Available online at www.sciencedirect.com
SciVerse ScienceDirect
Journal of Prosthodontic Research 57 (2013) 30–35
Journal of Prosthodontic Research
www.elsevier.com/locate/jpor

Original article

Effects of a fluoride etchant and a phosphate primer on bonding of veneering composite to Ti–6Al–4V alloy for CAD/CAM restorations

Yohsuke Taira DDS, PhD*, Tetsuro Odatsu DDS, PhD, Takashi Sawase DDS, PhD

Department of Applied Prosthodontics, Graduate School of Biomedical Sciences, Nagasaki University, 1-7-1 Sakamoto, Nagasaki 852-8588, Japan

Received 20 June 2012; accepted 8 August 2012
Available online 28 November 2012

Abstract

Purpose: Titanium abutments and superstructures are commonly veneered or covered with esthetic materials. The present investigation was carried out to evaluate the effects of an experimental surface treatment using etchant and primer on bond strength between a resin composite and Ti–6Al–4V alloy.

Methods: Disk-shaped Ti–6Al–4V alloy was machine milled, the surface was air abraded with alumina, and the alloy was chemically etched with 5wt% ammonium hydrogen fluoride (F-etch) for 30 s. A phosphate primer (MDP-primer) was applied to the bonding area, and then a resin composite, with or without milled-fiber resin composite (FRC), was veneered on the specimen. Shear bond strengths were determined after thermocycling for 20,000 cycles. Bond strength data were analyzed by means of ANOVA and a multiple comparison test ($\alpha = 0.05$). The surface of Ti–6Al–4V alloy was observed using a scanning electron microscope before and after the etching procedure.

Results: No-FRC/F-etch/MDP-primer exhibited the highest bond strength (28.2 MPa), followed by No-FRC/No-etching/MDP-primer (24.2 MPa), FRC/F-etch/MDP-primer (19.9 MPa), FRC/No-etching/MDP-primer (17.8 MPa), No-FRC/No-etching/No-primer (13.6 MPa), while FRC/No-etching/No-primer (2.5 MPa) resulted in the lowest value. Microphotographs showed that numerous micro and nano pits were created on the Ti–6Al–4V alloy surface modified with F-etch.

Conclusions: The bond strength between Ti–6Al–4V alloy and the veneering resin composite was the highest when the alloy surface was modified with alumina blasting, fluoride etchant, and phosphate primer successively.

Keywords: Adhesion; Titanium alloy; Surface modification; CAD/CAM

1. Introduction

With the development of computer-aided design and manufacturing (CAD/CAM) systems, the use of titanium for prosthodontic treatment has increased [1]. In addition to tooth-supported fixed partial dentures, multi-unit implant-supported prostheses could be fabricated with commercially pure titanium or titanium alloys [2]. Although conventional casting techniques involve a chemical reaction between metal alloys and investment materials, mechanical properties, and dimensional accuracy, this can be avoided through the use of CAD/CAM systems [3–5]. Since CAD/CAM restorations are machined from homogeneous and factory standardized blocks with high accuracy, they retain the original properties of the starting materials.

Several popular CAD/CAM systems, such as Aadva (GC Corp., Tokyo, Japan), GN-I (GC Corp.), KaVo Everest (Kavo Dental GmbH, Biberach, Germany), Smart Fit (DCS Dental AG, Allschwil, Switzerland), Zenotech (Wieland Dental GmbH, Pforzheim, Germany), Decsy (Media Inc., Tokyo, Japan), and NobelProcera (Nobel Biocare AB, Gothenburg, Sweden) employ commercially pure titanium blocks. In addition, the NobelProcera Crown and Bridge system (Nobel Biocare AB) is designed for the fabrication of a one-piece bridge from a titanium–aluminum–vanadium (Ti–6Al–4V) alloy block.

The metal framework is often veneered with resin composites in order to satisfy the esthetic demands of patients [6]. Strong and durable bonding between the resin composite and the metal framework is important to decrease detachment or fracture of the veneered resin composite in an oral environment. Various surface modifications including sandblasting [7,8], silica coating [9,10],

* Corresponding author at: Department of Applied Prosthodontics, Graduate School of Biomedical Sciences, Nagasaki University, 1-7-1 Sakamoto, Nagasaki 852-8588, Japan. Tel.: +81 95 819 7688; fax: +81 95 819 7689.
E-mail address: yohsuke@nagasaki-u.ac.jp (Y. Taira).

1883-1958 © 2012 Japan Prosthodontic Society. Published by Elsevier Ireland. Open access under CC BY-NC-ND license.
http://dx.doi.org/10.1016/j.jpor.2012.08.002

Table 1
Titanium alloy, etching agent, primers, and resin composites used in the present study.

Name (abbreviation)	Component	Manufacturer	Lot no.
Titanium alloy			
NobelProcera Titanium	Ti ≥88.478, Al 5.5–6.5%, V 3.5–4.5%, N ≤0.05%, C ≤0.08%, H ≤0.012%, Fe ≤0.25%, O ≤0.13%	Nobel Biocare AB, Gothenburg, Sweden	
Etching agent			
Experimental (F-etch)	5wt% ammonium hydrogen fluoride Distilled water	Wako Pure Chemical Ind. Ltd., Osaka, Japan	KSJ4437
Primer			
Estenia C&B Opaque Primer (MDP-primer)	MDP, methacrylate monomer, solvent, others	Kuraray Noritake Dental Inc., Tokyo, Japan	00166A
Resin composite			
Meta Color Prime Art Jacket Opaque (FRC)	UDMA, TEGDMA, silanized milled-glass fiber, aromatic amine, camphorquinone, others	Sun Medical Co. Ltd., Moriyama, Japan	TW2
Gradia Opaque OA3	UDMA, silica micro powder	GC Corp., Tokyo, Japan	1004211
Gradia Dentin DA3	Organic composite filler, UDMA, silica micro powder, glass powder	GC Corp.	1004011

MDP, 10-methacryloxydecyl dihydrogen phosphate; UDMA, urethane dimethacrylate, TEGDMA: triethyleneglycol dimethacrylate,

plasma exposure [11], and primer application [12–19], were investigated to improve the adhesive bonding of resin to commercially available pure titanium. With regard to Ti–6Al–4V alloy, a silica-coating technique was reported to have both positive [20] and negative [21] results. Some studies suggested that primers containing 10-methacryloxydecyl dihydrogen phosphate (MDP) or thiophosphate monomer (MEPS) were effective for chemical bonding between resin and Ti–6Al–4V alloy [22–24].

Increasing micro- or nano-mechanical retention is an attempt to improve adhesive bonding. An etching agent containing sodium fluoride with phosphoric acid has been evaluated as an alternative to sandblasting for titanium bonding [25]. The authors previously reported that the combined use of alumina blasting and chemical etching with fluorides significantly increased the bond strength of some resin-based self-curing luting agents to commercially pure titanium or Ti–6Al–7Nb alloy [26–29]. However, no information is available as to whether fluoride etching improves the adhesive bonding of light-curing veneering resin composite to Ti–6Al–4V alloy.

The purpose of this study was to evaluate the bond strength between a resin composite and Ti–6Al–4V alloy when the alloy surface was modified with alumina blasting, a fluoride etchant, and a phosphate primer. The hypothesis tested was that MDP primer improves the bond strength in cooperation with ammonium hydrogen fluoride etchant.

2. Materials and methods

The information on titanium alloy, etching agents, primers, and resin composites used in the present study are summarized in Table 1. A titanium alloy (NobelProcera Titanium, Nobel Biocare AB) designed for crowns and fixed partial dentures was used for the substrate material.

2.1. Specimen preparation

A total of 72 disk specimens of NobelProcera Titanium alloy, 10 mm in diameter and 2.5 mm thick, were fabricated using the NobelProcera CAD/CAM system. All disks were sanded with 600-grit silicon–carbide abrasive paper followed by air abrasion (Micro Blaster MB102, Comco Inc., Burbank, IL, U.S.A.) with 50 μm alumina (Hi-Aluminas, Shofu Inc., Kyoto, Japan) for 10 s. The supply side air pressure was 0.45 MPa, and the distance of the orifice from the metal surface was approximately 20 mm.

The disks were divided into three groups (No-etch/No-primer, No-etch/MDP-primer, and F-etch/MDP-primer), each of which consisted of 24 specimens. In the F-etch/MDP-primer group, 5 μl of F-etch liquid was applied on the alumina-blasted specimen with a micropipette for 30 s, rinsed with water for 15 s, and then air dried for 5 s. A 50-μm-thick piece of double-coated tape, with a circular hole of 5 mm diameter, was positioned on the surface of each specimen to delineate the bonding area, and 1 μl of primer was applied with a micropipette. One of the two control groups, MDP-primer, was prepared without F-etch. Another control group, No-etch/No-primer, used neither F-etch nor MDP-primer.

An acrylic ring (6 mm inside diameter, 0.5 mm in height, and 1 mm wall thickness) was placed so as to surround the bonding area. The acrylic ring was filled with a milled-fiber resin composite (Jacket Opaque, Sun Medical Co. Ltd., Moriyama, Japan) and light cured for 60 s using an apparatus (Dentacolor XS, Kulzer & Co GmbH, Wehrheim, Germany). Another acrylic mold (6 mm inside diameter, 2.5 mm in height, and 1 mm wall thickness) was adjusted on the acrylic ring, an opaque resin (Gradia OA3, GC Corp.) approximately 0.1 mm thickness was applied on the Jacket Opaque resin with a brush, and then the opaque resin was light cured for 60 s. The acrylic

Table 2
Results of analysis of variance.

Source of variation	d.f.	Sum of squares	Mean square	*F*-value	*P*-value
ANOVA corresponding to Table 3					
Surface treatment (ST)	1	3.9	3.9	0.7	0.4
Resin composite (RC)	2	900.6	450.3	77.9	0.0001
ST/RC	2	47.4	23.7	4.1	0.03
Residual	30	173.3	5.8		
ANOVA corresponding to Table 4					
Surface treatment (ST)	1	665.1	665.1	92.4	0.0001
Resin composite (RC)	2	1729.7	864.8	120.2	0.0001
ST/RC	2	34.4	17.2	2.4	0.1
Residual	30	215.9	7.2		

mold was filled with a veneering composite (Gradia DA3, GC Corp.) and light cured for 210 s. Six combinations of three surface treatments (No-etching/No-primer, No-etching/MDP-primer, and F-etch/MDP-primer) with and without Jacket Opaque resin were prepared.

2.2. Shear bond test

After the bonded specimens were stored at room temperature for 60 min, they were immersed in 37 °C water for 24 h, and this state was defined as thermocycle 0. Half of the specimens (six sets of six specimens) were tested for 24-h shear bond strength at thermocycle 0. The remaining six sets of six specimens were placed in a thermocycling apparatus (Rika Kogyo Corp., Tokyo, Japan) and cycled in water between 4 °C and 60 °C with a 1 min dwell time per bath for 20,000 cycles. Each specimen was embedded in an acrylic resin mold and seated in a shear-testing device (ISO/TR11405 jig, Wago Industrial Ltd., Nagasaki, Japan). Shear bond strengths were then determined with a mechanical testing machine (AGS-10kNG, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 0.5 mm/min. The shearing load was applied parallel to the bonded interface.

The mean bond strength and the standard deviation (SD) of six specimens were calculated for each condition. The data were analyzed by two-way analysis of variance (ANOVA). The mean values were compared by a *post hoc* Tukey Compromise test with the value of statistical significance set at 0.05 following one-way ANOVA. The debonded surfaces of all specimens were observed through an optical microscope (SMZ-10, Nikon Corp., Tokyo, Japan) at a magnification of 20× to assess bond failure. Failure modes were categorized as adhesive failure at the resin composite-titanium alloy interface (Ad), cohesive failure within the resin composite (Co), and complex adhesive failure at the resin composite–titanium alloy interface and cohesive failure within the resin composite (Ad/Co).

2.3. SEM observation

Two titanium specimens including a control were subjected to micro-photographic evaluation. The specimens were etched with the F-etch solution following alumina blasting, as described above. The surfaces were sputter coated with gold (Ion Coater IB-3, Eiko Engineering Co. Ltd., Mito, Japan) and then observed using a scanning electron microscope (S-3500N, Hitachi Corp., Tokyo, Japan) at a magnification of 5000×.

An additional titanium specimen was etched with F-etch for 30 s following alumina blasting. The etched specimen was veneered with the resin composites (Gradia OA3 and DA3), as described above. 60 min later, the specimen was cut perpendicular to the bonded interface. The specimen section was immersed in the F-etch solution for 360 min, rinsed with water, and dried for 24 h at room temperature. Following the sputter coating, the adhesive interface area was observed using a scanning electron microscope at 5000× magnification.

3. Results

Table 2 shows ANOVA results for shear bond strength corresponding to Tables 3 and 4. The mean bond strength varied from 12.6 to 25.3 MPa at thermocycling 0 (Table 3). The FRC/No-etching/MDP-primer, FRC/F-etch/MDP-primer, No-FRC/No-etching/MDP-primer, and No-FRC/F-etch/MDP-primer groups showed significantly higher bond strengths than the FRC/No-etching/No-primer and No-FRC/No-etching/No-primer groups. With regard to failure mode, the groups FRC/No-etching/No-primer and FRC/F-etch/MDP-primer exhibited only adhesive failure at the resin composite-titanium alloy interface (Ad). All specimens of No-FRC/No-etching/MDP-primer and No-FRC/F-etch/MDP-primer exhibited complex adhesive failure at the resin composite-titanium alloy interface and cohesive failure within the resin composite (Ad/Co). The FRC/No-etching/MDP-primer and No-FRC/No-etching/No-primer groups showed both Ad and Ad/Co modes.

After 20,000 thermocycles, the mean bond strength ranged from 2.5 to 28.2 MPa (Table 4). The No-FRC/F-etch/MDP-primer group exhibited the highest bond strength (28.2 MPa), followed by No-FRC/No-etching/MDP-primer, FRC/F-etch/MDP-primer and FRC/No-etching/MDP-primer, No-FRC/No-etching/No-primer, and FRC/No-etching/No-primer resulted in the lowest values (2.5 MPa). The failure mode observed in the FRC/No-etching/No-primer, FRC/No-etching/MDP-primer, FRC/F-etch/MDP-primer, and No-FRC/No-etching/No-primer groups was only adhesive failure. In contrast, all specimens of the No-FRC/No-etching/MDP-primer and No-FRC/F-etch/

Table 3
Shear bond strength and failure mode at thermocycle 0.

Group name	Mean (SD)* (MPa)	Failure mode** (Number of specimens)
FRC/No-etching/No-primer	12.6 (2.1)[a]	Ad(6)
FRC/No-etching/MDP-primer	25.3 (1.7)[b]	Ad(2), Ad/Co(4)
FRC/F-etch/MDP-primer	22.2 (2.2)[b]	Ad(6)
No-FRC/No-etching/No-primer	14.0 (3.1)[a]	Ad(3), Ad/Co(3)
No-FRC/No-etching/MDP-primer	22.9 (2.0)[b]	Ad/Co(6)
No-FRC/F-etch/MDP-primer	25.2 (2.9)[b]	Ad/Co(6)

* The identical small letters indicate that the values are not statistically different ($p > 0.05$).
** Ad: adhesive failure at the resin composite–titanium alloy interface; Ad/Co: complex adhesive failure at the resin composite–titanium alloy interface and cohesive failure within the resin composite.

Table 4
Shear bond strength and failure mode at thermocycle 20,000.

Group name	Mean (SD)* (MPa)	Failure mode** (number of specimens)
FRC/No-etching/No-primer	2.5 (2.3)[a]	Ad(6)
FRC/No-etching/MDP-primer	17.8 (1.9)[c]	Ad(6)
FRC/F-etch/MDP-primer	19.9 (2.8)[c]	Ad(6)
No-FRC/No-etching/No-primer	13.6 (3.3)[b]	Ad(6)
No-FRC/No-etching/MDP-primer	24.2 (2.9)[d]	Ad/Co(6)
No-FRC/F-etch/MDP-primer	28.2 (2.7)[e]	Ad/Co(6)

* The identical small letters indicate that the values are not statistically different ($p > 0.05$).
** Ad: adhesive failure at the resin composite–titanium alloy interface; Ad/Co: complex adhesive failure at the resin composite–titanium alloy interface and cohesive failure within the resin composite.

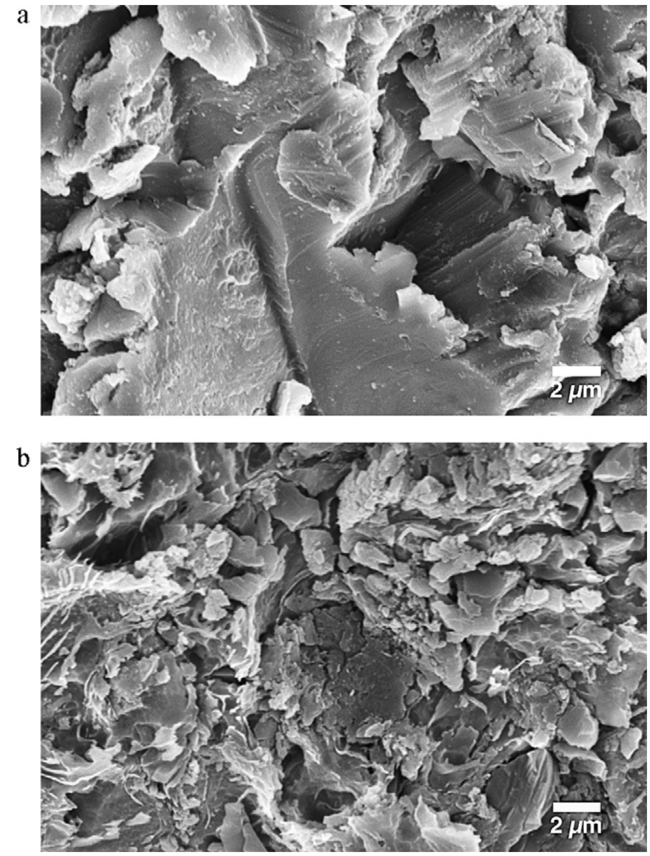

Fig. 1. Scanning electron micrographs (5000× original magnification) of Ti–6Al–4V alloy specimen surfaces: (a) air abraded with alumina; (b) modified with 5wt% ammonium hydrogen fluoride after alumina blasting.

MDP-primer groups were observed to fail in mixed adhesive and cohesive modes.

Representative titanium specimen surfaces consisting of (a) an alumina-blasted and non-etched control and (b) an alumina-blasted specimen modified with F-etch are shown in Fig. 1. Specimen (a) was scratched with the alumina particles to form relatively smooth grooves on the surface. Specimen (b) was obviously roughened and exhibited a greater number of micro and several hundred nano pits compared to specimen (a).

A micrograph and a schema of the partially dissolved bonded sample are shown in Figs. 2 and 3. A step was created between the cut resin surface and the partially dissolved titanium surface (Fig. 2). The exposed surface of resin was quite rough and sub-micron resin tags were observed at the bonded interface (Fig. 3).

4. Discussion

The present study revealed that the testable hypothesis was accepted. The concentration of ammonium hydrogen fluoride and the etching period were based upon previous studies in which etching with 0.5–10wt% ammonium hydrogen fluoride for 10–30 s was effective for improving the bond strength of resin to commercially pure titanium surfaces [28]. The titanium alloy surface was roughened with alumina blasting and further with F-etch, which should increase mechanical interlocking and the actual bonding area. Taking the standard reduction potential reported ($Al^{3+} + 3e^- = Al$, −1.66 V; $Ti^{3+} + 3e^- = Ti$, −1.37 V; $Ti^{2+} + 2e^- = Ti$, −1.63 V; and $V^{2+} + 2e^- = V$, −1.18 V) into account [30], these metal elements have different ionization tendency. Therefore, the local distribution of these metal elements may have relation to the morphology of the etched Ti–6Al–4V alloy surface.

Alumina-blasted Ti–6Al–4V alloy surfaces should be a contaminated surface containing titanium oxides, aluminum oxides, and vanadium oxides [31–33]. The corrosion resistance of Ti–6Al–4V alloy may originate from these metal oxide layers. It is considered that fluorides react with the surface of the titanium oxide layer and replace the titanium-bound oxygen to form titanium–fluoride compounds [34,35]. When F-etch was applied to the Ti–6Al–4V alloy specimen in this experiment, bubbles formed on the Ti–6Al–4V alloy surface. This bubbling is thought to have been due to the oxygen from the titanium oxide, which suggests that the titanium oxide layer was momentarily broken. Once the ammonium hydrogen fluoride has broken down the oxide layer on the surface, it may easily ionize the underlying Ti–6Al–4V alloy substance. An additional effect of the etching procedure may be the removal of loose alumina particles.

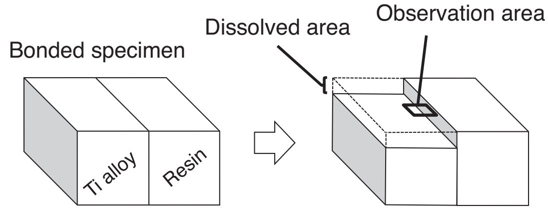

Fig. 2. Schematic illustration of preparation of a bonded specimen for microphotograph corresponding to Fig. 3. The surface of the bonded titanium alloy was dissolved with ammonium hydrogen fluoride for observation.

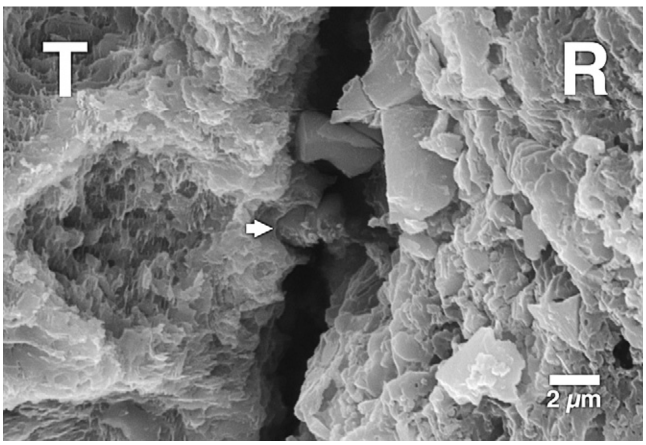

Fig. 3. Scanning electron micrograph (5000×original magnification) of the cross sectional view of the interface between resin (R) and titanium alloy (T). The titanium alloy of the sectioned specimen was partly dissolved with ammonium hydrogen fluoride for observation of the bonded interface. Arrow indicates a resin tag.

The SEM images (Figs. 1 and 2) let us to speculate that the MDP monomer of the primer wet to the Ti–6Al–4V alloy surface, not only generated adhesive force, but also promoted diffusion of the other monomer into the numerous pits, and then the diffused monomers were copolymerized *in situ.* When polymer exists in the micro and several hundred nano pits created on the surface, micro-mechanical retention and so-called nano-mechanical retention could be achieved.

Originally, FRC is a material to fabricate a coping of jacket crown, of which Young's modulus is lower than a conventional resin composite [36]. We had expected that the use of FRC at the interface relieved stress concentration due to implication of the materials' flexibility. Contrary to the expectation, no benefit was shown with FRC as a metal opaque. Thermal stress is generally derived from the difference between the thermal expansion coefficients of the substrate materials. Bigger difference of the thermal expansion coefficients makes experimental condition severer. The present data before and after the thermocycling, particularly in groups FRC/No-etching/No-primer and No-FRC/No-etching/No-primer, suggest that the discrepancy of thermal expansion coefficients of FRC and Ti–6Al–4V alloy is wider than that of the Gradia composites used.

The component of F-etch is quite similar to an etching agent containing 10wt% ammonium hydrogen fluoride, which was employed to a previous castable ceramic (Dicor, Dentsply International Inc., York, PA, U.S.A.). The ammonium hydrogen fluoride solution should not be directly applied to an oral cavity, because it is a deleterious substance. Clinicians and dental technicians could use F-etch in a dental laboratory. Not only the thermal stresses, but also various stresses, *i.e.*, load, wear, and hydrolysis, attack the adhesive bonding in oral environment. Accordingly, clinical evaluation is required to confirm the actual bonding durability.

In conclusion, the maximum bond strengths between Ti–6Al–4V alloy and the veneering resin composite was obtained when Ti–6Al–4V alloy was treated with alumina blasting, an etchant containing 5wt% ammonium hydrogen fluoride, and a phosphate primer successively. Additional use of milled-fiber resin composite as a metal opaque did not improve the bonding.

Acknowledgement

This work has been supported by Nobel Biocare with research grant study 2009-828.

References

[1] Kapos T, Ashy LM, Gallucci GO, Weber HP, Wismeijer D. Computer-aided design and computer-assisted manufacturing in prosthetic implant dentistry. Int J Oral Maxillofac Implants 2009;24 Suppl.:110–7.
[2] Hjalmarsson L, Örtorp A, Smedberg JI, Jemt T. Precision of fit to implants: a comparison of Cresco™ and Procera® implant bridge frameworks. Clin Implant Dent Relat Res 2010;12:271–80.
[3] Rodrigues RCS, Almeida EP, Faria ACL, Macedo AP, de Mattos MGC, Ribeiro RF. Effect of different investments and mold temperatures on titanium mechanical properties. J Prosthodont Res 2012;56:58–64.
[4] Guilin Y, Nan L, Yousheng L, Yining W. The effects of different types of investments on the alpha-case layer of titanium castings. J Prosthet Dent 2007;97:157–64.
[5] Drago C, Saldarriaga RL, Domagala D, Almasri R. Volumetric determination of the amount of misfit in CAD/CAM and cast implant frameworks: a multicenter laboratory study. Int J Oral Maxillofac Implants 2010;25:920–9.
[6] Fernandes CA, Ribeiro JC, Larson BS, Bonfante EA, Silva NR, Suzuki M, et al. Microtensile bond strength of resin-based composites to Ti–6Al–4V. Dent Mater 2009;25:655–61.
[7] White SN, Yu Z, Zhao XY. High-energy abrasion: an innovative esthetic modality to enhance adhesion. J Esthet Dent 1994;6:267–73.
[8] Kern M, Thompson VP. Effects of sandblasting and silica-coating procedures on pure titanium. J Dent 1994;22:300–6.
[9] Hansson O. Strength of bond with Comspan Opaque to three silicoated alloys and titanium. Scand J Dent Res 1990;98:248–56.
[10] Fujishima A, Fujishima Y, Ferracane JL. Shear bond strength of four commercial bonding systems to cpTi. Dent Mater 1995;11:82–6.
[11] Kibayashi H, Teraoka F, Fujimoto S, Nakagawa M, Takahashi J. Surface modification of pure titanium by plasma exposure and its bonding to resin. Dent Mater J 2005;24:53–8.
[12] 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;69:1614–6.
[13] 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;22:409–12.
[14] Taira Y, Imai Y. Primer for bonding resin to metal. Dent Mater 1995;11:2–6.
[15] Taira Y, Matsumura H, Atsuta M. Bonding of titanium with acidic primers and a tri-*n*-butylborane-initiated luting agent. J Oral Rehabil 1997;24:385–8.

[16] Taira Y, Yoshida K, Matsumura H, Atsuta M. Phosphate and thiophosphate primers for bonding prosthodontic luting materials to titanium. J Prosthet Dent 1998;79:384–8.

[17] Taira Y, Matsumura H, Yoshida K, Tanaka T, Atsuta M. Influence of surface oxidation of titanium on adhesion. J Dent 1998;26:69–73.

[18] 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: 456–60.

[19] Kadoma Y. Surface treatment agent for dental metals using a thiirane monomer and a phosphoric acid monomer. Dent Mater J 2002;21:156–69.

[20] Lee SY, Vang MS, Yang HS, Park SW, Park HO, Lim HP. Shear bond strength of composite resin to titanium according to various surface treatments. J Adv Prosthodont 2009;1:68–74.

[21] Wei AY, Sharma AB, Watanabe LG, Finzen FC. The effects of an airborne-particle abrasion and silica-coating on the bond strength between grooved titanium alloy temporary cylinders and provisional veneering materials. J Prosthet Dent 2011;105:158–63.

[22] Lim HP, Kim SS, Yang HS, Vang MS. Shear bond strength and failure types of polymethyl methacrylate denture base resin and titanium treated with surface conditioner. Int J Prosthodont 2010;23:246–8.

[23] Radhi A, Juszczyk AS, Curtis RV, Sherriff M, Radford DR, Clark RK. Effect of GC METALPRIMER II on bond strength of heat-cured acrylic resin to titanium alloy (Ti–6Al–4V) with two different surface treatments. Eur J Prosthodont Restor Dent 2008;16:132–7.

[24] 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;83:50–7.

[25] Lim BS, Heo SM, Lee YK, Kim CW. Shear bond strength between titanium alloys and composite resin: sandblasting versus fluoride-gel treatment. J Biomed Mater Res 2003;64B:38–43.

[26] 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;112:95–100.

[27] Yanagida H, Taira Y, Atsuta M. Effects of a fluoride etchant on resin bonding to titanium–aluminum–niobium alloy. Eur J Oral Sci 2004;112:384–7.

[28] Yang L, Taira Y, Atsuta M. Effect of an acidulated fluoride etchant on bonding between titanium and two luting materials. J Biomed Mater Res 2006;78B:161–6.

[29] Taira Y, Yang L, Atsuta M. Comparison of four fluoride etchants in bonding between titanium and a self-curing luting agent. Dent Mater J 2006;25:345–51.

[30] Vanýsek P. Electrochemical series. In: Haynes WM, editor. CRC handbook of chemistry and physics. 92nd ed., Boca Raton, U.S.A.: CRC Press; 2011–2012. 5-80–5-84.

[31] Darvell BW, Samman N, Luk WK, Clark RKF, Tideman H. Contamination of titanium castings by aluminium oxide blasting. J Dent 1995;23:319–22.

[32] Miyakawa O, Watanabe K, Okawa S, Kanatani M, Nakano S, Kobayashi M. Surface contamination of titanium by abrading treatment. Dent Mater J 1996;15:11–21.

[33] Papadopoulos T, Tsetsekou A, Eliades G. Effect of aluminium oxide sandblasting on cast commercially pure titanium surfaces. Eur J Prosthodont Restor Dent 1999;7:15–21.

[34] Ellingsen JE. Pre-treatment of titanium implants with fluoride improves their retention in bone. J Mater Sci Mater Med 1995;6:749–53.

[35] Nakagawa M, Matsuya S, Udoh K. Corrosion behavior of pure titanium and titanium alloys in fluoride-containing solutions. Dent Mater J 2001;20:305–14.

[36] Suzuki S, Saimi Y, Ono T. Evaluation of a new fiber-reinforced resin composite. J Biomed Mater Res 2006;76B:184–9.