Effects of silica-coating on surface topography and bond strength of porcelain fused to CAD/CAM pure titanium

Takushi FUKUYAMA, Naho HAMANO and Satoshi INO

Division of Minimal Intervention Prosthetic Dentistry, Department of Highly Advanced Stomatology, Kanagawa Dental University, Yokohama Clinic, 3-31-6 Tsuruya-cho, Kanagawa-ku, Yokohama, Kanagawa 221-0835, Japan

Corresponding author, Satoshi INO; E-mail: ino@kdu.ac.jp

The aim of this study was to evaluate the shear bond strength of porcelain fusing to titanium and the effects of surface treatment on surface structure of titanium. In the shear bond strength test, titanium surface treatments were: conventional, silica-coating without bonding agent, and silica-coating with bonding agent. Titanium surface treatments for analysis by the atomic force microscope (AFM) were: polishing, alumina sandblasting and silica-coating. The shear bond strength value of silica-coating with bonding agent group showed significantly higher than that of other groups. In AFM observation results, regular foamy structure which is effective for wetting was only observed in silica-coating. Therefore, this structure might indicate silicon. Silica-coating renders forms a nanoscopic regular foamy structure, involved in superhydrophilicity, to titanium surface, which is markedly different from the irregular surface generated by alumina sandblasting.

Keywords: Silica-coating, Nanostructure, Porcelain, CAD/CAM pure titanium, Shear bond strength

INTRODUCTION

Nickel chromium and gold alloys have been used for porcelain firing. However, in light of issues such as metal allergies caused by nickel-chromium alloy¹⁾ and soaring gold prices, titanium offers advantages such as high biocompatibility, corrosion resistance and low cost. It is also applied to a metal for porcelain firing and is clinically applied²⁻¹⁰⁾. However, titanium ceramic crowns have a lower bond strength than metal ceramic crowns containing conventional nickel-chromium or gold alloy¹¹⁻¹³⁾.

This is explained by the fact that titanium has powerful affinity for oxygen at high temperature and forms a thick oxide layer on a titanium surface. An oxide layer formed at less than 800°C is very thin and adherent; it markedly thickens at more than 900°C¹⁴⁾, forms a non-adherent oxide layer at 1,000°C and peels away from the titanium surface¹⁴⁾. Therefore, an oxide layer with a thick titanium surface reduces the bond strength of titanium and porcelain. In addition, since the thermal expansion coefficient of titanium is lower than that of either conventional nickel-chromium or gold alloys, porcelains applied to these metals cannot be used^{15,16)}. To compensate for these drawbacks, porcelains for low-temperature firing have been developed exclusively for use with titanium.

The melting points of conventional nickel-chromium and gold alloys are about 1,200°C, whereas that of titanium is 1,668°C¹⁶⁾, which precludes casting¹⁷⁾. Furthermore, the casting surface of titanium forms an α -case layer, which reduces the bond strength of porcelain^{18,19)}. Therefore, titan coping fabricated by

CAD/CAM, which does not form an α -case layer on the titanium surface, has recently been applied²⁻⁶⁾.

Various surface treatments of titanium have been attempted to improve bond strength, such as nitriding²⁰⁾, peroxidation^{21,22)} and chemical treatment^{23,24)}. All of these include alumina sandblasting. In 1989, Guggenberger described tribochemical silica-coating (Rocatec®, 3M ESPE, Seefeld, Germany) by sandblasting with silica-coated alumina powder to form a silicate layer on an adherent surface²⁵⁾. Kern *et al.* found that tribochemical silica-coating of a titanium surface improves adhesion^{26,27)}. However, they did not reveal the nanostructure of the treated surface, or the bond strength and mechanisms of action of CAD/CAM pure titanium and porcelain.

The present study examines the effects of tribochemical silica-coating on the surface of CAD/CAM pure titanium and the bond strength of porcelain.

MATERIALS AND METHODS

Table 1 shows the materials used in this study.

This study consists of two kinds of analyses, which are the bond strength test and the analysis of surface topography. The bond strength test was evaluated using shear bond strength measurement and analysis of fracture surface. The analysis of surface topography was examined by contact angle measurement and observation of treated surface.

Titanium specimen preparation

Thirty-seven test specimen (15×9×2 mm) were cut from a CAD/CAM pure titanium block (GN-1 TITANIUM BLOCK, GC, Tokyo, Japan) using a low-speed precision cutting machine (ISOMET®, Buehler, Chicago, IL,

Color figures can be viewed in the online issue, which is available at J-STAGE.

Received Sep 2, 2015; Accepted Dec 7, 2015

doi:10.4012/dmj.2015-290 JOI JST.JSTAGE/dmj/2015-290

Table 1 Materials used in this study

Brand name	Composition	Production no.	Manufacturer
GN-1 Titanium Block	Pure titanium	1111181	GC, Tokyo, Japan
Initial Ti Powder Opaque	Feldspathic porcelain	1110071	GC
Initial Ti Dentin	Feldspathic porcelain	812041	GC
Initial Ti Bonder, Bonder Liquid	B ₂ O ₃ , La ₂ O ₃	904301	GC
Rocatec® Pre	110 µm Al ₂ O ₃	572619	3M ESPE, Seefeld, Germany
Rocatec® Plus	Silica cont. 110 µm Al ₂ O ₃	572618	3M ESPE

Table 2 Firing Schedules of bonding agent and porcelain

	Start temperature (°C)	Rate of temperature rise (°C/min)	End temperature (°C)	Vacuum
Bonding agent	450	55	810	+
Opaque porcelain	450	55	810	+
Dentin porcelain	400	55	780	+

USA). The surfaces of the titanium test specimen were polished under running water using #600 waterproof abrasive papers (Sankyo Rikagaku, Saitama, Japan), then ultrasonically cleaned in ethanol for 15 min.

1. The bond strength test

1) Shear bond strength measurement

(1) Surface treatment

The surfaces of titanium test specimen were prepared as follows. Eight specimens were assigned for each group.

- ① Conventional group: After a bonding agent was mixed with a bonder liquid, a very thin bonding agent was applied to the titanium surface and fired according to manufacturer's recommendation²⁸⁾.
- ② Silica-coating without bonding agent group: Silica-coating was conducted with 110-µm silica-containing alumina powder (Rocatec® Plus, 3M ESPE).
- ③ Silica-coating with bonding agent group: Following the treatment ②, treatment ① was conducted.

Since sandblasting with alumina reduces the bond strengths of titanium and porcelain^{29,30)}, alumina sandblasting before the application of a bonding agent was omitted in the conventional group. The bonding agent was fired using a firing furnace (Programat P100, Evoclar Vivadent, Tokyo, Japan) according to manufacturer's recommendation²⁸⁾ (Table 2). Silica-coating was conducted using a sandblaster (Rocatec® delta, 3M ESPE) for 15 s at a distance of 10 mm from the specimen at a pressure of 0.6 MPa.

(2) Porcelain application (Fig. 1)

Porcelain was applied to the titanium surface after preparation as described above and fired according to

manufacturer's recommendation²⁸⁾ (Table 2). Dentine porcelain was applied using a circular polyoxymethylene mold (diameter, 4.6 mm; height, 2.0 mm) and fired to prepare a porcelain specimen (Fig. 1-a).

The bonding area was formed as a circle with a diameter of 4.6 mm using a masking tape. After the application of opaque porcelain (Fig. 1-b), the porcelain specimens were mounted on it (Fig. 1-c). An excess part of the opaque porcelain was removed, followed by firing using a firing furnace (Fig. 1-d) according to manufacturer's recommendation. (Table 2). Subsequently, a specimen was fixed in an autopolymerizing resin (Fig. 1-e) (Ostron II, GC).

(3) Shear bond strength measurement

A shear bond strength test was conducted using a universal testing machine (Autograph AGS 1000B, Shimadzu, Kyoto, Japan) at a crosshead speed of 1.0 mm/min. The results were subjected to one-way analysis of variance, followed by a Fisher's least significant difference (LSD) test ($p < 0.01$) (Fig. 1-f). The number of specimens was prepared by reference to standard ISO10477³¹⁾.

2) Analysis of fracture surface

After the shear bond strength test, five specimens each were randomly selected from the conventional and silica-coating with bonding agent groups. The La and Si mapping and Back Scattered Composition image (BSE image) of the fracture surface were observed with an electron probe microanalyzer (EPMA; EPMA8705, Shimadzu). Measurement parameters were set as follows: accelerating voltage, 20 kV; beam current, 2 nA; and measurement time, 0.01 s.

As a result of EPMA analysis, cohesive failure ratios

Fig. 1 Schema of porcelain application and shear-bond strength test.

and Si and La element-undetected areas in the bonding areas of each group were determined using NIH Image J software³². The results were analyzed using a Student's *t*-test ($p < 0.01$).

2. The analysis of surface topography

1) Contact angle measurement

Five titanium test preparations each were sandblasted with alumina (1) or coated with Si (2) as follows.

(1) Alumina sandblasting group: Alumina powder (110 μm , Rocatec® Pre, 3M ESPE) was injected using a sandblaster (Rocatec® delta, 3M ESPE) for 15 s at a distance of 10 mm from the specimen with a pressure of 0.6 MPa.

(2) Silica-coating group: Silica-coating was conducted in the same manner as the titanium surface treatment in the shear bond strength test.

Contact angles were measured with distilled water using an automatic dynamic contact analyzer (DCA-VZ, Kyowa Interface Science, Saitama, Japan). Each specimen was measured three times at room temperature. The contact angles were calculated using software (FAMAS, Kyowa Interface Science). The results were analyzed using a Student's *t*-test ($p < 0.01$).

2) Observation of treated surface

Each titanium test specimen was subjected to surface treatment as described below, and the titanium surfaces were observed using an Atomic Force Microscope (AFM; SPI3800n, Seiko Instruments, Chiba, Japan).

(1) Polishing: The titanium surfaces were polished under running water using #600 waterproof abrasive papers.

(2) Alumina sandblasting: Alumina sandblasting was conducted in the same manner as the

Fig. 2 Shear bond strength of each preparation.

* $p < 0.01$, statistically significant differences within groups.

treatment for titanium surface roughness.

(3) Silica-coating: Silica-coating was conducted in the same manner as the titanium surface treatment in the shear bond strength test.

RESULTS

The results of shear bond strength measurement showed significantly higher bond strengths in the conventional (22.1 ± 3.1 MPa) and silica-coating with bonding agent (26.0 ± 2.8 MPa) groups than in the silica-coating without bonding agent group (16.6 ± 1.0 MPa) (Fig. 2). Bond strength was significantly higher for the silica-coating with bonding agent group than for the conventional

Fig. 3 (a) BSE image, (b) Si mapping, (c) La mapping, (d) superimposed image Si and La mappings of fracture surface in conventional group. (e) BSE image, (f) Si mapping, (g) La mapping, (h) superimposed image of La and Si mappings of fracture surface in Si-coating with bonding agent group. Red and green area of superimposed image shows La and Si mapping. Circle in Figure shows bonding area.

Table 3 Cohesive failure ratios (%) in conventional group and silica-coating with bonding agent group

Surface treatment	Conventional	Silica-coating with bonding agent
Cohesive failure ratio (SD)	43.3 (15.3) ^a	67.4 (13.6) ^b

Significantly differences are visualized with different letters.

^{a,b} Significantly different ($p < 0.01$).

Table 4 Areas where elements were undetectable in conventional group and silica-coating with bonding agent group (%)

Surface treatment	Conventional	Silica-coating with bonding agent
Area of undetected elements (SD)	27.3 (15.3) ^a	8.9 (6.6) ^b

Significantly differences are visualized with different letters.

^{a,b} Significantly different ($p < 0.01$).

Table 5 Contact angles (°) of titanium surface for alumina sandblasting group and silica-coating group

Surface treatment	Alumina sandblasting	Silica-coating
Contact angle (°)	10.6 (0.3) ^a	3.4 (0.4) ^b

Significantly differences are visualized with different letters.

^{a,b} Significantly different ($p < 0.01$).

group (26.0 ± 2.8 vs. 22.1 ± 3.1 MPa; $p < 0.01$).

Residual porcelain was macroscopically obvious in the fracture surfaces of all specimens. Dark areas in BSE images indicated the cohesive failure of the porcelain (Figs. 3-a and e).

The results of element analysis of fracture surfaces are shown in Fig. 3. Element analysis were examined Si mapping (Figs. 3-b and f) and La mapping (Figs. 3-c and g). In addition, superimposed images of the Si and La were investigated (Figs. 3-d and h).

Element analysis of the fracture surfaces after the test revealed high levels of Si in both conventional and silica-coating with bonding agent groups (Figs. 3-b and f). High levels of La were also detected in both conventional and silica-coating with bonding agent groups (Figs. 3-c and g). Superimposed images of the Si and La detected on the fracture surface revealed areas where La and Si were detected in contrast to the conventional and silica-coating with bonding agent groups (Figs. 3-d and h). Black regions without Si or La were evident in the bonded area (Figs. 3-d and h).

The results of cohesive failure ratios are shown in Table 3. Silica-coating with bonding agent group ($67.4 \pm 13.6\%$) was significantly higher than the conventional group ($43.3 \pm 15.3\%$) ($p < 0.01$).

The conventional group ($27.3 \pm 15.3\%$) was significantly higher ratios of regions without Si or La in the bonding areas than silica-coating with bonding agent group ($8.9 \pm 6.6\%$) ($p < 0.01$) (Table 4).

The results of contact angles are summarized in Table 5. The silica-coating group ($3.4 \pm 0.4^\circ$) was smaller than alumina sandblasting group ($10.6 \pm 0.3^\circ$) ($p < 0.01$).

The results of observation of treated surface are shown in Fig. 4.

The specimens shown in Figs. 4-a, c and e were observed from above. In addition, the specimens shown in Figs. 4-b, d and f were observed at an angle of 60° . Less microscopic structural changes were evident after polishing titanium surfaces under running water using #600 waterproof abrasive papers (Figs 4-a and b). Rough irregular undulations were observed with grooves about 1,250-nm deep after alumina sandblasting (Figs. 4-c and d). After silica-coating, grooves about 1,250-nm deep, observed in alumina sandblasting, were not noted, and, instead, regular 200–300-nm nanoscopic foamy structures were observed (Figs. 4-e and f).

DISCUSSION

In generally, there is a three-point bending test (ISO 9693) as a major test of the bond strength of porcelain fused to the metal³³. However, Gilbert *et al.* used the shear bond strength test and three-point bending test to evaluate the bond strength of titanium and porcelain, and reported that the variation of the shear bond strength test was smaller than that of the three-point bending test³⁰. Therefore, the bond strength at the interface between titanium and porcelain was evaluated using the shear bond strength test in this study.

The porcelain specimens of the same size were fired, which were mounted on titanium specimens. These procedures enabled to stabilize mechanical properties of dentin porcelain. In addition, the bonding area could be standardized because an excess part of the opaque

Fig. 4 AFM image of surface in each groups.
(a) (b), Polishing; (c) (d), Alumina sandblasting; (e) (f) Silica-coating. Scale bar means depth.

porcelain was removed easily. Thus, the porcelain application procedure might reduce variation in this study.

Sandblasting is a simple method of mechanically interlocking a titanium surface with porcelain. Larger alumina particles lead to a rougher the titanium surface, which promotes the mechanical interlocking³⁴. Golebiowski *et al.* reported that 110-μm alumina particles are optimal for improving the bond strength of titanium and porcelain³⁵. However, Derand *et al.*

reported that sandblasting with alumina facilitates the embedding of alumina particles in the titanium surface, causing microcracks and reducing the bond strength of both the titanium and porcelain^{29,30}.

In the present study, we examined the effects of porcelain bond strengths on tribochemical silica-coated CAD/CAM pure titanium. Zinelis *et al.* reported that the bonding agent of initial Ti effectively controlled the oxidized layer, although a thick oxidized layer was observed on titanium surface depending on the type of

bonding agent³⁶⁾. Also, the results of the present study demonstrated that the bonding agent of initial Ti might effectively controlled the excessive oxidation of titanium.

Haag *et al.* reported that there were no significant differences between the bond strength of titanium and porcelain with and without thermo-cycling²¹⁾. Therefore, thermo-cycling did not be conducted in this study.

Element analysis of fracture surfaces was conducted to investigate fracture pattern. The Si-detected areas corresponded to the areas with residual porcelain observed with the naked eye and the dark areas on the BSE image (Figs. 3-a, b, e, and f). Thus, the Si detected on the fracture surface is derived from porcelain, suggesting that the cohesive failure of porcelain might have occurred in the Si-detected areas.

Some areas in both groups were devoid of both Si and La, indicating titanium exposure because neither porcelain nor bonding agent was present on the surface.

In the present study, black areas were observed in the fracture surface after testing in the silica-coating with bonding agent group, suggesting slight titanium exposure (Fig. 3-h). However, cohesive failure of porcelain accounted for the majority of the fracture surface, suggesting a small area with Si of the silicon layer peeled off from the titanium surface. Kern and Thompson reported that Si remains on the surface of tribochemical silica-coated titanium after ultrasonic cleaning, suggesting that Si is tightly bound to the titanium surface²⁶⁾. Thus, we presumed that the silica layer was firmly bound to the titanium surface after porcelain firing.

Oka *et al.* reported that sodium, silicon, calcium, and barium in porcelain diffuse into titanium oxide during porcelain firing³⁷⁾. These elements form complex oxides with titanium that become involved in titanium binding to porcelain³⁶⁻³⁸⁾. Wang *et al.* used TEM to investigate the bond strength of porcelain to a Si_3N_4 -coated titanium surface, and found that titanium silicide formed at the interface between the titanium and Si_3N_4 layer and silicon oxide (SiO_2) was formed at the interface with the outer surface where the Si_3N_4 layer was bound to porcelain³⁹⁾.

The cohesive failure ratio of porcelain was significantly higher in the silica-coating with bonding agent group than in the conventional group. This could be explained as element diffusion between the silicon layer and the porcelain and the formation of complex oxides that might have resulted in robust titanium binding to porcelain.

King *et al.* reported that close contact between metal and porcelain was obtained by improving the wetting of the metal surface⁴⁰⁾. In the present study, the titanium exposure rates on the fracture surface after testing were compared, demonstrating a significantly lower rate in the silica-coating with bonding agent group than in the conventional group (Table 3). Thus, in the silica-coating with bonding agent group, tribochemical silica-coating may have improved the wetting on titanium surface and increased compatibility between titanium and the

bonding agent.

Contact angles were measured to examine wetting on the treated surface, contact angle in the silica-coating group was smallest (Table 4). Thus, the silica-coated surface might be more hydrophilic than the sandblasted surface. In addition, the contact angle of the silica-coating was less than 10° , suggesting superhydrophilicity on the silica-coated surface.

Nanostructural changes due to improved wetting were examined using an atomic force microscope. Papadopoulos *et al.* reported that alumina becomes embedded in the titanium surface after sandblasting and forms a rough surface³⁴⁾. The present study also found that alumina sandblasting caused irregular undulations on the titanium surface.

Rammelsberg *et al.* reported that silica-coating was significantly higher bond strength of titanium and porcelain than alumina sandblasting⁴¹⁾. Surface structure analysis revealed silica-coating surface was different from alumina sandblasting surface. In addition, the foamy structure might have improved bond strength of titanium and porcelain.

Thus, after tribochemical silica-coating, besides deep irregular undulations, regular nanostructures may have been formed by particles with a foamy structure.

Surface wetting, as well as surface chemical properties, is influenced by the fine geometric structure of the surface⁴²⁾. Fine, regular grooves on the surface of snail shells range in size from nm to mm, form a fractal structure and render the shell hydrophilic. These structural properties have been industrially applied to develop a nanohydrophilic antifouling technology⁴³⁾. The regular silica layer formed by the nanoscopic foamy structure in the silica-coating also formed a fractal structure like that of the snail shell, suggesting that the nanostructure is involved in superhydrophilicity. The foamy particles seemed to be silicon, suggesting that superhydrophilicity was rendered through hydrogen bonding of the hydroxyl group of the silicon to water.

Thus, unlike routine alumina sandblasting, tribochemical silica-coating effectively modified CAD/CAM pure titanium into a superhydrophilic fractal structure that was involved in improving the bond strength of porcelain.

CONCLUSIONS

This study of the effects of a tribochemical silica-coating on the surface of CAD/CAM pure titanium and the bond strength of porcelain found the following.

1. Silica-coating results in a nanoscopic regular foamy structure that renders the surface of CAD/CAM pure titanium superhydrophilic, which is clearly different from the irregular surface generated by alumina sandblasting.
2. Silica-coating combined with a bonding agent can significantly improve the bond strength of CAD/CAM pure titanium and porcelain.

ACKNOWLEDGMENTS

We thank Shusaku OKADA, of Kanagawa Dental University, and Masahiko MITSUHASHI of the Kanagawa Industrial Technology Center for generous support and valuable advice.

REFERENCES

- Magnusson B, Bergman M, Bergman B, Söremark R. Nickel allergy and nickel-containing dental alloys. *Scand J Dent Res* 1982; 90: 163-167.
- Hey J, Beuer F, Bense T, Boeckler AF. Metal-ceramic-fixed dental prosthesis with CAD/CAM-fabricated substructures: 6-year clinical results. *Clin Oral Investig* 2013; 17: 1447-1451.
- Hey J, Beuer F, Bense T, Boeckler AF. Single crowns with CAD/CAM-fabricated copings from titanium: 6-year clinical results. *J Prosthet Dent* 2014; 112: 150-154.
- Boeckler AF, Lee H, Stadler A, Setz JM. Prospective observation of CAD/CAM titanium ceramic single crowns: a three-year follow-up. *J Prosthet Dent* 2009; 102: 290-297.
- Lovgren R, Andersson B, Carlsson GE, Odman P. Prospective clinical 5-year study of ceramic-veneered titanium restorations with the Procera system. *J Prosthet Dent* 2000; 84: 514-521.
- Boeckler AF, Lee H, Psoch A, Setz JM. Prospective observation of CAD/CAM titanium-ceramic-fixed partial dentures: 3-year follow-up. *J Prosthodont* 2010; 19: 592-597.
- Marklund S, Bergman B, Hedlund SO, Nilson H. An intraindividual clinical comparison of two metal-ceramic systems: a 5-year prospective study. *Int J Prosthodont* 2003; 16: 70-73.
- Kaus T, Probst L, Weber H. Clinical follow-up study of ceramic veneered titanium restorations—three-year results. *Int J Prosthodont* 1996; 9: 9-15.
- 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: 91-96.
- Bergman B, Nilson H, Andersson M. A longitudinal clinical study of Procera ceramic-veneered titanium copings. *Int J Prosthodont* 1999; 12: 135-139.
- Oyafuso DK, Ozcan M, Bottino MA, Itiniche MK. Influence of thermal and mechanical cycling on the flexural strength of ceramics with titanium or gold alloy frameworks. *Dent Mater* 2008; 24: 351-356.
- Yilmaz H, Dincer C. Comparison of the bond compatibility of titanium and an NiCr alloy to dental porcelain. *J Dent* 1999; 27: 215-222.
- Probst L, Maiwald U, Weber H. Three-point bending strength of ceramics fused to cast titanium. *Eur J Oral Sci* 1996; 104: 313-319.
- 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: 1230-1235.
- Togaya T, Suzuki M, Tsutsumi S, Ida K. An application of pure titanium to the metal porcelain system. *Dent Mater J* 1983; 2: 210-219.
- Akagi K, Okamoto Y, Matsuura T, Horibe T. Properties of test metal ceramic titanium alloys. *J Prosthet Dent* 1992; 68: 462-467.
- Kupper H. Pure titanium as an alternative material in restorative dentistry. *QDT Yearbook* 1992: 143-152.
- Miyakawa O, Watanabe K, Okawa S, Nakano S, Kobayashi M, Shiokawa N. Layered structure of cast titanium surface. *Dent Mater J* 1989; 8: 175-185.
- Boning K, Walter M. Ceramo-metallic bond of cast titanium. *Dtsch Zahnärztl Z* 1991; 46: 750-753.
- Oshida Y, Fung LW, Isikbay SC. Titanium-porcelain system. Part II: Bond strength of fired porcelain on nitrided pure titanium. *Biomed Mater Eng* 1997; 7: 13-34.
- Haag P, Andersson M, Nilner K. Porcelain bonding to titanium with two veneering principles and two firing temperatures. *Swed Dent J* 2013; 37: 143-151.
- Zhang CC, Ye JT, Zhang YP, Liao JK, Li BH. Effect of titanium preoxidation on wrought pure titanium to ceramic bond strength. *J Prosthet Dent* 2013; 109: 106-112.
- Lin MC, Tung KL, Lin SC, Huang HH. Bonding of dental porcelain to non-cast titanium with different surface treatments. *Dent Mater J* 2012; 31: 933-940.
- Troia MG Jr, Henriques GE, Mesquita MF, Fragoso WS. The effect of surface modifications on titanium to enable titanium-porcelain bonding. *Dent Mater* 2008; 24: 28-33.
- Guggenberger R. Rocatec system—adhesion by tribochemical coating. *Dtsch Zahnärztl Z* 1989; 44: 874-876.
- Kern M, Thompson VP. Effects of sandblasting and silica-coating procedures on pure titanium. *J Dent* 1994; 22: 300-306.
- Ino S, Toyoda M, Niiya T, Tamura T, Shibata T, Atsumi M, Hamano M. The effect of silica coating on the bonding strength of veneering composite resin to dental alloys. *J Jpn Prosthodont Soc* 2003; 47: 292-300.
- GC EUROPE. GC Initial Ti Technical Manual. 2008.
- Derand T, Hero H. Bond strength of porcelain on cast vs. wrought titanium. *Scand J Dent Res* 1992; 100: 184-188.
- Gilbert JL, Covey DA, Lautenschlager EP. Bond characteristics of porcelain fused to milled titanium. *Dent Mater* 1994; 10: 134-140.
- International Organization Standardization. Polymer-based crown and bridge materials: ISO 10477. ISO, 2004.
- Rasband WS. ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://imagej.nih.gov/ij/>, 1997-2012.
- International Organization Standardization. Metal-ceramic dental restorative systems: ISO 9693. ISO, 1999.
- 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.
- Golebiowski M, Wolowiec E, Klimek L. Airborne-particle abrasion parameters on the quality of titanium-ceramic bonds. *J Prosthet Dent* 2015; 113: 453-459.
- Zinelis S, Barmpagadaki X, Vergos V, Chakmakchi M, Eliades G. Bond strength and interfacial characterization of eight low fusing porcelains to cp Ti. *Dent Mater* 2010; 26: 264-273.
- Oka K, Hanawa T, Kon M, Lee HH, Kawano F, Tomotake Y, Matsumoto N, Asaoka K. Effect of barium in porcelain on bonding strength of titanium-porcelain system. *Dent Mater J* 1996; 15: 111-120.
- Hanawa T, Kon M, Ohkawa S, Asaoka K. Diffusion of elements in porcelain into titanium oxide. *Dent Mater J* 1994; 13: 164-173.
- Wang RR, Welsch GE, Monteiro O. Silicon nitride coating on titanium to enable titanium-ceramic bonding. *J Biomed Mater Res* 1999; 46: 262-270.
- King BW, Tripp HP, Duckworth WH. Nature of adherence of porcelain enamels to metals. *J Am Ceram Soc* 1959; 42: 504-525.
- Rammelsberg P, Aschl I, Pospiech P. Verbundfestigkeit niedrigschmelzender Keramiken zu Titan unter Berücksichtigung der Oberflächenkonditionierung. *Dtsch Zahnärztl Z* 53; 3: 1998.
- Onda T, Shibuichi S, Satoh N, Tsujii K. Application of fractals to surface science. *Oyobuturi* 1995; 64: 788-792.
- Isu N. Stain-free housing materials inspired from snail shell surface. *J Jpn Weld Soc* 2009; 78: 187-190.