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Influence of Surface Treatments on Adhesion of Porcelain to Titanium

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Bond strength; cp Ti; pretreatment; veneering porcelain; strain energy release rate; surface roughness.

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Abstract

Purpose: This study evaluated the effect of etching solution surface treatments on the surface characteristics of titanium and adhesion of titanium/porcelain system by means of strain energy release rate (G-value, J/m^2).
Materials and Methods: Two hundred and forty five specimens of cp Ti plates were prepared. The specimens were divided into five groups in each test according to the surface treatment used; Gr MC (machined control), Gr AP (airborne particle abrasion), Gr E15, Gr E30, and Gr E60 (etching solution applied for 15, 30, and 60 minutes, respectively). The treated surfaces were characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Three types of porcelains (Duceratin, Vita Titankeramik, Ti-22) were used to test adhesion with cp Ti. Following the four-point bending interfacial fracture test, the peeled fracture surfaces were examined using SEM. Data were analyzed using ANOVA and Tukey HSD test. Statistical significance was set at the 0.05 probability level.
Results: AFM and SEM analyses showed that the surface topography of cp Ti was modified after treatments. Bond strength values were significantly affected by surface treatment and by type of porcelain ($p < 0.05$). The cp Ti/Duceratin (E30 and E60 minutes) groups showed the highest G-value among the groups. Modes of failure were mixed and interfacial adhesive.
Conclusions: Adhesion between cp Ti and porcelain could be enhanced by the use of experimental hot etching solution prior to porcelain firing as an alternative modality to the airborne-particle abrasion method.

In recent years, the use of commercially pure titanium (cp Ti) and Ti alloys in restorative dentistry has increased due to their superior biocompatibility, corrosion resistance, high strength-to-weight ratio, and low cost.[1,2] However, due to the highly oxidative nature of Ti surfaces, Ti has a lower bond strength with low-fusing porcelain.[3,4] During porcelain firing, a thick, nonadherent layer of titanium oxide forms on the Ti surface, adversely affecting the Ti/porcelain bond.[4-6]

Enhancing the adhesion of porcelain to Ti is important for improving its clinical success.[7] Various surface treatments have been applied to the surface of titanium to improve its bond strength with porcelain, including airborne-particle abrasion, gold coating, chromium plating, chemical baths, silicon nitride, and ceramic coating.[8-14] Airborne-particle abrasion could distort the surface of Ti and contaminate it with alumina particles, which could weaken the interfacial bond strength between Ti and porcelain.[12,15] Chemical treatments of the Ti surface prior to porcelain firing have been recommended as alternative techniques to airborne-particle abrasion treatment.[12]

An experimental hot chemical etching solution has been applied to etch the wings, roughen the surface, and improve the bond strength of Maryland bridges.[16] The possibility of performing this technique in the dental office as well as in the laboratory[16-18] makes this method particularly useful for treating Ti substrate. The purpose of this study was to evaluate the effect of experimental chemical etching treatments on the surface roughness and topography of Ti surfaces as well as the bond strength of different low-fusing porcelains bonded to Ti compared with machining and airborne-particle abrasion methods. The null hypotheses tested were: (1) the surface pretreatments will not influence the surface characteristics of Ti; (2) the interfacial bond strength between Ti and veneering porcelain will not be affected by the surface pretreatments of Ti.

Materials and methods

Two hundred and forty five specimens of machined cp Ti plates (ASTM, Grade II, Modern Techniques and Materials

Engineering Center, Cairo, Egypt) were ground on a 600-grit silicon carbide paper (Leco Co., St. Joseph, MI) placed on a platform under running water for 5 minutes and then cleaned in an ultrasonic bath (Sonorex, Bandelin Electronics GmbH & Co. KG, Berlin, Germany) filled with distilled water for 5 minutes.

Specimen preparation

The specimens in each test were divided into five groups according to the method of surface treatment applied, as follows:

Group MC: Machined control group; the specimens were exposed only to grinding and ultrasonic cleaning as mentioned above.

Group AP: Airborne-particle abrasion group; the specimens were abraded with alumina particles (Al_2O_3) (110 μm) (Korox, Bego, Bremen, Germany) with a dental airborne-particle abrasion unit (Micro-Blaster; Daedong Industrial Co., Ltd., Daegu, Korea) at 2 bar pressure for 20 seconds, and the distance was maintained at 15 mm between the nozzle tip and the specimen surface.

Group E15: The specimens were immersed in experimental hot etching solution: A solution with 800 mL of methanol, 200 mL of 37% HCl, and 2 g of ferric chloride ($FeCl_3$) was heated to 70°C in a water bath during the etching process according to a protocol previously proposed by Ferrari et al for conditioning the wings of Maryland bridges.[16] The cp Ti plates were immersed in the solution for 15 minutes.

Group E30: The specimens were immersed in the experimental hot etching solution for 30 minutes.

Group E60: The specimens were immersed in the experimental hot etching solution for 60 minutes.

After surface treatments of cp Ti plates, the specimens were cleaned in an ultrasonic bath filled with distilled water for 5 minutes.

Atomic force microscopy (AFM) evaluation

The surface microtopography of the treated cp Ti plates (10 mm × 10 mm × 1 mm) (n = 10/group) was characterized by contact-mode AFM (Autoprobe CP- II, Veeco, Santa Clara, CA). The radius of curvature of the scanning tip was 10 nm. Images were recorded with a scan rate of 1 Hz at a resolution of 512 × 512 pixels per image and scanning area of 10 μm × 10 μm. The average surface roughness (R_a) of the cp Ti specimen after different treatments was recorded in nanometers. R_a for each specimen was measured at three sites, and the mean roughness average was then calculated. Surface roughness mean values were compared with one-way ANOVA and a Tukey HSD test. Statistical significance was set at the 0.05 probability level.

Scanning electron microscopy (SEM) evaluation

The surface morphology of the treated cp Ti plates (10 mm × 10 mm × 1 mm) (n = 3/group) were imaged using SEM (JEOL, JXA-840A, JEOL Ltd., Tokyo, Japan) at magnifications of 750× to assess changes in surface topography.

Strain energy release rate test

One hundred and eighty rectangular specimens of cp Ti plates (30 mm × 8 mm × 1.5 mm) were divided into five groups according to surface modification procedures as described earlier (n = 36/group). Each group was further subdivided into three subgroups according to the type of low-fusing porcelain used (n = 12/group). Three brands of low-fusing porcelains were used in combination with cp Ti, namely Duceratin Kiss (DK) (DeguDent GmbH, Dentsply International, Hanau, Germany), Vita Titankeramik (VT) (Vita Zahnfabrick, Bad Säckingen, Germany), and Super Porcelain Ti-22 (ST) (Noritake, Nagoya, Japan). A split Teflon mold (30 mm × 8 mm × 1.5 mm) was used to apply each type of porcelain onto the Ti plate according to the manufacturer's instructions in a dental vacuum porcelain furnace (Programat P500, Ivoclar Vivadent, Jagst, Germany). Both surfaces (30 mm × 8 mm) of the specimens were ground to achieve flat and smooth surfaces using 240-grit and 320-grit silicon carbide paper (Leco Co.), respectively.[3] The porcelain surface that would be in contact with the rollers of the four-point bending jig was additionally polished with 45 μm diamond abrasive using a rotary polishing machine (Cooke Throughton, Simms Ltd., York, UK).

After that, notching across the width and entirely through the depth of the porcelain layer and in the center of the specimen was made using a water-cooled low-speed diamond wafering saw blade (Isomet, Buehler GmbH, Düsseldorf, Germany), on which a micrometer was attached. This technique provides an accurate notch of 0.4 mm width and 1.5 mm depth (the thickness of porcelain). A pre-crack was created in a specially designed bending apparatus, on which the applied load is controlled by a screw-knob, and the specimen is supported completely on rubber. The pre-crack started from the base of the notch, and it extended along the interface with a total length of approximately 2 mm.[3] The initiation of cracking from the base of the notch and along the interface was identified under a light microscope.

The pre-cracked specimens were then placed in a four-point-bending apparatus mounted in a universal testing machine (Model TT-B, Instron Corp., Canton, MA) with the inner rollers 14 mm and the outer rollers 26 mm. The diameter of the rollers was 1.7 mm, and the rollers were made of stainless steel. They were subjected to load at a 0.05 mm/min crosshead speed until the crack reached the inner rollers. The load and crosshead displacement data were collected for calculation of the strain energy release rate, G.

The strain energy release rate, G, is given by[19]

$$G = \frac{\eta\left[P^2 l^2\left(1 - \nu_t^2\right)\right]}{E_t b^2 h^3} \quad (1)$$

where P is the load to stably propagate the crack, l the moment arm or distance between inner and outer load line (rollers) on the same side, ν_t and E_t are Poisson's ratio and elastic modulus of Ti substructure (0.3 and 107.2 GPa),[20] respectively, and b and h are the specimen width and total thickness, respectively.

Table 1 Mean and standard deviations of the strain energy release rate (G values, J/m^2) of cp Ti/porcelain combinations with different treatments and surface roughness values (R_a, nm) of cp Ti plates

	cp Ti/porcelain (G value, J/m^2)†			
Surface treatment	cp Ti/DK	cp Ti/VT	cp Ti/ST	cp Ti (R_a, nm)*
MC	10.13 ± 1.47^{Aa}	8.49 ± 1.03^{Aab}	6.56 ± 0.90^{Ab}	40.64 ± 3.02^{A}
AP	18.39 ± 1.68^{Ba}	19.18 ± 1.85^{Ba}	12.09 ± 1.31^{Bb}	351.75 ± 30.77^{B}
E15	19.72 ± 1.78^{Ba}	15.61 ± 1.29^{Cb}	14.14 ± 1.54^{Bb}	92.18 ± 7.88^{C}
E30	30.74 ± 2.54^{Ca}	29.73 ± 2.20^{Da}	18.66 ± 2.03^{Cb}	142.81 ± 18.09^{D}
E60	34.52 ± 3.17^{Da}	32.31 ± 2.56^{Da}	24.38 ± 2.38^{Db}	217.5 ± 17.52^{E}

†Mean values represented with same superscript uppercase letters (column) or lowercase letters (row) are not significantly different according to Tukey's test ($p > 0.05$) for G-values (J/m^2).

*Mean values with different superscript uppercase letter (column) are significantly different ($p < 0.05$) for R_a (nm) values.

The non-dimensional parameter η will be calculated as follows:

$$\eta = \left(\frac{3}{2}\right) \times \left[\frac{1}{\left(h_t/h\right)^3} - \frac{\lambda}{\left\{\left(h_p/h\right)^3 + \lambda\left(h_t/h\right)^3 + 3\lambda\left(h_p h_t/h^2\right)\left[\left(h_p/h\right) + \left(\lambda h_t/h\right)\right]^{-1}\right\}}\right] \quad (2)$$

With

$$\lambda = \frac{E_{t(1-\nu_p^2)}}{E_{p(1-\nu_t^2)}} \quad (3)$$

where ν_p and E_p are Poisson's ratio and elastic modulus of porcelain (DK: 0.2, 67.8 GPa; VT: 0.2, 66.3 GPa; ST: 0.2, 59.1 GPa),[21] respectively, and h_p and h_t are thickness of porcelain and Ti, respectively. A statistical analysis of the strain energy release rate (G) values was conducted using two-way ANOVA considering two factors (surface treatment and type of porcelain) and their interaction. Multiple comparisons were made by Tukey HSD test. Statistical significance was set at the 0.05 probability level. Following the four-point bending interfacial fracture test, three representative specimens of each group of titanium/porcelain systems were used to examine the peeled fracture surfaces using SEM at magnification of 500×.

Results

Means and standard deviations of the cp Ti average surface roughness (R_a) are presented in Table 1. In general, E15, E30, and E60 groups showed significantly higher R_a (nm) values compared with the MC group ($p < 0.05$); however, the AP group revealed significantly higher R_a value than the other groups ($p < 0.05$).

Representative AFM and SEM images of the treated cp Ti plates are presented in Figures 1 and 2, respectively. The surfaces of specimens treated by AP showed macro-sized elevated and depressed areas, which possibly resulted from the high impact force of blasting particles (Figs 1B and 2B). Experimental etching treatments of the cp Ti surfaces resulted in a rough and irregular surface with numerous fine surface elevations (Figs 1C-E and 2C-E).

The mean of the strain energy release rate (G-value, J/m^2) and standard deviations are presented in Table 1. The results of bond strength values achieved with E30 and E60 groups were significantly higher than the MC and AP groups for the three types of veneering porcelains tested ($p < 0.05$). Two-way ANOVA of the strain energy release rate (G-value) testing data revealed that there were significant interactions between the surface treatment and type of veneering porcelain ($p < 0.001$). The cp Ti/DK (etching for 30 and 60 minutes) groups showed the highest G-value among the groups. The cp Ti/VT (etching for 30 and 60 minutes) groups were statistically significantly different from the MC and AP groups ($p < 0.05$) (Table 1). For cp Ti/ST, the MC group showed the lowest bond strength value among the groups. The mode of failure was mixed adhesive and cohesive within the porcelain and interfacial adhesive failure between cp Ti and porcelain for the differently tested groups (Fig 3).

Discussion

The results of this study require the rejection of the null hypothesis, as differences in surface characteristics of titanium substrate and bond strengths between titanium and veneering porcelain were recorded between the experimental groups. The present study verified the effect of the experimental hot etching solution treatment on the surface topography of cp Ti plates as revealed by AFM and SEM evaluation (Figs 1 and 2). Surface roughness enhances mechanical interlocking with veneering porcelain, considered as a significant factor that could influence bond strength.[22] Airborne-particle abrasion is expected to enhance the bond strength by providing mechanical interlocking, increasing wettability, and surface area.[8,23] On the other hand, it was reported in previous studies that airborne-particle abrasion contaminates the Ti surface, possibly compromising its corrosion resistance and biocompatibility.[15,24] AP produced a higher roughness of Ti surface than the other groups (Table 1). Surface roughness should increase surface area and, accordingly, may enhance the titanium/porcelain bond.[12] For the groups etched for 30 or 60 minutes, the surface roughness was 142.81 ± 18.09 and 217.5 ± 17.52 nm, respectively; however, the bond strength for these groups was higher than the AP group (Table 1). This means that roughening of the Ti surface by airborne-particle abrasion does not essentially enhance the bond

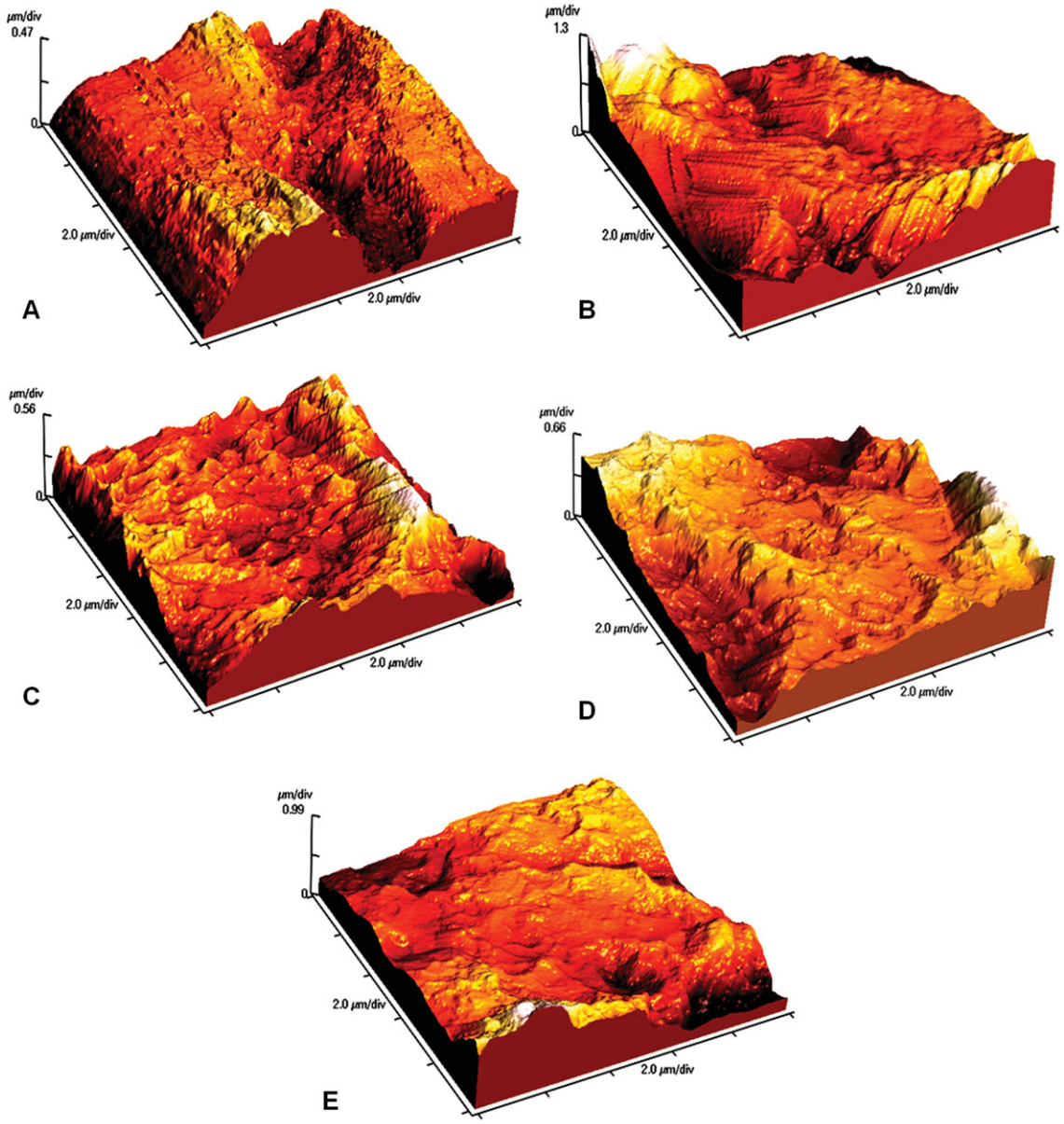

Figure 1 AFM images of cp Ti plates: (A) Machined control; (B) Airborne-particle abrasion; (C-E) Experimental hot-etching solution applied for 15, 30, and 60 minutes, respectively.

strength as compared with E30 and E60 groups. Additionally, the surface roughness could increase the stress concentration at the metal/porcelain interface and produce sharp angles about asperities that could prevent complete wetting and cause voids at metal/porcelain interfaces.[25]

The adhesion between Ti and porcelain was determined by means of strain energy release rate (G-value) using a four-point bending test based on a fracture mechanics approach. It has been shown that a fracture mechanics approach is more accurate to evaluate the adhesive bonded interface.[26] The interfacial strain energy release rate determined in this study showed that the cp Ti/DK etching for 30- and 60-minutes groups showed the highest G-value among the groups. This finding was supported by the SEM photomicrographs of the peeled Ti surface, which showed that the mode of failure was mixed for these groups (Fig 3A and D). On the other hand, for cp Ti/VT and cp Ti/ST, the control groups showed the lowest bond strength values among their groups, and the modes of failure were interfacial adhesive (Fig 3E and F). The inference of these outcomes is that the porcelain bonding layer could not entirely prevent the oxidation of Ti, thus weakening the interfacial bonding.[11] A sandwich layer of Ti oxide formed at the interface during

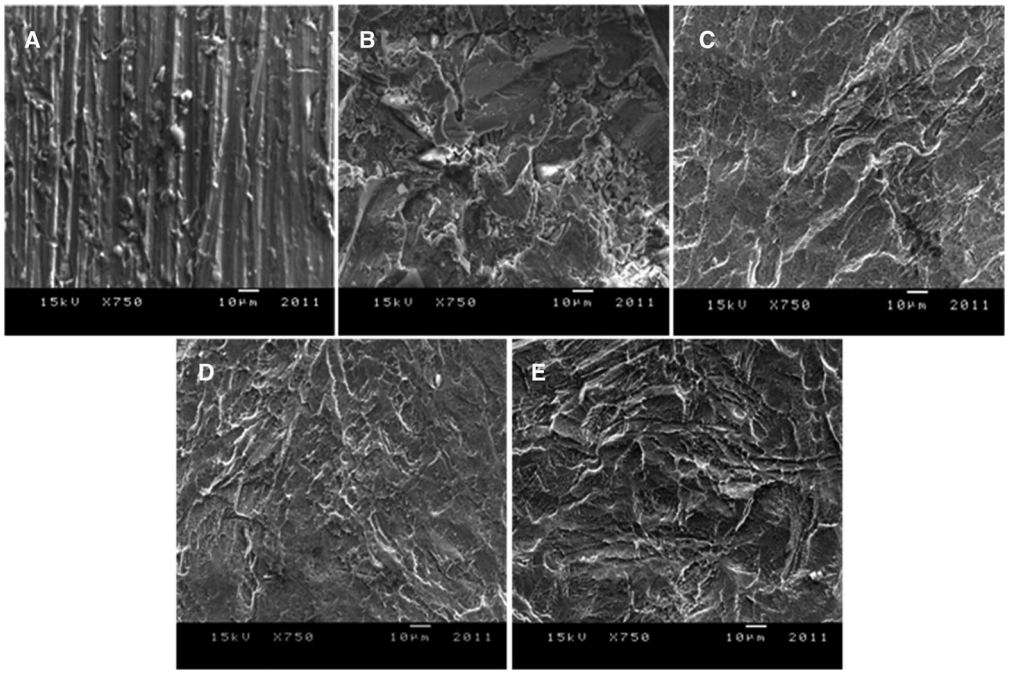

Figure 2 SEM photomicrographs of cp Ti plates: (A) Machined control; (B) Airborne-particle abrasion; (C-E) Experimental hot-etching solution applied for 15, 30, and 60 minutes, respectively.

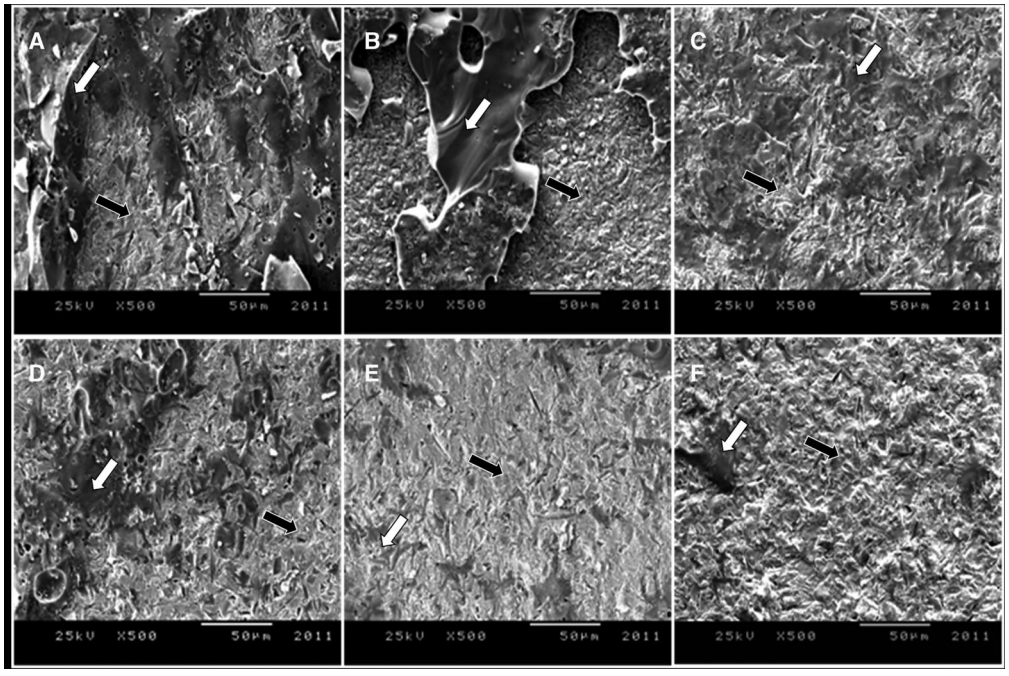

Figure 3 Representative SEM photomicrographs of the peeled surface of cp Ti/veneering porcelain system: (A-D) Mixed bond failure for cp Ti/DK (etching for 30 minutes), cp Ti/VT (etching for 15 minutes), cp Ti/ST (etching for 60 minutes), and cp Ti/DK (etching for 60 minutes) groups, respectively. (E, F) Adhesive bond failure for cp Ti/VT (machined control) and cp Ti/ST (machined control) groups, respectively. White arrows indicate retained porcelain; black arrows indicate Ti.

porcelain firing cycles at which failure occurs. These oxidation processes could also make stresses in the oxide scale as well as in Ti, causing reduction or loss of adherence.[11,27] This explanation is in agreement with previous studies.[4,10-13,28]

It could be assumed that surface alterations by chemical solutions altered the natural chemical composition of the cp Ti surfaces, enhancing the bonding of porcelain to the Ti through the chemical adhesion mechanism.[29] Since the composition of oxide layer is a significant aspect for enhancing the bond strength between metal and porcelain,[2] the modification of the Ti surface could modify the feature of the oxide layer produced prior to and during porcelain firing.[29] Apparently, the chemical solution treatments resulted in a modified surface that produced an oxide layer of improved quality and capability to prevent adhesion problems during the porcelain sintering cycles, including the growth of the oxide layer at higher temperatures or poor adherence of the self-formed oxide on the Ti substrate.[29,30]

A limitation of this study was that the effect of other factors that could have a significant influence on Ti/porcelain bonding systems, such as long-term storage under simulated oral conditions and fatigue loading, which were not investigated in this study, could also affect adhesion and durability of Ti/porcelain bonding systems. Moreover, further studies are needed for more clear evaluation of their performance during clinical service.

Conclusions

Based on the results presented and within the limitations of this study, the following conclusions can be made. The use of the experimental hot-etching solution (30 or 60 minutes) as a pretreatment for cp Ti prior to porcelain firing will provide enhanced bond strength by improving the micromechanical retention. This treatment could be considered as an alternative modality to the airborne-particle abrasion method.

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