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Microtensile bond strength of resin-based composites to Ti–6Al–4V

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ABSTRACT

Objective. The purpose of this study was to determine the microtensile bond strength of various resin composite/adhesive systems to alumina particle abraded Ti–6Al–4V substrate after aging for 24 h, 10 days, and 30 days in distilled water at 37 °C.

Methods. Four laboratory resin composite veneering systems (Gradia, GR; Solidex, SOL; Cera-mage, CER; and Sinfony, SF) were bonded to 25 mm diameter machined disks of Ti–6Al–4V with their respective adhesive and methodology, according to the manufacturer's instructions. Microtensile bars of approximate dimensions 1 mm × 1 mm × 6 mm were prepared for each resin composite/adhesive system. After cutting, groups (n = 12) from each adhesive system were separated and either stored in water at 37 °C for 24 h (baseline) or aged for 10 or 30 days prior to loading to failure under tension at a cross head speed of 1.0 mm/min. Failure modes were determined by means of scanning electron microscopy (SEM). Statistical analysis was performed through one-way ANOVA and Tukey's test at 95% level of significance.

Results. Significant variation in microtensile bond strength was observed for the different systems and aging times. SOL and GR showed the highest mean bond strength values followed by SF and CER at baseline. Aging specimens in water had an adverse effect on bond strength for SOL and CER but not for the SF and GR groups.

Significance. *In vitro* bond strength of laboratory resin composites to Ti–6Al–4V suggests that strong bonds can be achieved and are stable for certain systems, making them useful as an alternative for esthetic fixed prosthetic restorations.

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1. Introduction

The use of titanium and its alloys for cast restorations and fixed partial denture frameworks has increased substantially over the last years. This trend can be mainly attributed to the development of casting technology for titanium alloys,

such as new casting machines and investment materials and the extensively reported advantages of titanium over other base metal alloys [1–3]. Also, excellent biocompatibility, high strength to weight ratio, low density, high corrosion resistance and low cost compared to noble metals are attractive properties which have favored the application of titanium alloys in

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Table 1 – Materials utilized in this study.

Material	Description	Manufacturer	Mode of application
Ceramage™	Light curing composite system with UDMA matrix and zirconium silicate micro ceramic filling.	Shofu Dental Corp., San Marcos, CA, USA.	Apply two thin coats of ML metal primer and allow to air dry for 10 s between layers; apply a thin coat of pre-opaque and light cure for 3 min with GC Labolight LV-III; apply two layers of opaque and light cure for 3 min each; apply cervical, body and incisal and light cure each layer for 2 min.
Gradia™	Light curing composite system with bis-(methacryloyloxy)-propoxy-carbonylamino-hexane-triazine-trione, aluminoborosilicate and silica filling.	GC America Inc., Alsip, IL, USA.	Apply two thin coatings of Metal Primer II and allow them to dry for 30 s; apply three layers of opaque and light cure it for 1 min each with GC Labolight LV-III; apply opaque dentin, dentin and enamel layers and light cure each layer for 3 min.
Synfony™	Light curing composite resin with aliphatic and cycloaliphatic monomers, strontium aluminium borosilicate glass and pyrogenic silica fillers.	Pentron Laboratory Technologies, Wallingford, CT, USA.	Microblast metal surface with Rocatec Pre and silicoat it with Rocatec Plus; apply ESPE Sil and allow it to air dry for 5 min; mix opaque liquid and powder and apply a thin light curing it for two cycles of 5 s with Visio Alpha Unit; apply opaque dentin, dentin, transparent opal and enamel layers, light-curing each layer for four to six cycles of 5 s; cure with vacuum in 3M ESPE Beta Vario unit for 15 min.
Solidex™	Light-curing indirect ceramic polymeric composite system.	Shofu Dental Corp., San Marcos, CA, USA.	Microblast and silicoat metal surface with Rocatec system; apply Solidbond and allow it to dry; apply opaque liquid and light cure it in DentaColor XS for 1 min; apply two layers of flow opaque and light cure each layer for 3 min with GC Labolight LV-III; apply cervical, body and incisal layers of composite and light cure each layer for 3 min.

prosthetic restorations [4–12]. However, problems with porcelain bonding have been reported when titanium is used in metal–ceramic restorations as thick and non-adherent layers of titanium oxide are formed at the high temperatures used for porcelain fused to metal (PFM) technique [13–15]. For this reason, special low fusing porcelains have been developed [12,13,15,16]. Resin composite veneering on titanium castings has been considered as an alternative for esthetic anterior restorations [1].

Metal–composite restorations have long been used as an alternative to PFM restorations [17–19]. Indirect light-cured composite resins have been extensively used in tooth restoration because they can provide acceptable aesthetics, wear resistance similar to tooth structure, and are easy to manipulate in the laboratory and to repair [20–23]. However, durable bonding between composite resins and metal frameworks has been a challenge. Years ago, macro- or micro-mechanical retention on the metal substructures such as beads, loops and pits, or sandblasting and etching, were the only mechanisms for bonding composite materials to metallic substrates. However, recent developments resulting in chemical bonding have been achieved [20,21,24,25], including silicoating systems and functional monomers systems [2,20,23,24]. The former covers the metal surface with a thin layer of silica and is followed by a bi-functional silane-coupling agent which bonds the silanol-groups of the silica layer with monomers of the composite

[24,26–28]. The latter utilizes organic sulphur and phosphoric acids (thiophosphate derivatives) that bond to the oxides of the metal surface. These monomer acids are dissolved in solvents or in methacrylate-based liquids to bond to the composites [6,19,23,29,30].

Several studies have shown that silicoating and functional monomer systems improve the composite-to-metal bond strength with noble and non-noble dental alloys [17–20,23,26,28,30] and with titanium and its alloys [1–3,28,31–33]. However, the stability of composite–titanium bond is still questionable. While studies have shown that shear bond strength results were considerably affected by thermal cycling or long-term water storage [2,6,24,34–41], other studies have demonstrated that a number of the composite/adhesive systems evaluated under various metal surface conditioning methods exhibited considerably high and durable bond strength values after thermocycling [20,23,25,30].

Such controversial and limited results concerning adhesive performance between indirect composite and titanium alloys has led to the lack of an informed design rationale for bonding composite materials to titanium alloys [1,2,35]. The current study evaluated the bond strength of four commercially available indirect composite/adhesive systems to a titanium alloy (Ti–6Al–4V) subjected to different times of water storage. The bond strength was determined by microtensile testing and

failure mode analysis was performed by SEM to investigate potential weak links in the resin composite–titanium interface/interphase.

2. Materials and methods

Specific information concerning the materials used for this study is presented in Table 1. For the present study, 25 mm diameter and 3 mm thick disks ($n = 12$, 3 for each material) of ASTM Grade V Ti–6Al–4V alloy (as-machined) were immersed in ethanol for 1 min in an ultrasonic cleaner (Accusonic, Patterson, Saint Paul, MN, USA), dried in air stream and sandblasted on the upper side with 50 μm grain-sized alumina using a grit-blaster (Pony Sandblaster, Buffalo Dental, Syosset, NY, USA) for 30 s at a distance of 1.5 cm from each disk surface. Following sandblasting, the samples were again immersed in ethanol for 1 min in an ultrasonic cleaner and dried in air stream before receiving one of the following procedures prior to resin composite build-up:

- Ceramage™ (CER) (Shofu Dental Corp., San Marcos, CA, USA): ultrasonic bath with ethyl alcohol (5 min); application of two layers of proprietary ML Metal Primer (allowed to dry for 10 s between layers); application of a thin layer of Ceramage Pre-Opaque adhesive and light cured for 3 min with GC Labolight LV III (GC America Inc., Alsip, IL, USA).
- Gradia™ (GR) (GC America Inc., Alsip, IL, USA): air cleaning of disk surface; application of two layers of GC Metal Primer II (allowed to dry for 30 s between layers).
- Sinfony™ (SF) (Pentron Laboratory Technologies, Wallingford, CT, USA): ultrasonic bath with ethyl alcohol (5 min); tribochemical silica coating with Rocatec™ system (RocactorDelta, 3M Espe, Seefeld, Germany); application of EspeSil™ (3M Espe, Seefeld, Germany) silane coupling agent and allow to dry for 5 min; metal coupler application (air dried).
- Solidex™ (SOL) (Shofu Dental Corp., San Marcos, CA, USA): ultrasonic bath with ethyl alcohol (5 min); tribochemical silica coating with Rocatec™ system; application of proprietary Solidbond silane coupling agent (allowed to air dry); application of a thin coat of Solidex Opaquer liquid adhesive and light cure for 1 min with Dentacolor XS (Heraeus-Kulzer GmbH, Wehrheim, Germany).



Fig. 1 – Four different composite systems were directly bonded to Ti–6Al–4V according to the manufacturer’s guidelines.

Subsequently, resin composite build-up was completed by applying small increments, including the opaque, body, and incisal material for each system according to the manufacturer’s recommendation (Table 1). Customized circular molds (25 mm in diameter and 6 mm height) were used for inserting the composite on titanium disks and placement of the specimens in its respective curing unit. The final disk-shaped specimens of approximately 9 mm height (3 mm of titanium and 6 mm of composite) (Fig. 1) were polished with 300-grit SiC paper to achieve uniform thickness throughout the specimens and then stored in distilled water at 37 °C.

The specimens were then cross-sectioned perpendicular to the composite–titanium interface with a diamond wafering blade (Buehler series 20HC N° 11-4215) mounted on an IsoMet® low speed diamond saw (Buehler, Lake Bluff, IL, USA) under copious water, to produce a series of rectangular beams with mean cross-sectional area of $\sim 0.85 \text{ mm}^2$, according to the “non-trimming” technique for microtensile bond strength testing [36] (Fig. 2). After exclusion of the beams from the peripheral areas of the disks, 36 bars were randomly selected from each group of 3 disks and then divided into three subgroups for each material ($n = 12$). Subgroup 1 was tested for microtensile bond strength (μTBS) at baseline (24 h). Subgroup 2 was aged in distilled water at 37 °C for 10 days and subgroup 3 was aged for 30 days before bond strength testing.

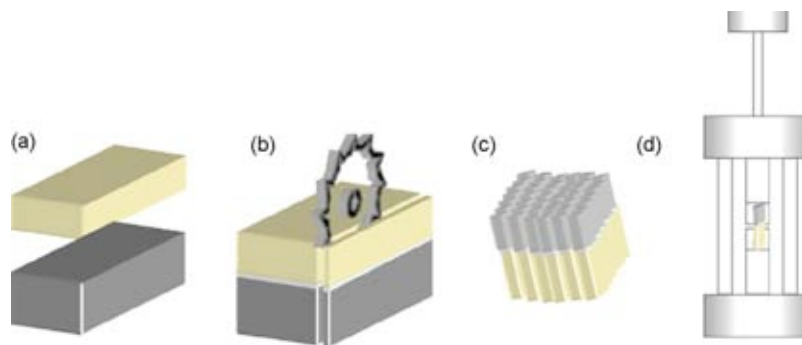


Fig. 2 – Microtensile specimen preparation. (a) Composite system bonded to Ti–6Al–4V, (b and c) the composite-metallic substrate were reduced by means of a diamond saw under irrigation, and (d) the microtensile bars were mounted and tested in a universal testing machine.

Table 2 – Microtensile bond strength testing results.

Group	Mean μ TBS (\pm 95% confidence interval) (MPa) (three disk specimens per group)		
	Subgroup 1 (baseline)	Subgroup 2 (10 days water aging)	Subgroup 3 (30 days water aging)
CER	19.18 (3.85) ^b	6.10 (1.63) ^d	4.80 (1.49) ^d
GR	29.96 (5.74) ^{a,b}	21.52 (3.53) ^b	23.18 (2.72) ^b
SF	20.90 (3.46) ^b	23.27 (3.40) ^b	25.90 (2.42) ^b
SOL	38.32 (3.65) ^a	20.10 (2.91) ^b	15.30 (3.58) ^c

Letters indicate statistical significance. Groups with the same letter denote no significant difference ($p > 0.05$).

Each specimen had the cross-sectional area measured with a digital caliper (Mitutoyo, Tokyo, Japan). Beams were individually attached to the flat grips of a Bencor Multi-T testing device (Danville Engineering, San Ramon, CA, USA) using cyanoacrylate adhesive (Krazy Glue Gel, Advanced Formula-Elmer's Products, Inc., USA) (Fig. 2). The bars were loaded to failure under tension at a crosshead speed of 1.0 mm/min using a tensile testing machine (TSD 500, Chatillon-Ametek, Agawam, MA, USA). The bond strength data were converted to MPa and analyzed by one-way ANOVA ($n = 3$). Multiple comparisons between groups were evaluated by Tukey test at a 95% level of significance.

The mode of failure of each specimen was determined using a Stereomicroscope (Olympus SZX – ILLB100 – Olympus Optical Co. Ltd., Tokyo, Japan). The fracture modes were classified according to the following categories: (1) adhesive at opaque–metal interface; (2) adhesive at opaque–composite interface; (3) cohesive in composite; (4) cohesive in metal; (5) mixed fractures. SEM analysis was performed in selected samples for higher magnification verification of failure modes and

evaluation of fractured surfaces. After sputter-coating with gold (Emitech K650, Emitech Products Inc., Houston, TX, USA), the specimens were observed under SEM (Hitachi S-3500N, Hitachi Science Systems Ltd., Japan).

3. Results

The results summary for the μ TBS of the different composites under the various storage conditions are presented in Table 2.

One-way ANOVA showed significant differences among the μ TBS values for the various composite systems and storage conditions. When comparing all composite systems at baseline (subgroup 1), SOL group showed the highest mean μ TBS values compared to all other groups ($p \leq 0.05$) but not significantly different from the GR group ($p > 0.05$). The latter presented higher bond strength than CER and SF groups, but the difference did not reach statistical significance ($p > 0.05$).

Regarding the influence of storage condition, the composite systems were affected differently. After 10 days of water

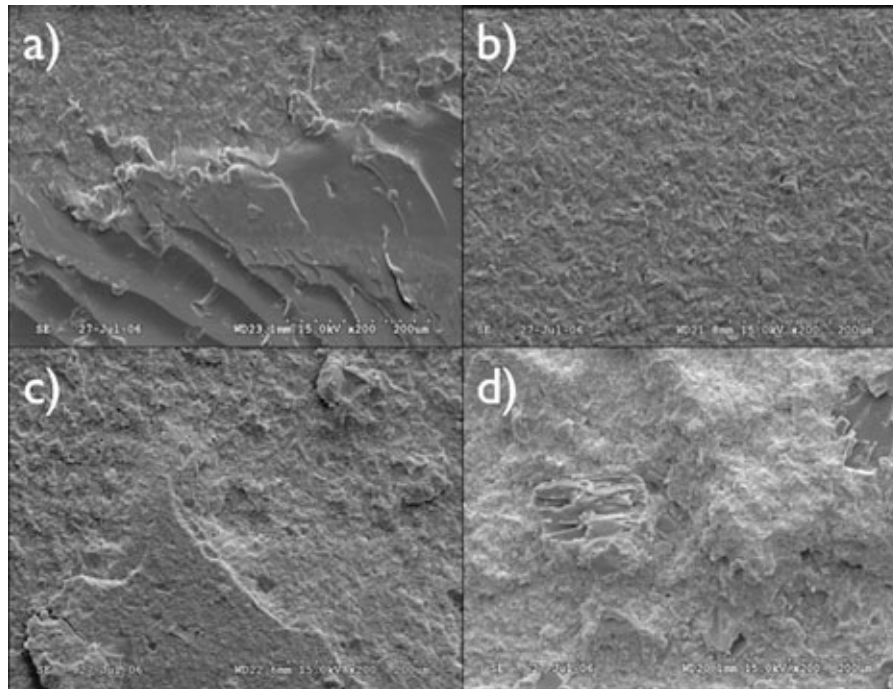


Fig. 3 – Representative scanning electron micrographs of the metal side of fractured specimens. (a) SOL specimen presenting a mixed fracture mode; (b) Ceramage specimens presented adhesive fracture mode for all subgroups; (c) Gradia sample fractured between the opaque layer and composite; and (d) Sinfony samples presented fractures between the opaque layer and composite for all subgroups investigated.

storage (subgroup 2), μ TBS values of SOL and CER groups were significantly reduced ($p \leq 0.05$) compared to their bond strength at baseline. Bond strength mean values of GR and SF groups were not affected by aging. In subgroup 2, SOL, GR, and SF showed significantly higher μ TBS values than CER ($p \leq 0.05$), but not significantly different from each other ($p > 0.05$).

When the specimens were stored in distilled water for 30 days (subgroup 3), only SOL and CER groups exhibited lower μ TBS values than their respective subgroups 1 and 2. GR and SF groups were not affected by aging time and showed significantly higher bond strength values than SOL and CER groups. GR and SF did not have significantly different mean bond strength from each other within subgroup 3 ($p > 0.05$).

The scanning electron micrographs of the metal side of the fractured specimens showed that SOL groups had 50% of fractures between the opaque layer and metal (type 1), 20% of cohesive fractures in composite (type 3), 20% of mixed fractures (Fig. 3a) and 10% of adhesive fractures between opaque layer and composite (type 2). CER groups exhibited type 1 fractures in all specimens observed (Fig. 3b). GR groups presented type 2 fractures (Fig. 3c). SF groups presented cohesive failures of type 3 for all subgroups (Fig. 3d).

4. Discussion

Metal–composite restorations have not been well accepted generally due to what has been perceived as an insufficient ability to bond resin to metal castings [1]. However, several systems have been developed over the last two decades in order to improve the bond strength of composites to metals, including titanium. These systems involve treatment of titanium surface to render it more reactive to bonding agents either by coating the metal surface with silicate (enabling bonding through a silane coupling agent) or by conditioning the metal surface with organic acids in solvents or embedded in methacrylate-based liquids that bond to the titanium oxides and to the resin composites [2,23,25].

The current study evaluated four indirect composite and adhesive systems employing different methods of metal treatment to enhance bonding to Ti–6Al–4V alloy. The μ TBS tests showed that at baseline all of the composite systems exhibited bond strength values to Ti–6Al–4V that exceeded the 15–20 MPa level (Table 2). These range of values have been suggested by *in vitro* studies as adequate for resisting masticatory forces [1,2,24,42,43]. However it is desirable that this level should be maintained or preferably surpassed after water storage since these systems will be subjected to the oral environment during function. Such results were only achieved with GR and SF groups, which were not affected by water aging.

The μ TBS results suggest that bond strength between GR and SF to titanium alloy was effective and resistant to hydrolysis after 30 days of water storage. These two systems employ different methods for the treatment of titanium. GR system employs a methacrylate thiophosphoric acid (GC Metal Primer II™) for metal surface treatment. This dual functional primer has shown to be effective for bonding composites to titanium alloys in several studies [2,3,6,19,24,25,30,31,44], which are in agreement with the present work. The SF system utilizes tribochemical silica coating and a silane coupling agent (Rocatec™

and EspeSil™) to create a bond between the monomers of the composite and the silica layer on the titanium surface. Previous studies have reported that silicoating promotes a high and durable bond between titanium and composites [2,24,32,33]. The results of the present study are in partial agreement with these findings, since SOL decreased bond strength after aging.

The CER and SOL groups exhibited bond strength results that were significantly affected by water aging. CER system showed a reduction of ~75% in bond strength after 30 days of water storage, while SOL system presented ~60% of reduction with the same aging time. Although the GR and SF systems employ different treatment methods (Table 1) for metal surface preparation, their bond strength were not significantly different within experimental subgroups.

In the CER system, a proprietary metal primer (ML Primer) is employed for titanium surface conditioning. The specific composition of this primer is not described by the manufacturer and refers to a phosphonate monomer and a thioacetic acid. These constituents may be substantially different from Metal Primer II™ used in GR system [2,3,30]. Thus, differences in chemical composition and perhaps concentration may account for the different bond strength between the two systems to titanium since this bond is based on the interaction of the organic acid with the oxides of the titanium surface [24,25].

The titanium surface in SOL groups was treated in the same way as for SF groups, with silica coating (Rocatec™) and silane coupling agent. However, instead of EspeSil™ used in SF, the silane agent used for SOL system was Solidbond, a proprietary silane provided in the Solidex kit. The composition of this silane agent is not described by the manufacturer, while EspeSil™ is a 10% solution of 3-methacryloyloxypropyltrimethoxy-silane in ethanol [45]. Matinlinna et al. [45–47] have demonstrated that commercial dental silanes show differences in chemical composition, pH, solvent system and silane concentration that can provide different bond strengths to titanium surfaces. This may explain why μ TBS values of SOL groups were substantially different from the SF groups, being more prominently affected by water aging.

Fractographic analysis of GR and SF specimens revealed that none of the fractures occurred at the interface between opaque layer and titanium, which suggests that the bond strength between these two substrates was high enough to resist the tensile stress applied in μ TBS test. This interface is considered the critical link in metal–composite bonding since it joins two essentially dissimilar materials together; an inorganic metallic substrate and an organic polymeric substrate [28,33,46,48]. Thus, the absence of fractures at this interface suggests an effectiveness of bonding between these substrates and is coherent with the bond strength results of GR and SF groups, which exhibited the highest μ TBS mean values after 30 days of water aging. On the other hand, the fracture modes of CER and SOL, in all subgroups, were predominantly adhesive at the interface between opaque layer and titanium, indicating that interaction between these substrates seems to be the weak point with these systems. This is also in agreement with the bond strength results since CER and SOL were the systems with the highest reduction in μ TBS mean values after water storage. Alternatively, condensation of the silane on the sur-

face may have resulted in a thick layer that is susceptible to hydrolysis [10].

Although shear testing is the most commonly used method to assess metal–composite bond strength, several studies suggest it can produce misleading results from high stress concentration within the substrates, leading to a high incidence of cohesive failures [36,42,49,50]. Tensile strength tests and in particular the microtensile testing method, has been considered to be more appropriate for bond strength evaluation since it allows a more uniform distribution of the stress, a reduction of the incidence of premature cohesive failures, and consequently a more realistic measurement of bond strength of the adhesive interface [25,36,51–53]. The use of microtensile testing in this study resulted in low occurrence of cohesive failures.

The present *in vitro* work suggest that the composite systems Gradia™ and Sinfony™ would be acceptable for achieving clinically high and stable bond strength to titanium alloy, surpassing the minimum level of 20 MPa for resisting masticatory forces [36]. These two systems were not significantly affected by water aging and may represent a viable alternative for metal–ceramic restorations on titanium with regard to adhesion. However, it should be noted that a minimum bond strength level for clinical long-term bond stability of composites to titanium has not yet been determined and further clinical research should be undertaken to investigate these materials.

5. Conclusions

Within the limitations of this experiment, the following conclusions could be made:

1. The resin composite adhesive systems exhibited significantly different bond strengths to titanium. All the systems showed high initial bond strength and water aging had an adverse effect on bond strength of CER and SOL, but did not affect GR and SF systems.
2. CER and SOL exhibited failures at the opaque–titanium interface, which is the weak-link of metal–composite bonding. For GR and SF systems, this interface resisted the tensile load and was not affected by water storage.

REFERENCES

- [1] Fujishima A, Fujishima Y, Ferracane JL. Shear bond strength of four commercial bonding systems to cp Ti. *Dent Mater* 1995;11(2):82–6.
- [2] Yanagida H, Matsumura H, Taira Y, Atsuta M, Shimoe S. Adhesive bonding of composite material to cast titanium with varying surface preparations. *J Oral Rehabil* 2002;29(2):121–6.
- [3] Yanagida H, Taira Y, Shimoe S, Atsuta M, Yoneyama T, Matsumura H. Adhesive bonding of titanium–aluminium–niobium alloy with nine surface preparations and three self-curing resins. *Eur J Oral Sci* 2003;111(2):170–4.
- [4] Adell R, Lekholm U, Rockler B, Branemark PI. A 15-year study of osseointegrated implants in the treatment of the edentulous jaw. *Int J Oral Surg* 1981;10(6):387–416.
- [5] Taira Y, Matsumura H, Yoshida K, Tanaka T, Atsuta M. Influence of surface oxidation of titanium on adhesion. *J Dent* 1998;26(1):69–73.
- [6] Taira Y, Yanagida H, Matsumura H, Yoshida K, Atsuta M, Suzuki S. Adhesive bonding of titanium with a thione-phosphate dual functional primer and self-curing luting agents. *Eur J Oral Sci* 2000;108(5):456–60.
- [7] Zavanelli RA, Pessanha Henriques GE, Ferreira I, De Almeida Rollo JM. Corrosion-fatigue life of commercially pure titanium and Ti–6Al–4V alloys in different storage environments. *J Prosthet Dent* 2000;84(3):274–9.
- [8] Atsu S, Berksun S. Bond strength of three porcelains to two forms of titanium using two firing atmospheres. *J Prosthet Dent* 2000;84(5):567–74.
- [9] Da Silva L, Martinez A, Rilo B, Santana U. Titanium for removable denture bases. *J Oral Rehabil* 2000;27(2):131–5.
- [10] 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(6):636–9.
- [11] Troia Jr MG, Henriques GE, Nobilo MA, Mesquita MF. The effect of thermal cycling on the bond strength of low-fusing porcelain to commercially pure titanium and titanium–aluminium–vanadium alloy. *Dent Mater* 2003;19(8):790–6.
- [12] Troia Jr MG, Henriques GE, Mesquita MF, Frago WS. The effect of surface modifications on titanium to enable titanium–porcelain bonding. *Dent Mater* 2008;24(1):28–33.
- [13] Adachi M, Mackert Jr JR, Parry EE, Fairhurst CW. Oxide adherence and porcelain bonding to titanium and Ti–6Al–4V alloy. *J Dent Res* 1990;69(6):1230–5.
- [14] Pang IC, Gilbert JL, Chai J, Lautenschlager EP. Bonding characteristics of low-fusing porcelain bonded to pure titanium and palladium–copper alloy. *J Prosthet Dent* 1995;73(1):17–25.
- [15] Kononen M, Kivilahti J. Fusing of dental ceramics to titanium. *J Dent Res* 2001;80(3):848–54.
- [16] Al Hussaini I, Al Wazzan KA. Effect of surface treatment on bond strength of low-fusing porcelain to commercially pure titanium. *J Prosthet Dent* 2005;94(4):350–6.
- [17] 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(9):1697–706.
- [18] Tanaka T, Hirano M, Kawahara M, Matsumura H, Atsuta M. A new ion-coating surface treatment of alloys for dental adhesive resins. *J Dent Res* 1988;67(11):1376–80.
- [19] Matsumura H, Nakabayashi N. Adhesive 4-META/MMA-TBB opaque resin with poly(methyl methacrylate)-coated titanium dioxide. *J Dent Res* 1988;67(1):29–32.
- [20] Yoshida K, Taira Y, Matsumura H, Atsuta M. Effect of adhesive metal primers on bonding a prosthetic composite resin to metals. *J Prosthet Dent* 1993;69(4):357–62.
- [21] Touati B, Aidan N. Second generation laboratory composite resins for indirect restorations. *J Esthet Dent* 1997;9(3):108–18.
- [22] Suzuki S, Nagai E, Taira Y, Minesaki Y. *In vitro* wear of indirect composite restoratives. *J Prosthet Dent* 2002;88(4):431–6.
- [23] Shimoe S, Tanoue N, Yanagida H, Atsuta M, Koizumi H, Matsumura H. Comparative strength of metal–ceramic and metal–composite bonds after extended thermocycling. *J Oral Rehabil* 2004;31(7):689–94.
- [24] Behr M, Rosentritt M, Groger G, Handel G. Adhesive bond of veneering composites on various metal surfaces using silicoating, titanium-coating or functional monomers. *J Dent* 2003;31(1):33–42.

- [25] Behr M, Rosentritt M, Bettermann K, Handel G. Influence of electron beam irradiation on the alloy-to-resin bond strength. *Eur J Oral Sci* 2005;113(5):429–35.
- [26] Moulin P, Degrange M, Picard B. Influence of surface treatment on adherence energy of alloys used in bonded prosthetics. *J Oral Rehabil* 1999;26(5):413–21.
- [27] Robin C, Scherrer SS, Wiskott HW, de Rijk WG, Belser UC. Weibull parameters of composite resin bond strengths to porcelain and noble alloy using the Rocatec system. *Dent Mater* 2002;18(5):389–95.
- [28] Matinlinna JP, Lassila LV, Kangasniemi I, Yli-Urpo A, Vallittu PK. Shear bond strength of Bis-GMA resin and methacrylated dendrimer resins on silanized titanium substrate. *Dent Mater* 2005;21(3):287–96.
- [29] 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(9):1614–6.
- [30] Ohkubo C, Watanabe I, Hosoi T, Okabe T. Shear bond strengths of polymethyl methacrylate to cast titanium and cobalt–chromium frameworks using five metal primers. *J Prosthet Dent* 2000;83(1):50–7.
- [31] Taira Y, Yanagida H, Matsumura H, Atsuta M. Effects of a metal etchant and two primers on resin bonding durability to titanium. *Eur J Oral Sci* 2004;112(1):95–100.
- [32] Matinlinna JP, Ozcan M, Lassila LV, Vallittu PK. The effect of a 3-methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane blend and tris(3-trimethoxysilylpropyl)isocyanurate on the shear bond strength of composite resin to titanium metal. *Dent Mater* 2004;20(9):804–13.
- [33] Matinlinna JP, Lassila LV, Vallittu PK. The effect of three silane coupling agents and their blends with a cross-linker silane on bonding a bis-GMA resin to silicized titanium (a novel silane system). *J Dent* 2006;34(10):740–6.
- [34] Kim JY, Pfeiffer P, Niedermeier W. Effect of laboratory procedures and thermocycling on the shear bond strength of resin–metal bonding systems. *J Prosthet Dent* 2003;90(2):184–9.
- [35] Watanabe I, Watanabe E, Yoshida K, Okabe T. Effect of surface contamination on adhesive bonding of cast pure titanium and Ti–6Al–4V alloy. *J Prosthet Dent* 1999;81(3):270–6.
- [36] Pashley DH, Carvalho RM, Sano H, Nakajima M, Yoshiyama M, Shono Y, et al. The microtensile bond test: a review. *J Adhes Dent* 1999;1(4):299–309.
- [37] Zinelis S, Tsetsekou A, Papadopoulos T. Thermal expansion and microstructural analysis of experimental metal–ceramic titanium alloys. *J Prosthet Dent* 2003;90(4):332–8.
- [38] Yilmaz H, Dincer C. Comparison of the bond compatibility of titanium and an NiCr alloy to dental porcelain. *J Dent* 1999;27(3):215–22.
- [39] Low D, Sumii T, Swain M. Thermal expansion coefficient of titanium casting. *J Oral Rehabil* 2001;28(3):239–42.
- [40] Coffey JP, Anusavice KJ, DeHoff PH, Lee RB, Hojjatie B. Influence of contraction mismatch and cooling rate on flexural failure of PFM systems. *J Dent Res* 1988;67(1):61–5.
- [41] Walter M, Reppel PD, Boning K, Freesmeyer WB. Six-year follow-up of titanium and high-gold porcelain-fused-to-metal fixed partial dentures. *J Oral Rehabil* 1999;26(2):91–6.
- [42] Pashley DH, Sano H, Ciucchi B, Yoshiyama M, Carvalho RM. Adhesion testing of dentin bonding agents: a review. *Dent Mater* 1995;11(2):117–25.
- [43] Goracci C, Sadek FT, Monticelli F, Cardoso PE, Ferrari M. Microtensile bond strength of self-etching adhesives to enamel and dentin. *J Adhes Dent* 2004;6(4):313–8.
- [44] Taira Y, Yoshida K, Matsumura H, Atsuta M. Phosphate and thiophosphate primers for bonding prosthodontic luting materials to titanium. *J Prosthet Dent* 1998;79(4):384–8.
- [45] Matinlinna JP, Lassila LV, Vallittu PK. The effect of five silane coupling agents on the bond strength of a luting cement to a silica-coated titanium. *Dent Mater* 2007;23(9):1173–80.
- [46] Matinlinna JP, Lassila LV, Kangasniemi I, Vallittu PK. Isocyanato- and methacryloxysilanes promote Bis-GMA adhesion to titanium. *J Dent Res* 2005;84(4):360–4.
- [47] Matinlinna JP, Lassila LV, Vallittu PK. Evaluation of five dental silanes on bonding a luting cement onto silica-coated titanium. *J Dent* 2006;34(9):721–6.
- [48] 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(4):287–93.
- [49] Della Bona A, van Noort R. Shear vs. tensile bond strength of resin composite bonded to ceramic. *J Dent Res* 1995;74(9):1591–6.
- [50] Versluis A, Tantbirojn D, Douglas WH. Why do shear bond tests pull out dentin? *J Dent Res* 1997;76(6):1298–307.
- [51] Sano H, Shono T, Sonoda H, Takatsu T, Ciucchi B, Carvalho R, et al. Relationship between surface area for adhesion and tensile bond strength—evaluation of a micro-tensile bond test. *Dent Mater* 1994;10(4):236–40.
- [52] Phrukkanon S, Burrow MF, Tyas MJ. The influence of cross-sectional shape and surface area on the microtensile bond test. *Dent Mater* 1998;14(3):212–21.
- [53] Armstrong SR, Boyer DB, Keller JC. Microtensile bond strength testing and failure analysis of two dentin adhesives. *Dent Mater* 1998;14(1):44–50.