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Adhesive performance of silver-palladium-copper-gold alloy and component metals bonded with organic sulfur-based priming agents and a tri-*n*-butylborane initiated luting material

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Abstract

Objective. The purpose of the current study was to evaluate the effect of thione-based metal priming agents on the adhesive behavior of a Ag-Pd-Cu-Au alloy and component metals bonded with an acrylic resin. ***Materials and methods.*** Disk specimens (10 mm in diameter by 3 mm thick) were prepared from a silver-palladium-copper-gold (Ag-Pd-Cu-Au) alloy (Castwell M.C.12), high-purity silver, palladium, copper and gold. Four single-liquid priming agents containing organic sulfur compound (Alloy Primer, Metaltite, M.L. Primer and V-Primer) and three acidic priming agents (All Bond II Primer B, Estenia Opaque Primer and Super-Bond Liquid) were assessed. The metal specimens were flat-ground with abrasive papers, primed with one of the agents and bonded with a tri-*n*-butylborane initiated resin. The shear bond strengths were determined both before and after repeated thermocycling (5°C and 55°C, 1 min each, 20,000 cycles). The results were statistically analyzed with a non-parametric procedure ($p = 0.05$ level). ***Results.*** The post-thermocycling bond strengths in MPa (median; $n = 11$) associated with the Alloy Primer, Metaltite, M.L. Primer and V-Primer materials were, respectively, 20.8, 22.8, 17.8 and 18.4 for the Ag-Pd-Cu-Au alloy; 19.6, 21.9, 14.4 and 20.1 for silver; 5.4, 4.5, 12.8 and 5.3 for palladium; 17.1, 19.2, 0.7 and 6.6 for copper; and 18.5, 17.7, 22.8 and 15.4 for gold. ***Conclusions.*** It can be concluded that the use of the four priming agents, which are based on organic sulfur compounds, effectively enhanced bonding to the Ag-Pd-Cu-Au alloy and the component metals, although the bonding performance varied among the priming agents and metal elements. The priming agents appeared to have more of an effect on the alloy, silver and gold than on the palladium and copper.

Key Words: *thiol, thione, thiouracil, tri-n-butylborane*

Introduction

Over the last decade, the use of prosthodontic adhesives for cementing cast restorations and fixed partial dentures (FPDs) has increased considerably. This trend is due to development of adhesive functional monomers and initiation systems. Representative functional monomers are organic acids for hard tissues [1], base metal alloys [2,3] and metal oxide ceramics [4]. Silanes are used for bonding silica-based ceramics [5], whereas thiones or thiols are used for noble metal alloys [6,7]. The initiation systems that are currently applicable to acidic bonding agents are a tri-*n*-butylborane (TBB) derivative [8], benzoyl peroxide (BPO)-amine-sodium sulfinate [9] and others.

Silver-palladium-copper-gold (Ag-Pd-Cu-Au) alloys are being used as an alternative to gold alloys for cast restorations, FPDs and the framework of removable partial dentures. Because of its age-hardenability and improved bonding characteristics, the Ag-Pd-Cu-Au alloy has been used in the fabrication of resin-bonded FPDs. Atsuta et al. [7] reported on the adhesive bonding of type 3 gold and Ag-Pd-Cu-Au alloys. Their results showed that priming with a thione monomer considerably enhanced bonding between a TBB-initiated opaque resin and noble metal alloys. Four thione or thiol-based priming

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agents designed for noble metal alloys are currently available. Laboratory evaluations demonstrated the effectiveness of these priming agents in application to noble metals [10–18]. In addition, clinical results demonstrate considerably long survival periods for resin-bonded restorations and FPDs [19-24] made of noble alloys and bonded with thione primers.

Although the usefulness of thiol and thione priming agents for bonding noble alloys appears to be confirmed, limited information is available about the relationship, if any, between the type of priming agent and the characteristics of their bonding to metal elements. The purpose of the current study therefore is to evaluate the effect of thiol/thione-based metal priming agents on the bonding behavior of both an Ag-Pd-Cu-Au alloy and the component metals, under the condition that the specimens were bonded with a TBB-initiated acrylic resin.

Materials and methods

Materials

A silver-palladium-copper-gold alloy (Ag-Pd-Cu-Au alloy, Castwell M.C.12; GC, Tokyo, Japan) designed for cast restorations and denture frameworks was used as the adherend material. In addition, high-purity silver (Ag), copper (Cu), palladium (Pd) (The Nilaco, Tokyo, Japan) and gold (Au) (Kojundo Chemical Laboratory, Saitama, Japan) metals were employed as controls (Table I). Seven metal priming agents, including Alloy Primer, Estenia Opaque Primer (Kuraray Medical, Tokyo, Japan), All Bond II Primer B (Bisco, Schaumburg, IL), M.L. Primer (Shofu, Kyoto, Japan), Metaltite (Tokuyama Dental, Tokyo, Japan), Super-Bond Liquid and V-Primer (Sun Medical, Moriyama, Japan) were assessed as the bonding promoter. Figure 1 shows the structural formulae of four adhesive functional monomers. All primers were single-liquid and contained at least one functional monomer (Table I, Figure 1). A self-polymerizing acrylic resin initiated with partially oxidized tri-*n*-butylborane (TBB) was selected as the luting material. The TBB initiator and the powder component of this material were identical to Super-Bond C&B resin (Sun Medical). A commercially available methyl methacrylate (MMA; Tokyo Kasei, Tokyo, Japan), which did not contain any functional monomers, was selected as the monomer liquid of the MMA-TBB resin used in the study because our purpose was to evaluate the functional monomers in the priming agents. Information regarding the materials is summarized in Table I.

Specimen preparation and shear bond strength

A total of 176 disk specimens (10 mm in diameter and 3 mm thick) were prepared for the Ag-Pd-Cu-Au alloy, Ag and Cu and a total of 110 disk specimens were prepared for Pd and Au. The Ag-Pd-Cu-Au ingot was cast with a cristobalite investment material and a high-frequency induction heating machine (Argoncaster-AE; Shofu), whereas the pure metals cut from rods were supplied by the manufacturers. All disks were wet-ground with a series of silicon-carbide abrasive paper (#800, #1000 and #1500; Wet or Dry Tri-M-ite; 3M, St. Paul, MN).

The 176 disk specimens were divided into eight sets (seven primers and an unprimed control). The Au and Pd disk specimens were divided into five sets (four primers and unprimed control). A piece of double-sided tape with a circular hole 5 mm in diameter was placed on the disk surface to define the bonding area. The disk specimens, excluding the 22 control specimens, were primed with one of the priming agents and air-dried. A stainless steel ring (SUS303) 2 mm high with 6 mm inner diameter and a 1-mm-thick wall was positioned surrounding the 5-mm-diameter circular hole. The steel ring was filled with the MMA-TBB resin using a brush-dip technique.

After 30 min of bonding, the prepared specimens were immersed in 37°C distilled water for 24 h. This state was considered to be 0 thermocycles and one-half of the specimens were tested at this stage. The remaining half of the specimens were subsequently thermocycled in water between 5–55°C for 20,000 cycles with a 60 s dwell time per bath (Thermal shock tester TTS-1 LM; Thomas Kagaku, Tokyo, Japan). The specimens were then set in a steel mold and seated in a bond test jig. The shear bond strengths were determined with a mechanical testing device (Type 5567; Instron, Canton, MA) at a crosshead speed of 0.5 mm/min.

Statistical analysis

The shear bond strength and standard deviation of 11 replications were calculated for each group. The results were primarily analyzed by the Kolmogorov-Smirnov normal distribution test (IBM SPSS Statistics ver. 19; IBM, Somers, NY). When the results of the Kolmogorov-Smirnov test did not show a normal distribution in at least one category, the results were analyzed with the non-parametric Kruskal-Wallis test (IBM SPSS Statistics). Based on the Kruskal-Wallis test, Steel-Dwass multiple comparisons (Kyplot 5.0; KyensLab, Tokyo, Japan) were also performed to compare the priming groups for each of the pre- and post-thermocycling conditions. The differences between the pre- and post-thermocycling bond strength within an identical primer-metal combination were analyzed with the Mann-Whitney *U*-test (IBM SPSS Statistics). *p*-values less than 0.05 were considered to be statistically significant.

Table I. Materials assessed.

Material	Abbr.	Manufacturer	Lot number	Composition
Alloy				
Ag-Pd-Cu-Au casting alloy		GC Corp., Tokyo, Japan	812161	Ag 46, Pd 20, Cu 20, Au 12, mass%
Pure metal				
High-purity sliver	Ag	The Nilaco Corp., Tokyo, Japan.	44326511	Ag 99.9, mass%
High-purity copper	Cu	The Nilaco Corp.	44225602	Cu 99.9, mass%
High-purity palladium	Pd	The Nilaco Corp.	44151201	Pd 99.9, mass%
High-purity gold	Au	Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan	282443	Au 99.9, mass%
Primer				
Alloy Primer	AP	Kuraray Medical Inc., Tokyo, Japan	00337A	MDP, VTD, Acetone
All Bond II Primer B	BP	Bisco Inc., Schaumburg, IL, USA	0900000247	BPDM
Estenia Opaque Primer	EP	Kuraray Medical Inc.	00161A	MDP, Solvent
M.L. Primer	ML	Shofu Inc., Kyoto, Japan	030937	10-MDDT, 6-MHPA, Acetone
Metaltite	MT	Tokuyama Dental Corp., Tokyo, Japan	027	MTU-6, Ethanol
Super-Bond Liquid	SB	Sun Medical Co., Ltd., Moriyama, Japan	SV3	4-META, MMA
V-Primer	VP	Sun Medical Co., Ltd.	SX1	VTD, acetone
Luting material				
Super-Bond C&B Catalyst		Sun Medical Co., Ltd.	TV41	Tri-*n*-butylborane (TBB)
Super-Bond C&B Opaque Ivory Powder		Sun Medical Co., Ltd.	SR2	PMMA, TiO_2
Methyl methacrylate	MMA	Tokyo Kasei Co., Ltd., Tokyo, Japan	KWP4267	MMA 99.8%

MDP, 10-methacryloyloxydecyl dihydrogen phosphate; VTD, 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione, -dithiol tautomer; BPDM, Adduct of 2-HEMA and 3,4,4',5'-biphenyl tetracarboxylic anhydride; 10-MDDT, 10-methacryloyloxydecyl 6,8-dithiooctanoate; 6-MHPA, 6-methacryloyloxyhexyl phosphonoacetate; MTU-6, 6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate; 4-META, 4-methacryloyloxyethyl trimellitate anhydride; MMA, methyl methacrylate; PMMA, poly(methyl methacrylate).

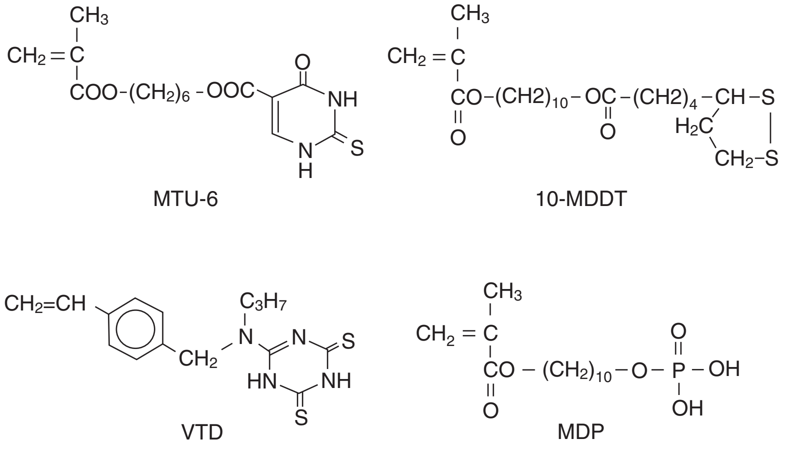
MTU-6
10-MDDT
VTD
MDP

Figure 1. Structural formulae of three sulfur-based monomers and a phosphate monomer.

Failure mode analysis

After shear bond testing, the debonded surfaces were observed through an optical microscope at 8× magnification (SZX9; Olympus, Tokyo, Japan). Failure modes were classified into one of the following three categories: A—adhesive failure at the luting material-alloy interface, C—cohesive failure within the luting material, and CA—a combination of adhesive and cohesive failures.

X-ray diffraction analysis

The crystalline phases in the ground copper surface and in the debonded surface of the thermocycled copper primed with the Estenia Opaque Primer were analyzed using an X-ray diffractometer (XRD, Miniflex II; Rigaku, Tokyo, Japan) operated at 15 mA and 30 kV. The XRD analysis was conducted using Ni-filtered Cu Kα radiation. The scan rate was 2.0°/min and the range of 2θ was between 20–80°. Peak analysis was performed using computer software (PDXL ver. 1.0.7.1; Rigaku) and the index of the International Centre for Diffraction Data (ICDD; Newton Square, PA).

Results

The Kolmogorov-Smirnov test of the bond strength results did not demonstrate a normal distribution for several of the groups. The Kruskal-Wallis test revealed significant differences in bond strengths for both the pre- and post-thermocycling stages of five of the metal groups ($p < 0.05$). Therefore, both the pre- and post-thermocycled groups were analyzed independently with the Steel-Dwass non-parametric multiple comparison method. In addition, the differences between the pre- and post-thermocycling bond strengths for each of the primers were analyzed with the Mann-Whitney *U*-test.

The results of the shear bond strength tests and the statistical analyses are summarized in Table II. The 24-h median bond strengths without thermocycling ranged from 2.1–28.0 MPa for the Ag-Pd-Cu-Au alloy, 2.7–29.5 MPa for Ag, 2.3–30.1 for Cu, 3.2–26.1 MPa for Pd and 2.8–26.5 MPa for Au. The pre-thermocycling bond strengths were categorized into five groups for the Ag-Pd-Cu-Au alloy (B-a to B-e), five groups for Ag (B-f to B-j), six groups for Cu (B-k to B-p), three groups for Pd (B-q to B-s) and four groups for Au (B-t to B-w). The unprimed control specimens showed the lowest bond strengths of all of the metals. The median bond strengths after 20,000 thermocycles ranged from 0.1–22.8 MPa for the Ag-Pd-Cu-Au alloy, 0.1–21.9 MPa for Ag, 0.5–19.2 for Cu, 0.1–12.8 MPa for Pd and 0.1–22.8 MPa for Au. The post-thermocycling bond strengths were categorized into three groups for the Ag-Pd-Cu-Au alloy (A-a to A-c), three groups for Ag (A-d to A-f), three groups for Cu (A-g to A-i), three groups for Pd (A-j to A-l) and four groups for Au (A-m to A-p). The Mann-Whitney U-test revealed that the bond strengths in 33 of the groups were reduced by the application of 20,000 thermocycles, whereas the bond strengths in the M.L. Primer-Au group were not significantly reduced ($p = 0.324 > 0.05$). The post-/pre-thermocycling bond strength ratios varied from 0.6–80.5% for the Ag-Pd-Cu-Au alloy, from 0.3–85.3% for Ag, from 1.9–61.9% for Cu, from 2.9–63.2% for Pd and from 3.7–97.4% for Au.

The results of the failure mode analysis are summarized in Table III. Optical microscope observations of the debonded specimen surfaces revealed that a reduction in cohesive failure and an increase in adhesive failures were observed for the majority of the groups after thermocycling.

Figure 2A shows a typical ground copper surface; this surface shows overall coppertone. Figure 2B shows a debonded copper surface that was primed with the Estenia Opaque Primer and then thermocycled; this surface shows adhesive failure at the resin/copper interface. It is notable that corrosion of the copper occurred along the margin of the adhesive. Corroded copper was also attached to the debonded resin surface (Figure 2C).

Figure 3 shows the XRD patterns of the ground copper and debonded copper surfaces. The principal specific peaks for the ground copper are at 43.1°, 50.3° and 74.1° (Figure 3A, Table IV). Copper peaks are evident. Figure 3B shows the XRD pattern of the debonded copper surface. The specific peaks for the debonded copper surface are at 29.3°, 36.3°, 43.2°, 50.3°, 61.4° and 74.0°. Both copper and copper (I) oxide were detected from the specimen which was primed with the Estenia Opaque Primer and thermocycled (Table IV).

Discussion

In this study, the adhesive characteristics of single-liquid priming agents in bonding to a Ag-Pd-Cu-Au alloy were evaluated. The groups that were primed with the four priming agents (Table II, categories A-a and A-b) showed higher post-thermocycling bond strengths than the other groups. As shown in Table I, the four priming agents contain thiones (MTU-6, Metaltite, VTD, Alloy Primer and V-Primer) or a sulfide (10-MDDT, M.L. Primer). MTU-6, VTD and 10-MDDT contain one or two sulfur atoms in the monomer structure (Figure 1). It is speculated that either bonding or adsorption of the sulfur atom occurred at the alloy surface after application of the priming agents. Using the surface-enhanced Raman scattering technique, Suzuki et al. [25] suggested that structural changes involving the $C = S$ bonds occurred in VTD upon adsorption onto Au and that the molecule

Table II. Shear bond strength mean, standard deviation and median in MPa.

		0 thermocycle				20,000 thermocycles				Post-/Pre-bs
Metal	Primer	Mean (SD)	Median	IQR	Category B*	Mean (SD)	Median	IQR	Category A*	Ratio (%)
Ag-Pd-Cu-Au	MT	27.7 (1.4)	28.0	1.9	B-a	22.3 (1.8)	22.8	3.3	A-a	80.5
	AP	27.1 (1.3)	27.7	2.4	B-a	20.6 (1.7)	20.8	2.0	A-a, A-b	76.0
	ML	27.0 (1.1)	27.2	1.4	B-a	17.8 (2.2)	17.8	3.7	A-b	66.0
	VP	23.2 (2.6)	22.5	4.8	B-b	18.4 (0.9)	18.4	1.8	A-b	79.3
	EP	18.1 (3.3)	18.6	4.7	B-c	0.1 (0.1)	0.1	0.2	A-c	0.6
	BP	15.8 (1.3)	16.4	2.2	B-c	0.1 (0.1)	0.1	0.1	A-c	0.6
	SB	12.3 (3.1)	12.5	2.9	B-d	0.1 (0.1)	0.1	0.2	A-c	1.0
	UP	1.7 (0.9)	2.1	1.6	B-e	0.1 (0.1)	0.1	0.1	A-c	5.9
Ag	MT	27.9 (2.3)	28.2	4.0	B-f, B-g	21.9 (1.6)	21.9	2.5	A-d	78.5
	VP	23.1 (3.0)	22.1	4.5	B-h, B-i	19.7 (2.5)	20.1	4.7	A-d	85.3
	AP	27.5 (2.1)	27.0	3.7	B-f, B-h	19.3 (1.9)	19.6	2.2	A-d	70.2
	ML	26.7 (2.5)	25.9	3.9	B-f, B-i	14.5 (1.0)	14.4	1.8	A-e	54.3
	SB	23.3 (2.8)	23.7	3.3	B-i	0.3 (0.2)	0.3	0.4	A-f	1.3
	BP	25.1 (1.9)	25.3	3.6	B-g, B-h, B-i	0.1 (0.1)	0.1	0.2	A-f	0.4
	EP	29.4 (2.0)	29.5	3.6	B-f	0.1 (0.1)	0.1	0.1	A-f	0.3
	UP	2.3 (0.9)	2.7	1.5	B-j	0.1 (0.2)	0.1	0.3	A-f	4.3
Cu	MT	30.6 (1.9)	30.1	3.1	B-k	18.6 (2.8)	19.2	4.5	A-g	60.8
	AP	26.5 (1.4)	26.4	2.5	B-l, B-o	16.4 (2.3)	17.1	5.0	A-g	61.9
	VP	25.9 (1.4)	26.4	2.5	B-n, B-o	6.1 (1.7)	6.6	3.0	A-h	23.6
	EP	28.7 (1.1)	28.8	1.5	B-k, B-m	1.3 (1.2)	0.7	1.0	A-i	4.5
	ML	28.9 (1.8)	29.5	3.2	B-k, B-l	1.0 (0.8)	0.7	2.1	A-i	3.5
	SB	26.5 (1.7)	26.4	2.9	B-l, B-m, B-n	0.5 (0.2)	0.6	0.2	A-i	1.9
	BP	26.2 (2.0)	25.9	2.2	B-l, B-m, B-o	0.5 (0.2)	0.5	0.4	A-i	1.9
	UP	2.3 (0.4)	2.3	0.7	B-p	0.5 (0.3)	0.6	0.5	A-i	21.7
Pd	ML	18.2 (2.1)	18.6	2.5	B-r	11.5 (2.7)	12.8	4.3	A-j	63.2
	AP	17.5 (1.9)	17.0	3.5	B-r	6.3 (3.2)	5.4	3.5	A-k	36.0
	VP	16.2 (2.1)	16.1	2.6	B-r	5.1 (1.2)	5.3	1.8	A-k	31.5
	MT	25.5 (3.0)	26.1	4.6	B-q	4.8 (2.1)	4.5	3.4	A-k	18.8
	UP	3.5 (1.3)	3.2	2.0	B-s	0.1 (0.1)	0.1	0.1	A-l	2.9
Au	ML	22.8 (1.9)	23.0	2.8	B-u, B-v	22.2 (2.1)	22.8	2.5	A-m	97.4 NS
	AP	23.6 (2.5)	23.3	4.7	B-t, B-u	18.7 (2.0)	18.5	3.3	A-n	79.2
	MT	25.7 (3.0)	26.5	5.4	B-t	17.2 (2.9)	17.7	4.2	A-n, A-o	66.9
	VP	20.1 (2.3)	20.5	4.1	B-v	15.3 (2.7)	15.4	5.4	A-o	76.1
	UP	2.7 (0.9)	2.8	0.5	B-w	0.1 (0.1)	0.1	0.1	A-p	3.7

$n = 11$; UP, Unprimed control; SD, Standard deviation; Post-/Pre-bs ratio, Post-/Pre-thermocycling bond strength ratio (%); IQR, interquartile range; Statistic categories B (Pre-thermocycling bond strength) and A (Post-thermocycling bond strength). * Identical capital-lower case letters for each of five metals indicated that the values are not significantly different ($p < 0.05$). NS, Difference between pre- and post-thermocycling bond strengths was not significant (Mann-Whitney U-test; $p > 0.05$).

underwent thione-thiol-type tautomerization during the adsorption process. They also suggested that specific interactions existed between the sulfur atoms of VTD and the Au surface that led to the formation of interfaces that were similar to chemical bonds. Suzuki et al. [26] thereafter reported that the Raman and infrared reflection absorption spectroscopic evaluations indicated that the VTD in the primer is primarily chemisorbed onto the Au, Ag and Cu surfaces. The results of Suzuki et al. [25,26] support our speculation that either bonding or adsorption of the sulfur atoms occurred at the alloy surface after application of the Alloy Primer or V-Primer that contain VTD. In contrast, Silikas et al. [27] reported that the chemical bonding of the Alloy Primer (VTD) with the noble alloys under the environmental conditions is difficult.

Table III. Failure modes after shear bond testing.

Metal	Primer	0 thermocycle			20,000 thermocycles		
	Mode	A	CA	C	A	CA	C
Ag-Pd-Cu-Au	MT	0	3	8	0	9	2
	AP	0	9	2	0	11	0
	ML	0	6	5	0	11	0
	VP	0	7	4	0	11	0
	EP	0	11	0	11	0	0
	BP	0	11	0	11	0	0
	SB	1	10	0	11	0	0
	UP	11	0	0	11	0	0
Ag	MT	0	1	10	0	0	11
	VP	0	2	9	0	4	7
	AP	0	9	2	0	9	2
	ML	0	7	4	2	8	1
	SB	0	7	4	11	0	0
	BP	0	9	2	11	0	0
	EP	0	9	2	11	0	0
	UP	11	0	0	11	0	0
Cu	MT	0	9	2	0	11	0
	AP	0	10	1	0	11	0
	VP	0	10	1	7	4	0
	EP	0	11	0	11	0	0
	ML	0	11	0	8	3	0
	SB	0	11	0	11	0	0
	BP	0	10	1	11	0	0
	UP	11	0	0	11	0	0
Pd	ML	0	4	7	0	11	0
	AP	0	10	1	0	11	0
	VP	0	10	1	4	7	0
	MT	0	1	10	5	6	0
	UP	11	0	0	11	0	0
Au	ML	0	3	8	0	2	9
	AP	0	7	4	3	6	2
	MT	0	1	10	0	0	11
	VP	0	3	8	4	2	5
	UP	11	0	0	11	0	0

A, Adhesive failure at the resin-metal interface; C, Cohesive failure within the resin material; CA, Combination of adhesive and cohesive failures. Optical microscope: 8× magnification.

Considering the previous bond strength test results [7,11,15] and spectroscopic evaluation concerning the VTD-TBB bonding system and noble metal alloys [25,26], the current study focused on bonding between sulfur-based functional monomers and noble metal elements. The bonding characteristics of the Ag-Pd-Cu-Au alloy (categories A-a, A-b and A-c) and silver (A-d, A-e and A-f) using the seven priming agents and the TBB resin were similar. This result probably derives from the fact that silver is the main component (46%) of the Ag-Pd-Cu-Au alloy. It is also possible that the compatibility of a functional monomer and an alloy depends upon the structure of the functional group in the monomer and the main component of the alloy.

Palladium exhibited somewhat lower post-thermocycling bond strength than the other metals (categories A-j, A-k and A-l). This result agreed in

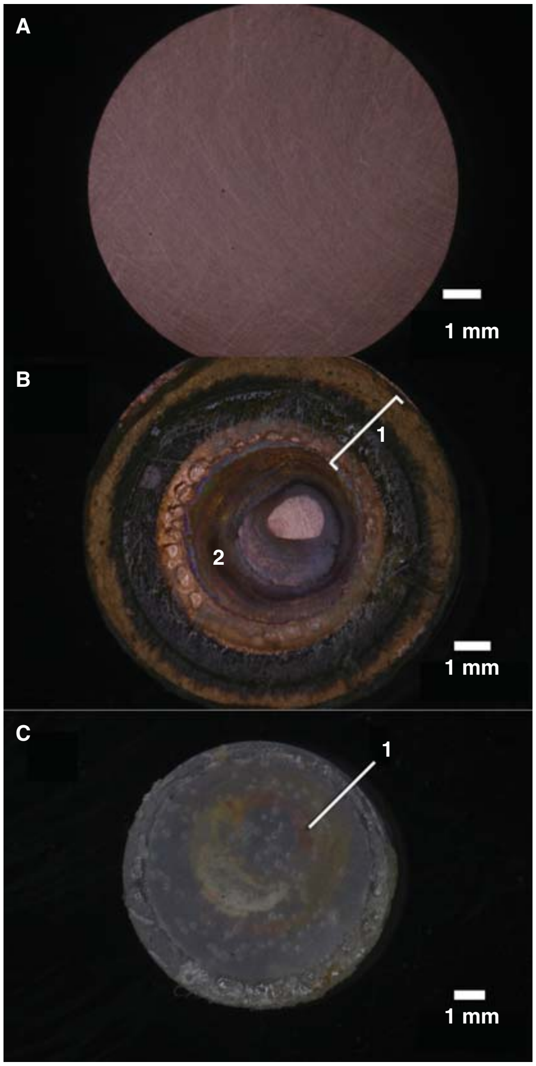

Figure 2. Copper specimens and debonded resin, (A) Ground with #1500 SiC paper. (B) Debonded surface of the copper specimen. This specimen was primed with the Estenia Opaque Primer material, bonded with the TBB resin and thermocycled. The surface shows: (1) double-sided tape and (2) the copper surface. (C) Debonded luting material. The surface shows: (1) predominant adhesive failure and corroded copper. Digital photographic system: 8× magnification.

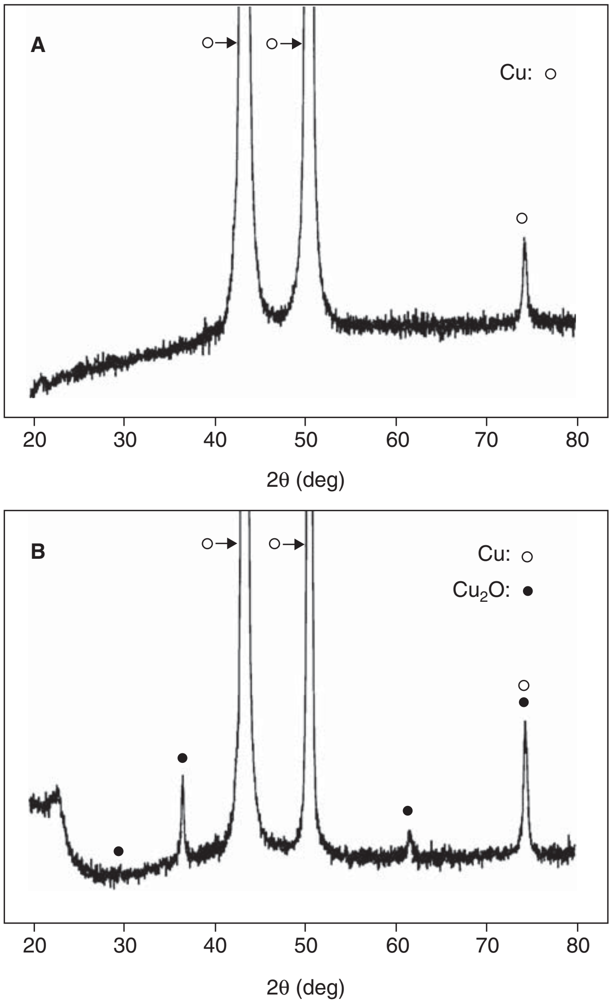

Figure 3. X-ray diffraction patterns of the copper specimens: (A) ground copper surface and (B) debonded surface of the copper. The debonded specimen was primed with the Estenia Opaque Primer and thermocycled.

part with the results of Okuya et al. [16], in which they employed three priming agents and a carboxylic TBB resin (Super-Bond C&B). Palladium stores or occludes hydrogen [28], which is a phenomenon whereby a considerable amount of hydrogen is occluded in elemental palladium. If hydrogen were released from the palladium metal surface under specific conditions, such as thermocycling, storage in water or electrochemical treatment, the transfer of hydrogen would negatively affect bonding between the resin materials and the alloys.

Although copper showed high bond strength before the application of thermocycling (categories B-k, B-l, B-m, B-n and B-o), the reduction in bond strength after thermocycling was remarkable (categories A-g, A-h and A-i). As revealed by photographs and the XRD analysis of the debonded specimens, corrosion was detected for the unalloyed copper. The authors believe that the reduction in the bond strength of the primed copper after application of thermocycling is a

Table IV. X-ray diffraction analysis, 2θ, cps and crystal phase.

Specimen	2θ (°)	Intensity (cps)	Crystal phase
Ground copper	43.1	90,508	Copper (1, 1, 1)
	50.3	2,044	Copper (2, 0, 0)
	74.1	194	Copper (2, 2, 0)
Debonded copper	29.3	13	Copper(I) oxide (1, 1, 0)
	36.3	235	Copper(I) oxide (1, 1, 1)
	43.2	53,899	Copper (1, 1, 1)
	50.3	10,715	Copper (2, 0, 0)
	61.4	72	Copper(I) oxide (2, 2, 0)
	74.0	403	Copper(I) oxide (3, 1, 1); copper (2, 2, 0)

result of the penetration of water into the adhesive interface associated with the corrosion of copper metal. It is also believed that a strong bond is achieved between the sulfur compound and copper when the corrosion of copper is suppressed by alloying the component metals.

The four priming agents effectively bonded high-purity gold using the TBB resin (categories A-m, A-n and A-o). The results can be explained in part by the report of Suzuki et al. [25]. Specifically, the post-thermocycling bond strengths associated with the Alloy Primer (18.5 MPa) and the V-Primer (15.4 MPa) VTD are a result of the adsorption interaction between the sulfur atoms of VTD and the surface of the gold, which leads to the formation of an interface that is similar to a chemical bond.

As shown in Table II, the three acidic priming agents (BPDM, All Bond II Primer (BP); MDP, Estenia Opaque Primer (EP); and 4-META, Super-Bond Liquid (SB)) showed lower post-thermocycling bond strengths than the other groups (Table II, categories A-c, A-f and A-i). It is speculated that the acidic monomers were not effective for bonding noble metals (Ag-Pd-Cu-Au alloy and silver). The ineffectiveness of a MDP monomer for bonding noble metals (gold and silver) has been proposed by Suzuki et al. [26] and the bond strength results of the silver in this study support their finding. The current study therefore omitted evaluation of the bond to palladium and gold of three carboxylic agents (BP, EP and SB).

Conclusions

Within the limitations of the current experimental conditions, the following conclusions can be drawn.

(1) Four priming agents containing organic sulfur compounds enhanced the bonding durability of the tri-*n*-butylborane-initiated resin joined to either the Ag-Pd-Cu-Au casting alloy or to high-purity gold.
(2) Silver exhibited bonding behavior that was similar to the Ag-Pd-Cu-Au alloy.
(3) The durability of the bond to unalloyed copper was not high, which was probably a result of the corrosion of the metal.
(4) For the bonding systems used in this study, the pre- and post-thermocycling bond strengths with palladium were not particularly good.

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