

Comparative Evaluation of Thione and Phosphate Monomers on Bonding Gold Alloy and Ti-6Al-7Nb Alloy with Tri-*n*-butylborane initiated Resin

Takaya ISHII¹, Hiroyasu KOIZUMI^{2,3}, Takayuki YONEYAMA⁴, Naomi TANOUE⁵, Yumi ISHIKAWA² and Hideo MATSUMURA^{2,3}

¹Nihon University Graduate School of Dentistry, 1-8-13, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8310, Japan

²Department of Fixed Prosthodontics, Nihon University School of Dentistry, 1-8-13, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8310, Japan

³Division of Advanced Dental Treatment, Dental Research Center, Nihon University School of Dentistry, 1-8-13, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8310, Japan

⁴Department of Metallurgy, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan

⁵Department of Specialized Dentistry, Nagasaki University Hospital of Medicine and Dentistry, 1-7-1, Sakamoto, Nagasaki 852-8501, Japan

Corresponding author, Hiroyasu KOIZUMI; E-mail: koizumi@dent.nihon-u.ac.jp

Received March 2, 2007/Accepted August 6, 2007

This study aimed to evaluate the bonding behaviors of a gold alloy and a titanium-aluminum-niobium (Ti-6Al-7Nb) alloy after priming with three metal conditioners. Cast alloy disks were ground and divided into the following four conditions: (1) unprimed control *versus* priming with (2) Alloy Primer, (3) Estenia Opaque Primer, or (4) V-Primer. The disks were bonded with tri-*n*-butylborane (TBB) initiated methacrylic resin, and shear bond strengths were determined both before and after 20,000 times of thermocycling. Alloy Primer and V-Primer — which contained a vinyl-thione monomer — were effective for bonding the Au-Pt-Pd alloy. As for the hydrophobic phosphate monomer contained in Alloy Primer and Estenia Opaque Primer, it was effective for bonding the Ti-6Al-7Nb alloy. Further, when specimens were primed with Alloy Primer that contained both functional monomers, bond strength to Ti-6Al-7Nb alloy was greater than that to Au-Pt-Pd alloy.

Keywords: Phosphate, Thione, Ti-6Al-7Nb alloy

INTRODUCTION

The use of adhesive luting systems for bonding dental casting alloys has increased substantially. This trend is attributed to the development of a wide range of functional monomers. A representative carboxylic monomer effectively bonded nickel-chromium alloy, cobalt-chromium alloy, and titanium¹⁻³. Bond strength to base metal alloys has improved thereafter with the use of a hydrophobic phosphate monomer⁴⁻⁹. In addition, bonding to titanium-aluminum-niobium (Ti-6Al-7Nb) alloy has been widely evaluated as this alloy is applicable to both fixed and removable dentures¹⁰⁻¹⁶. A thiol monomer was originally developed for coating copper¹⁷, but its bonding to dental noble metal alloys has also been evaluated¹⁸⁻²¹.

With regard to the currently available single-liquid metal priming agents, they can be categorized into three types: (1) for base metal alloys; (2) for noble metal alloys; and (3) for both base and noble metal alloys. Although quite a number of single-liquid metal priming agents are available, only limited information is available about the relation between combined use of functional monomers and resultant bond strength to noble and base metal alloys. Therefore, this study aimed to evaluate the bonding characteristics of three metal priming agents when used to bond a gold alloy or Ti-6Al-7Nb alloy using a tri-*n*-butylborane derivative (TBB) initiated

resin luting agent.

MATERIALS AND METHODS

Materials used

Two casting alloys — a gold alloy designed for porcelain-fused-to-metal (PFM) procedure (Au-Pt-Pd; DeguDent Universal, Degussa AG, Hanau, Germany) and a titanium alloy consisting of titanium, niobium, and aluminum (Ti-6Al-7Nb; T-Alloy Tough, GC Corp., Tokyo, Japan) — were selected as adherend materials.

As for the metal priming agents selected for evaluation in this study, they were namely Alloy Primer (Kuraray Medical Inc., Tokyo, Japan), Estenia Opaque Primer (Kuraray Medical Inc.), and V-Primer (Sun Medical Co. Ltd., Moriyama, Japan). These three agents were of the single-liquid type and which contained at least one functional monomer in the solvent. Alloy Primer consisted of acetone solvent with a small amount of 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithione (VTD), whereas Estenia Opaque Primer consisted of the MDP monomer and monomer solvent. As for V-Primer, it consisted of acetone solvent with VTD.

A self-polymerizing resin — based on methyl methacrylate (MMA), pigmented PMMA, and TBB initiator — was used as the luting agent. Unlike

Table 1 Materials assessed

Material / Trade name	Abbreviation	Manufacturer	Lot number	Composition (mass %)
Gold alloy				
Degudent Universal	Au-Pt-Pd	Degussa AG, Hanau, Germany	B013339	77.3 Au, 9.8 Pt, 8.9 Pd, 1.2 Ag, 0.1 Ir
Titanium alloy				
T-Alloy Tough	Ti-6Al-7Nb	GC Corp., Tokyo, Japan	408041	86.5 Ti, 7 Nb, 6 Al
Primer				
Alloy Primer		Kuraray Medical Inc., Tokyo, Japan	00232A	MDP, VTD, Acetone
Estenia Opaque Primer		Kuraray Medical Inc.	00145A	MDP, Monomer solvent
V-Primer		Sun Medical Co. Ltd., MoriYama, Japan	ML1	VTD, Acetone
Luting Agent				
Super-Bond Catalyst		Sun Medical Co. Ltd.	MG120	Tri- <i>n</i> -butylborane (TBB)
Super-Bond Opaque powder		Sun Medical Co. Ltd	MK2	PolyMMA (PMMA), TiO ₂
Methyl methacrylate	MMA	Wako Pure Chemical Ind. Ltd., Osaka, Japan	DPJ7276	99.8 MMA

MDP: 10-methacryloyloxydecyl dihydrogen phosphate; VTD: 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione

the commercially available SuperBond resin (Sun Medical Co. Ltd.), this luting agent did not contain any functional monomer. This was because the purpose of this study was to evaluate the functional monomers in the priming agents. Table 1 summarizes the information of the materials used in this study.

Specimen preparation

A total of 64 pairs of disk specimens, 10 mm and 8 mm in diameter by 2.5 mm in thickness, were cast from Ti-6Al-7Nb alloy using a magnesia-based investment material (Selevest CB, Selec, Osaka, Japan) and a centrifugal casting apparatus (Ticast Super R, Selec). In addition, a total of 64 pairs of disk specimens, also 10 mm and 8 mm in diameter by 2.5 mm in thickness, were cast from Au-Pt-Pd alloy using a phosphate-bonded investment material (Univest Silky, Shofu Inc., Kyoto, Japan) and a centrifugal casting apparatus (Argoncaster-C, Shofu Inc.). All disks were sanded with a series of silicon-carbide abrasive papers and finished with 800-grit paper.

The 64 disks of each alloy were divided into eight sets of eight specimens according to the combination of four priming conditions (three primers and unprimed control) and two thermocycling conditions. The four priming conditions were: (1) unprimed control; (2) priming with Alloy Primer; (3) priming with Estenia Opaque Primer; and (4) priming with V-Primer. For the three primed groups, the three priming agents were separately applied to the ground metal surfaces with a sponge pellet and then air-dried. After surface preparation, a piece of tape with a circular hole of 5 mm diameter was positioned on each 10-mm-diameter alloy specimen to define the bonding area. The paired disks with identical alloy composition (10- and 8-mm-diameter) were then bonded together with the MMA-TBB resin using brush-dip technique.

Shear bond strength test

After 30 minutes, the bonded specimens were

immersed in water at 37°C for 24 hours. This state was defined as 0 thermocycles, and half of the specimens (four sets of eight pairs for two alloys) were subjected to shear bond testing at this stage. The remaining half of the specimens (four sets of eight pairs for two alloys) were subsequently thermocycled in water between 5°C and 55°C for 20,000 cycles with a 60-second dwell time per bath (Thermal Shock Tester TTS-1 LM, Thomas Kagaku Co. Ltd., Tokyo, Japan).

Each specimen was positioned in a steel mold and seated in a bond testing jig (ISO TR 11405)²²⁾. Shear bond strength was determined using a mechanical testing device (Type 5567, Instron Corp., Canton, MA, USA) at a crosshead speed of 0.5 mm/minute. Average shear bond strength and standard deviation (SD) of eight replications were calculated for each group. Bond strength of the specimens that showed pre-testing failure (PTF) was defined as 0 MPa, and the results were included in the statistical analysis. The results were primarily analyzed by Kruskal–Wallis test, followed by Steel–Dwass test with the value of statistical significance set at 0.05. Difference between pre- and post-thermocycling bond strengths within an identical primer-alloy combination was analyzed using Mann–Whitney U test with the value of statistical significance also set at 0.05.

Failure mode analysis

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

RESULTS

Shear bond strength

Shear bond strength results are summarized in

Table 2 Shear bond strength results in MPa with statistical categories

Alloy	Primer	0 thermocycles			Category*	20,000 thermocycles				Reduction from 0 to 20,000**	
		Median	Mean	SD		Median	Mean	SD	PTF		
Au-Pt-Pd	None	7.7	7.0	2.3	a	0.1	0.2	0.2	3	h	Significant
	V-Primer	31.6	31.2	4.2	c	16.3	16.9	4.8		i	Significant
	Estenia	13.7	13.8	2.1	b	0.1	0.1	0.1	2	h	Significant
	Alloy Primer	37.1	36.2	2.2	d	11.5	12.3	4.2		i	Significant
Ti-6Al-7Nb	None	9.1	8.7	1.8	e	0.0	0.1	0.1	5	j	Significant
	V-Primer	12.7	12.8	1.9	f	0.0	0.1	0.1	5	j	Significant
	Estenia	43.0	42.2	4.2	g	30.6	30.1	1.6		k	Significant
	Alloy Primer	46.5	47.3	4.2	g	28.8	29.0	3.0		k	Significant

SD: Standard deviation; PTF: Number of pre-testing failures (PTF). *Category: Identical letters indicate that the values are not significantly different (Steel–Dwass test; $p>0.05$). **Reduction from 0 to 20,000: Significant difference between pre- and post-thermocycling bond strengths was found for all groups (Mann–Whitney U test; $p<0.001$).

Table 3 Failure modes after shear bond testing

Alloy	Primer	0 thermocycles			20,000 thermocycles		
		A	AC	C	A	AC	C
Au-Pt-Pd	None	8	0	0	8	0	0
Au-Pt-Pd	V-Primer	7	1	0	8	0	0
Au-Pt-Pd	Estenia	8	0	0	8	0	0
Au-Pt-Pd	Alloy Primer	6	2	0	8	0	0
Ti-6Al-7Nb	None	8	0	0	8	0	0
Ti-6Al-7Nb	V-Primer	8	0	0	8	0	0
Ti-6Al-7Nb	Estenia	4	4	0	6	2	0
Ti-6Al-7Nb	Alloy Primer	5	1	2	6	2	0

A: Adhesive failure at the alloy-luting agent interface;
C: Cohesive failure within the luting agent;
AC: Combination of adhesive and cohesive failures.

Table 2. For Au-Pt-Pd alloy, 24-hour bond strengths without thermocycling ranged from 7.0 to 36.2 MPa — and they were statistically different from each other (categories a–d). For Ti-6Al-7Nb alloy, 24-hour bond strengths ranged from 8.7 to 47.3 MPa. Two groups (category g) showed the highest bond strength, followed by the other two groups (categories e and f).

Post-thermocycling bond strength varied from only 0.1 MPa to 16.9 MPa for Au-Pt-Pd alloy, and 0.1 MPa to 30.1 MPa for Ti-6Al-7Nb alloy. For Au-Pt-Pd alloy, two groups treated with the VTD thione-based primers (category i) showed greater bond strengths than the other two groups (category h). For Ti-6Al-7Nb alloy, two groups treated with the MDP phosphate-based primers (category k) showed greater bond strengths than the other two groups (category j). Thus, it was clearly shown that thermocycling significantly reduced the bond strength of all the

eight groups ($p<0.001$). In addition, post-thermocycling bond strength to Ti-6Al-7Nb alloy was greater than that to Au-Pt-Pd alloy when the alloys were primed with the VTD- and MDP-based Alloy Primer ($p<0.001$).

Failure mode

Failure mode analysis results are summarized in Table 3. Cohesive failure reduced substantially following the application of thermal stress. After the aging process, adhesive-cohesive failure was detected only in two groups of Ti-6Al-7Nb alloy, whereby the specimens were treated with MDP-based primers.

DISCUSSION

This study evaluated the differences in bonding characteristics between a gold alloy and a Ti-6Al-7Nb alloy using three priming agents and a TBB-initiated resin. As shown in Table 2, application of thermal stress revealed the bonding characteristics of the two alloys. Alloy Primer and V-Primer effectively bonded the Au-Pt-Pd alloy. It is noteworthy that both primers contained the VTD thione monomer. These results agreed with previous investigations which found VTD monomer to be effective for bonding noble metal alloys¹⁸⁻²¹. As for the bonding mechanism between the Alloy Primer or V-Primer and noble metals, it is considered to be chemical interaction between sulfur and noble metal elements^{23,24}.

In addition, the current study clearly revealed that MDP monomer was ineffective for bonding gold alloy. Post-thermocycling bond strength yielded with Estenia Opaque Primer (with MDP alone) was only 0.1 MPa for the gold alloy. In contrast, bond strength yielded with Alloy Primer (with MDP and VTD) was 12.3 MPa. In a study by Suzuki *et al.*²⁴, the reason for ineffectiveness of MDP monomer for bonding noble metals has been proposed — although

titanium alloy was not included in their assessment. The bond strength results of the present study thus supported their finding.

The Alloy Primer and Estenia Opaque Primer effectively bonded the Ti-6Al-7Nb alloy. Both primers contained the hydrophobic phosphate monomer, MDP. These results agreed with previous investigations which found MDP monomer to be effective for bonding Ti-6Al-7Nb alloy^{10,12-16}. As for the bonding mechanism between the Alloy Primer or Estenia Opaque Primer and base metal alloys, it is considered to be chemical interaction between MDP phosphate monomer and chromium²⁴.

It should be highlighted that in this study, the Ti-6Al-7Nb alloy did not contain chromium although high bond strength results were yielded with MDP-containing primers. Separately, in a recent study by Tsuchimoto *et al.*²⁵, it was reported that strong bond to titanium could be achieved when the luting agent contained MDP monomer and when MDP adsorption occurred on the titanium surface. In view of these results and findings, the authors speculated that a corrosion-resistant passive film was present on base metal alloys, which then promoted effective bonding between MDP monomer and titanium alloy.

In addition, the current study revealed that VTD monomer was ineffective for bonding Ti-6Al-7Nb alloy. Post-thermocycling bond strength yielded with V-Primer (with VTD alone) was only 0.1 MPa for the Ti-6Al-7Nb alloy. In contrast, bond strength yield with Alloy Primer (with MDP and VTD) was 29.0 MPa. In a study by Suzuki *et al.*²⁴, the reason for ineffectiveness of VTD monomer for bonding chromium has been reported. The bond strength results of the present study supported in part their finding, with the understanding that VTD thione monomer was ineffective for bonding corrosion-resistant base metal alloys.

Failure mode analysis (Table 3) showed that majority of the specimens resulted in adhesive failure after thermocycling. Moreover, the number of specimens that showed combined adhesive and cohesive (AC) failures was smaller for the post-thermocycling state than for the pre-thermocycling state. Indeed, the reduction in bond strength coupled with an increase in adhesive failure suggested that the bonding interface was negatively affected by thermocycling. Therefore, it was clear that thermocycling was an effective means to evaluate adhesive durability of resin-to-metal bonded specimens for a limited testing period.

With due consideration to the clinical longevity of restorations and fixed partial dentures, it is beneficial for clinicians to select the best combination of casting alloy and adhesive system. Within the limitations of the current experimental settings, it might be concluded that the combination of an MDP-

containing priming agent with Ti-6Al-7Nb alloy was an optimum bonding system. Further investigation, however, is required using other types of priming agents, luting agents, and casting alloys, since reduction after thermocycling is remarkable for all combinations.

ACKNOWLEDGEMENTS

This work was supported in part by a Grant-in-aid for Young Scientists (B) (18791454) from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT-Japan), and by Special Research Grants for the Development of Distinctive Education from the Promotion and Mutual Aid Corporation for Private Schools of Japan. This project was also supported in part by Sato Fund and Grant from the Dental Research Center, Nihon University School of Dentistry.

REFERENCES

- 1) Tanaka T, Nagata K, Takeyama M, Atsuta M, Nakabayashi N, Masuhara E. 4-META opaque resin --a new resin strongly adhesive to nickel-chromium alloy. *J Dent Res* 1981; 60: 1697-1706.
- 2) Tanaka T, Fujiyama E, Shimizu H, Takaki A, Atsuta M. Surface treatment of nonprecious alloys for adhesion-fixed partial dentures. *J Prosthet Dent* 1986; 55: 456-462.
- 3) Matsumura H, Yoshida K, Tanaka T, Atsuta M. Adhesive bonding of titanium with a titanate coupler and 4-META/MMA-TBB opaque resin. *J Dent Res* 1990; 69: 1614-1616.
- 4) Hansson O, Moberg LE. Evaluation of three silicoating methods for resin-bonded prostheses. *Scand J Dent Res* 1993; 101: 243-251.
- 5) Taira Y, Matsumura H, Yoshida K, Tanaka T, Atsuta M. Adhesive bonding of titanium with a methacrylate-phosphate primer and self-curing adhesive resins. *J Oral Rehabil* 1995; 22: 409-412.
- 6) Matsumura H, Tanaka T, Taira Y, Atsuta M. Bonding of a cobalt-chromium alloy with acidic primers and tri-*n*-butylborane-initiated luting agents. *J Prosthet Dent* 1996; 76: 194-199.
- 7) Matsumura H, Tanaka T, Atsuta M. Effect of acidic primers on bonding between stainless steel and auto-polymerizing methacrylic resins. *J Dent* 1997; 25: 285-290.
- 8) Tsuchimoto Y, Yoshida Y, Mine A, Nakamura M, Nishiyama N, Van Meerbeek B, Suzuki K, Kuboki T. Effect of 4-MET- and 10-MDP-based primers on resin bonding to titanium. *Dent Mater J* 2006; 25: 120-124.
- 9) Ban S, Taniki T, Sato H, Kono H, Iwaya Y, Miyamoto M. Acid etching of titanium for bonding with veneering composite resins. *Dent Mater J* 2006; 25: 382-390.
- 10) Yanagida H, Matsumura H, Atsuta M. Bonding of prosthetic composite material to Ti-6Al-7Nb alloy with eight metal conditioners and a surface modifi-

- cation technique. *Am J Dent* 2001; 14: 291-294.
- 11) Matsumura H, Yoneyama T, Shimoe S. Veneering technique for a Ti-6Al-7Nb framework used in a resin-bonded fixed partial denture with a highly filled indirect composite. *J Prosthet Dent* 2002; 88: 636-639.
 - 12) Yanagida H, Taira Y, Shimoe S, Atsuta M, Yoneyama T, Matsumura H. Adhesive bonding of titanium-aluminum-niobium alloy with nine surface preparations and three self-curing resins. *Eur J Oral Sci* 2003; 111: 170-174.
 - 13) Sugawara H, Yanagida H, Tanoue N, Koishi Y, Nagano K, Atsuta M, Matsumura H. Effect of alumina abrasion for bonding between Ti-6Al-7Nb alloy and an indirect composite. *Int Chin J Dent* 2004; 4: 8-14.
 - 14) Suzuki T, Takahashi H, Arksornnukit M, Oda N, Hirano S. Bonding properties of heat-polymerized denture base resin to Ti-6Al-7Nb alloy. *Dent Mater J* 2005; 24: 530-535.
 - 15) Shimizu H, Kurtz KS, Tachii Y, Takahashi Y. Use of metal conditioners to improve bond strengths of autopolymerizing denture base resin to cast Ti-6Al-7Nb and Co-Cr. *J Dent* 2006; 34: 117-122.
 - 16) Koizumi H, Furuchi M, Tanoue N, Yanagida H, Yoneyama T, Matsumura H. Bond strength to primed Ti-6Al-7Nb alloy of two acrylic resin adhesives. *Dent Mater J* 2006; 25: 286-290.
 - 17) Mori K, Nakamura Y. Study on triazine thiols. V. Polymerization of 6-(4-vinylbenzyl propyl) amino-1,3,5-triazine-2,4-dithiol on copper plates and their corrosion resistance. *J Polym Sci Polym Lett Ed* 1983; 21: 889-895.
 - 18) Atsuta M, Matsumura H, Tanaka T. Bonding fixed prosthodontic composite resin and precious metal alloys with the use of a vinyl-thiol primer and an adhesive opaque resin. *J Prosthet Dent* 1992; 67: 296-300.
 - 19) Matsumura H, Leinfelder KF. Effect of an adhesive primer on the integrity of occlusal veneer-metal interface and wear of composite resin veneered restorations. *J Prosthet Dent* 1993; 70: 296-299.
 - 20) Matsumura H, Taira Y, Atsuta M. Adhesive bonding of noble metal alloys with a triazine dithiol derivative primer and an adhesive resin. *J Oral Rehabil* 1999; 26: 877-882.
 - 21) Matsumura H, Kamada K, Tanoue N, Atsuta M. Effect of thione primers on bonding of noble metal alloys with an adhesive resin. *J Dent* 2000; 28: 287-293.
 - 22) International Organization for Standardization. ISO TR 11405, Dental materials — Guidance on testing of adhesion to tooth structure, 1994.
 - 23) Suzuki M, Fujishima A, Miyazaki T, Hisamitsu H, Kojima K, Kadoma Y. A study on the adsorption structure of an adhesive monomer for precious metals by surface-enhanced Raman scattering spectroscopy. *Biomaterials* 1999; 20: 839-845.
 - 24) Suzuki M, Yamamoto M, Fujishima A, Miyazaki T, Hisamitsu H, Kojima K, Kadoma Y. Raman and IR studies on adsorption behavior of adhesive monomers in a metal primer for Au, Ag, Cu, and Cr surfaces. *J Biomed Mater Res* 2002; 62: 37-45.
 - 25) Tsuchimoto Y, Yoshida Y, Takeuchi M, Mine A, Yatani H, Tagawa Y, Van Meerbeek B, Suzuki K, Kuboki T. Effect of surface pre-treatment on durability of resin-based cements bonded to titanium. *Dent Mater* 2006; 22: 545-552.