoelectron spectroscopy has shown that oxides of Ag, Al, and Cu are present on the noble metal alloy surface.[14,30] Adhesive force seems to be generated between these elements on the noble metal alloy surface and the acidic monomer in the metal primer. This may be the reason for the higher SBS shown by the combined use of an acidic monomer and a sulfur containing monomer (AP) than the single use of a sulfur containing monomer (VP) on an Au-Ag-Pd alloy.

In Ti alloys, types of primer and tarnish treatment did not cause any significant effects on the adhesion of titanium and composite resins. A similar trend has been reported previously.[10,15] The SBS of groups using MDP (AP) was slightly higher than that of specimens using MAC-10 (MB), although the difference was statistically insignificant. This suggests the possibility that the chemical bonding of MDP to titanium oxide is superior to that of MAC-10.[15] However, this trend did not appear distinctly when the Co-Cr alloy is considered, which is caused by the thick chromium oxide layer, which MDP may be more strongly combined with than titanium oxide. For this reason, the difference between the MDP and MAC-10 may not be seen clearly in the Ti alloy samples compared to Co-Cr alloys.

Polyvinylpyrrolidone is a strong tarnish solution. Takasusuki et al.[27] reported that the concentration of Au, Ag, and Cu ions released in polyvinylpyrrolidone solution is to 5 - 40 times higher than that released in Fusayama artificial saliva.[25] There are no clear standards for tarnish solutions; however, polyvinylpyrrolidone solution, because of its strong corrosive effect, was sufficient as a tarnish solution.

In the Co-Cr alloy group, the SBS significantly reduced after tarnishing both in the case of AP and MB application.

Table 4. Failure mode experimental groups (cohesive failure / mixed failure / adhesive failure)

Metal	Primer	No tarnish	Tarnish
Co-Cr alloys	AP	1 / 1 / 10	0 / 1 / 11
	MB	0 / 1 / 11	0 / 0 / 12
	Total	1 / 2 / 21	0 / 1 / 23
Ti alloys	AP	1 / 2 / 9	0 / 1 / 11
	MB	1 / 0 / 11	0 / 2 / 10
	Total	2 / 2 / 20	0 / 3 / 21
Au-Ag-Pd alloys	AP	0 / 1 / 11	0 / 1 / 11
	VP	0 / 0 / 12	0 / 0 / 12
	Total	0 / 1 / 23	0 / 1 / 23

AP = Alloy Primer, MB = MAC Bond II, VP = V-Primer.

In the SEM image, smooth surface features of the tarnished Co-Cr surface can be observed. The sharp scratches on the Co-Cr surface disappeared after the tarnish treatment. Changes in the surface roughness due to chemical attack by the polyvinylpyrrolidone solution could have led to the reduced SBS.

In the Ti alloy samples, the SBS slightly increased after the tarnish treatment, although the change was statistically insignificant. In the SEM image, the Ti alloy surface changed similar to the chemically etched surface after the tarnish treatment. The effect of MDP on bonding to the cast Ti alloy showed poor results because of the presence of a brittle oxide layer on the titanium surface formed during the heating process.[16] The Ti specimen used in this experiment was produced by machining; however, unintended heating could have occurred during machining the disk-shaped samples. The bonding strength to the machined Ti in the case of using the MDP primer was significantly reduced when titanium was heated to temperatures $\geq$ 500°C.[16] However, the bond strength of the Ti alloy reduced by heating or casting can be recovered by blasting the surfaces with aluminum oxide.16 The SBS increase observed after tarnishing of Ti alloy samples in the present study can be explained on the basis of the chemical attack of the titanium surface by polyvinylpyrrolidone solution, which induced an effect similar to that generated by airborne-particle abrasion.

In the case of Au-Ag-Pd alloys, the SBS significantly reduced after tarnishing both in specimens using AP and VP. In the SEM image, the surface features smoothened and numerous corrosion products were observed on the alloy surface, which is estimated to be silver iodide (AgI). Takasusuki et al.[27] showed that the surface of pure Ag was completely covered with small crystalline corrosion products of AgI after static immersion in a polyvinylpyrrolidone solution. In the iodine-based solution, pure Au dissolve into the solution, whereas pure Ag and Cu corroded to form insoluble corrosion products i.e., AgI and CuI, respectively.[27] The Au-Ag-Pd alloy used in this study also contained silver (19.9%); therefore, silver iodide could be generated in the tarnish process. Therefore, noble metal surfaces tarnished by iodine-based solutions should be treated by airborne-particle abrasion, chemical etching, or grinding with a diamond bur for resin bonding repair.

The failure mode was predominantly adhesive, suggesting that the resin to metal bond strength is lower than the cohesive strength of the composite resin for all surface treatments. This can be attributed to the insufficient strength of the macromechanical bonding to the metal surface. In clinical situations, a three-dimensional structure of the resin-metal restoration is used to increase the retention of the veneering resin and pure shear failure may not occur as observed in the experiments here. It is to be noted that the adhesive resin was omitted in this study. The adhesive resin included in the Tecera ATL II system contains a metal primer. To avoid confusion and to evaluate the unique effect of the metal primer type, an opaque resin was directly applied on the metal surface without applying an adhesive resin. Matsumura et al.[17] suggest that a SBS greater than 10 MPa is sufficient for veneering materials. The bond strength exhibited by the use of AP exceeded 10 MPa in all metal alloy specimens, which is clinically acceptable.

In this study, the combined use of an acidic monomer and a sulfur-containing monomer improved the bonding between the resin composite and metal. This evidence implies that clinicians may consider the use of a metal primer to both the base and noble metals. Moreover, the tarnished surface can disturb the bonding between the metal and the resin. Additional metal surface treatments are required before applying a metal primer, especially on metals used for long time in the oral cavity.

CONCLUSION

This study evaluated the efficacy of three metal primers and the tarnishing effect of a polyvinylpyrrolidone solution on the bonding of the resin to base and noble metals. Within the limitations of this study, the following conclusions can be drawn.

Specimens with MDP (AP) showed significantly higher SBS than specimens with MAC-10 (MB) in the case of Co-Cr alloys ($P < .05$). The type of metal primer and tarnish treatment did not affect the SBS in Ti alloys ($P > .05$). The SBS of the Au-Ag-Pd alloys significantly improved when VBATDT was used in combination with MDP (AP), compared to the single use of VBATDT (VP) only ($P < .05$). Tarnishing by the polyvinylpyrrolidone solution significantly decreased the SBS of the Co-Cr and Au-Ag-Pd alloys ($P < .05$).

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