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Acid Etching of Titanium for Bonding with Veneering Composite Resins

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Commercially pure titanium (cpTi) was etched using three concentrated acids: 18% HCl, 43% H_3PO_4, and 48% H_2SO_4. The bond strengths between five types of veneering composite resin and eight cpTi treatments (involving combinations of sandblasting, acid etching in 48% H_2SO_4, and vacuum firing) were determined before and after 10,000 and 20,000 thermal cycles. There were no significant differences in the bond strength of resin to cpTi after etching in 48% H_2SO_4 at 90℃ for 15 minutes, at 60℃ for 15, 30, or 60 minutes, and after sandblasting with and without vacuum firing ($p>0.05$); moreover, these treatments yielded the highest values. As for vacuum firing, it had no significant effect on resin bond strength to cpTi before or after 10,000 and 20,000 thermal cycles. We therefore concluded that acid etching in concentrated H_2SO_4 is a simple and effective surface modification method of titanium for bonding to veneering composite resins.

Key words: Titanium, Acid etching, Composite resin

INTRODUCTION

Commercially pure titanium (cpTi) and its alloys are frequently used for dental prosthetic devices[1)]. When they are used to restore anterior teeth, titanium prostheses are generally covered with an esthetic material, such as a composite resin. To obtain good retention between the metal core and resin, retention beads are generally cast on the metal surface to promote mechanical retention — and this form of mechanical retention has the highest survival rate in clinical prostheses[2)]. However, a non-mechanical retention method for the metal core is preferred to minimize the removal of sound enamel and dentin when preparing the tooth for cementation. Furthermore, a machining method — versus casting — was developed recently for the fabrication of titanium prostheses. Consequently, there arose an intense, two-pronged effort to develop a new adhesive system that would deliver improved adhesion with the titanium substrate produced by machining. The two key approaches were: focus on the development of adhesion-promoting monomers[3,4)], as well as explore pretreatment methods that would modify the substrate surface for optimal adhesion[5–7)].

In the quest for an optimal pretreatment method for titanium, the authors have examined supercritical water[8)] and alkaline[9)] treatments. Both treatments significantly increased the bond strength of treated titanium to veneering resins. Essentially, these treatments depend on the roughened, tough oxide texture on the surface of treated titanium. However, it was reported[10)] that after thermal cycling, the bonding strength decreased remarkably such that the bonding durability was no longer considered sufficient for long-term restorations. On the other hand, the authors have also reported that etching in concentrated H_2SO_4 at 40 to 90℃ produced a highly roughened surface on cpTi and Ti-6Al-4V alloy[11,12)]. Therefore, acid etching might be an alternative, effective pretreatment for titanium for the purpose of promoting better bonding to veneering resins.

However, acid etching of Ti-6Al-4V alloy provides only adequate dry strength with reportedly poor durability[13)]. In this study, therefore, we examined whether etching in concentrated acid enhanced the bond strength durability between cpTi and veneering resin. To this end, we measured the bond strength of acid-etched cpTi to veneering resins before and after thermal cycling, and then discussed the possibility of using acid etching as a pretreatment method for dental restoratives comprising titanium substrate and veneering composite resins.

MATERIALS AND METHODS

Substrate metal

CpTi plates (KS-50, JIS type 2, Kobelco, Kobe, Japan) were used as the substrate. Metal plates measuring 20 × 15 × 1 mm were sandblasted (Hi-Blaster II, Shofu, Kyoto, Japan) with alumina powder (70 μm), cleaned in distilled water supersonically, and dried in air at room temperature.

Acid etching

CpTi plates were etched using 11 treatments involving differences in the acid solution (18% HCl, 43% H_3PO_4, and 4.8 and 48% H_2SO_4), soaking temperature (RT, 40, 60, and 90℃), and soaking time (15, 30, and 60 minutes). After etching, specimens were rinsed thoroughly with distilled water and air-dried at room temperature. A composite veneering resin (Solidex) was attached to the cpTi specimens for the bonding test. In addition, eight surface treatments (involving combinations of sandblasting, acid etching, and vacuum firing, as shown in Table 1) were tested to determine the conditions that provide the optimal bonding durability between the treated cpTi and the veneering composite resin. Some of the etched and sandblasted specimens were heated at 600℃ in a vacuum for 10 minutes using a dental porcelain furnace (Jelenko Cerafusion VPF, J. Morita, Tokyo, Japan). Five types of composite resin, listed in Table 2, were veneered to these cpTi specimens for the bonding test.

Surface roughness of the dried specimens was analyzed using a surface roughness tester (Surfcom 130A, Accretech, Tokyo, Japan). Three measurements were performed for each specimen according to ISO 4287:1997 recommendation. The arithmetic mean deviation of the profile (Ra) was measured with a cutoff value of 0.8 mm, a measurement length of 5.0 mm, a measurement speed of 0.6 mm/s, and a Gaussian filter. The X-ray diffraction (XRD) patterns of treated and untreated cpTi were recorded with an X-ray diffractometer (RINT-2500, Rigaku, Tokyo, Japan) at 40 kV and 120 mA. Scans were conducted over a 2θ angular range between 20 and 60° at 1°/min. The surfaces and sections of cpTi after etching were observed under a scanning electron microscope (JSM-5510LV, JEOL, Tokyo, Japan).

Veneering resins

Table 2 lists the product names, manufacturers, and polymerization conditions for the five light-cured composite resins used in this study. For Solidex, the primer resin paste was painted on the treated surface of the substrate using a small brush and polymerized for one minute using a visible light-curing unit (α-light, GC Corp., Tokyo, Japan). The body resin was used to fill a hole 6 mm in diameter in a transparent acrylic plate of 2-mm thickness on the opaque, treated metal plate, and then polymerized for three minutes using the same visible light-curing unit. For Cesead II, the metal primer paste was painted on the treated surface of the substrate using a small brush. After air-drying, the opaque primer was also

Table 1 CpTi treatment conditions used in this study

No.	Code	Sandblasting with 70-μm alumina	Etching in 48% H_2SO_4 at 60℃ for 60 min	Vacuum firing at 600℃ for 10 min
1	A	–	–	–
2	B	–	–	Vacuum firing
3	C	–	Etching	–
4	D	–	Etching	Vacuum firing
5	E	Sandblasting	–	–
6	F	Sandblasting	–	Vacuum firing
7	G	Sandblasting	Etching	–
8	H	Sandblasting	Etching	Vacuum firing

Table 2 Veneering resins used in this study

Product	Manufacturer		Lot number	Drying and irradiation conditions
Solidex	Shofu Inc.	Primer paste	060348	α-Light, 1 min
		Body paste	080232	α-Light, 3 min
Ceramage	Shofu Inc.	Metal Link	010406	Natural dry, 10 sec
		Pre-Opaque	010402	α-Light, 1 min
		Opaque	010402	α-Light, 3 min
		Body resin	010410	α-Light, 1 min
Cesead II	Kuraray Co. Ltd.	Alloy primer	0051AA	Natural dry
		Opaque primer	0086BA	Natural dry, 30 sec
		Body opaque	0081EB	α-Light, 3 min
		Body resin	0603AA	α-Light, 3 min
Epricord	Kuraray Co. Ltd.	Alloy primer	0151AA	Natural dry
		Opaque primer	0125AA	Natural dry, 30 sec
		Opaque resin	0128AA	α-Light, 3 min
		Body resin	0007BA	α-Light, 3 min
Sirius	Heraeus-Kulzer GmbH	Retention flow	030031	α-Light, 1 min
		Opaque	030030	α-Light, 3 min
		Dentine	010023	α-Light, 3 min

painted on and dried in the same manner. After drying, the opaque body was painted and polymerized for three minutes using the light-curing unit. Subsequently, the hole in the acrylic plate was filled with the body resin and polymerized for three minutes using the light-curing unit. The other resins were prepared in a similar manner.

Bonding test

Shear bond strength between the titanium substrate and veneering resin was determined after a 24-hour immersion in water at 37℃ and after 10,000 and 20,000 thermal cycles at 60℃ and 4℃ with a dwelling time of one minute each. The substrate metal was clamped in a vise. By means of a universal testing machine (TCM-1kNB, Minebea, Tokyo, Japan) at a crosshead speed of 5 mm/min, the resin disk was pulled with a stainless steel orthodontic wire with a rectangular cross-section. Four specimens were used for each condition before thermal cycling, and two specimens for each condition after 10,000 and 20,000 thermal cycles. Five-way analysis of variance was applied to determine the effect on bond strength with sandblasting, acid etching, vacuum firing, veneering composite resin, and thermal cycling as factors.

RESULTS

Fig. 1 shows the SEM photographs of cpTi surface after etching in 18% HCl, 43% H_3PO_4, and 48% H_2SO_4 at 60℃ for 60 minutes, followed by sandblasting with 70-μm alumina powder. A dendrite pattern was observed on the cpTi surface etched in 18% HCl. The surface etched in 43% H_3PO_4 showed clearer grain boundaries and smoother grains than with 18% HCl. After etching in 48% H_2SO_4, the grain boundary was remarkably distinct and micropores measuring less than 1μm were formed in the crystal grain. After sandblasting, sharp edges and sharp grooves were formed due to the mechanical action.

Fig. 2 shows the X-ray diffraction patterns of cpTi before and after etching in 48% H_2SO_4 at 60℃ for 60 minutes with and without vacuum firing at 600℃ for 10 minutes. The untreated cpTi showed only the diffraction peaks assigned to α-Ti, while the diffraction peaks of both α-Ti and TiH_2 were observed after etching in 48% H_2SO_4. After vacuum firing, the TiH_2 peaks disappeared and those of TiO_2 (rutile) were observed.

Fig. 3 shows the surface roughness (Ra) of cpTi before and after etching in various ways as well as after sandblasting. The Ra values of cpTi after etching in 43% H_3PO_4 at 90℃ for 60 minutes or in 48% H_2SO_4 at 60℃ for 30 minutes were slightly higher than that with no treatment ($p<0.05$). The Ra values of cpTi after etching in 48% H_2SO_4 at 90℃ for 15 minutes and at 60℃ for 60 minutes and after sandblasting were significantly higher than that with no treatment ($p<0.01$). In particular, the Ra value of cpTi after etching in 48% H_2SO_4 at 60℃ for 60 minutes ranked the highest.

Fig. 4 shows the shear bond strengths of a veneering resin (Solidex) to cpTi before and after etching under various conditions and after sandblasting with and without vacuum firing, but before thermal cycling. There were no significant differences in the

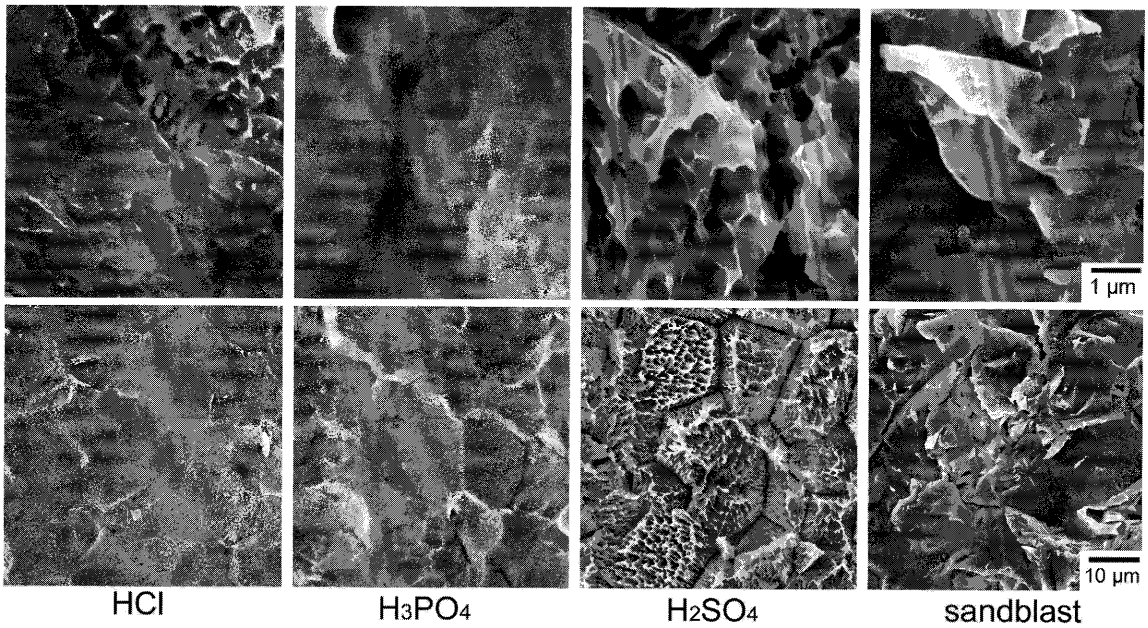

Fig. 1 SEM photographs of cpTi surface after etching in 18% HCl, 43% H_3PO_4, and 48% H_2SO_4 at 60℃ for 60 min, followed by sandblasting. Magnification of upper-row photos is 10 times greater than that of the lower-row ones.

bond strength of resin to cpTi after etching in 48% H_2SO_4 at 90℃ for 15 minutes, at 60℃ for 15, 30, or 60 minutes, or after sandblasting with and without vacuum firing ($p>0.05$). These values were the highest among all the treatments. The bond strengths of the other treatments with vacuum firing were significantly greater than without it ($p<0.05$).

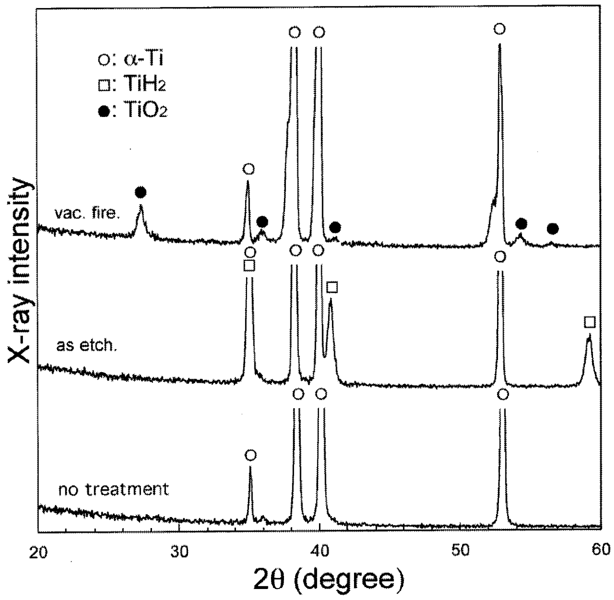

Fig. 2 X-ray diffraction patterns of cpTi before and after etching in 48% H_2SO_4 at 60℃ for 60 min with and without vacuum firing at 600℃ for 10 min.

Fig. 5 shows the relationship between surface roughness (Ra) and the bond strength of as-treated (left) and vacuum-fired cpTi (center), and the ratio of the vacuum-fired to the as-treated cpTi (right). The bond strengths were the same as shown for the 13 conditions in Fig. 4. Bond strength was independent of surface roughness and vacuum firing for Ra over 0.6 μm.

Subsequently, we focused on the effect of etching in 48% H_2SO_4 on bonding durability to several veneering resins. Fig. 6 shows the shear bond strengths of cpTi treated under eight conditions (Table 1) for five veneering resins (Table 2) before and after 10,000 and 20,000 thermal cycles. Table 3 shows the five-way analysis of variance for the bond strengths of the five veneering resins to cpTi treated under eight conditions before and after thermal cycling. Vacuum firing had no significant effect on bond strength ($p>0.05$). Sandblasting, acid etching, resin type, and thermal cycling all had a significant effect on bond strength ($p<0.01$). In particular, acid etching made the greatest contribution whereas sandblasting contributed the least. While condition G (sandblasting and etching) ($p>0.05$) gave the strongest bond out of the eight conditions, there were no significant differences in bond strength between conditions C (only etching) and G. Cesead II and Ceramage had a greater bond strength than Sirius, Solidex, and Epricord. In particular, Cesead II had excellent bonding durability even after 20,000 thermal cycles, whereas Sirius had poor durability.

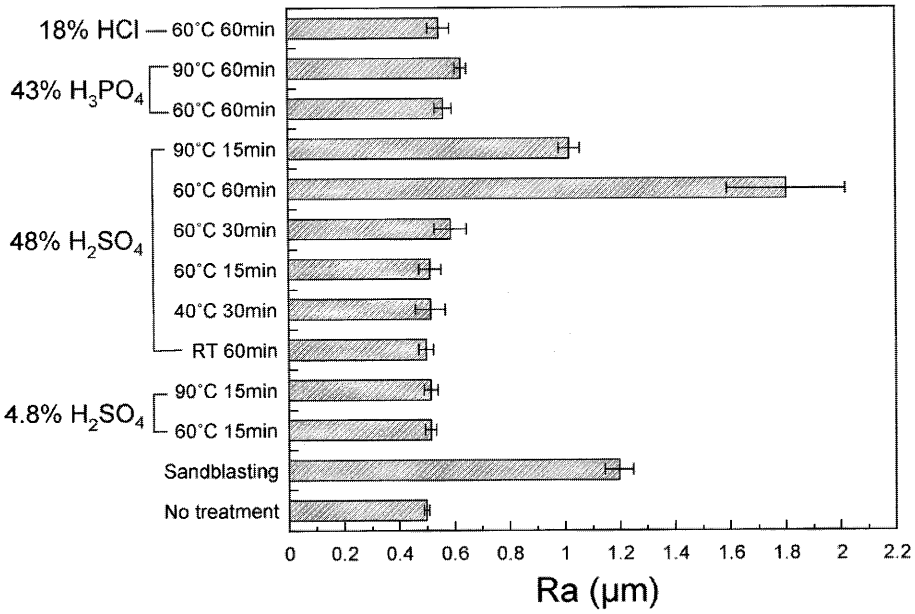

Fig. 3 Surface roughness (Ra) of cpTi before and after etching in 18% HCl at 60℃ for 60 min, 43% H_3PO_4 at 60 and 90℃ for 60 min, 48% H_2SO_4 at RT-90℃ for 15-60 min, and 4.8% H_2SO_4 at 60 and 90℃ for 15 min, and after sandblasting.

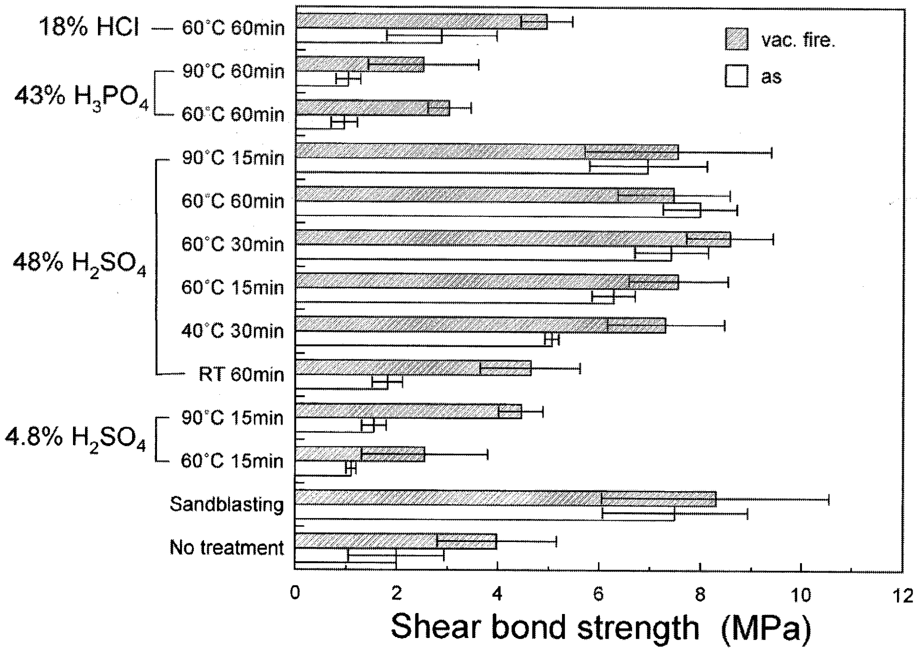

Fig. 4 Shear bond strength of a veneering resin (Solidex) to cpTi before and after etching in 18% HCl at 60℃ for 60 min, 43% H_3PO_4 at 60 and 90℃ for 60 min, 48% H_2SO_4 at RT-90℃ for 15-60 min, 4.8% H_2SO_4 at 60 and 90℃ for 15 min, and after sandblasting with and without vacuum firing.

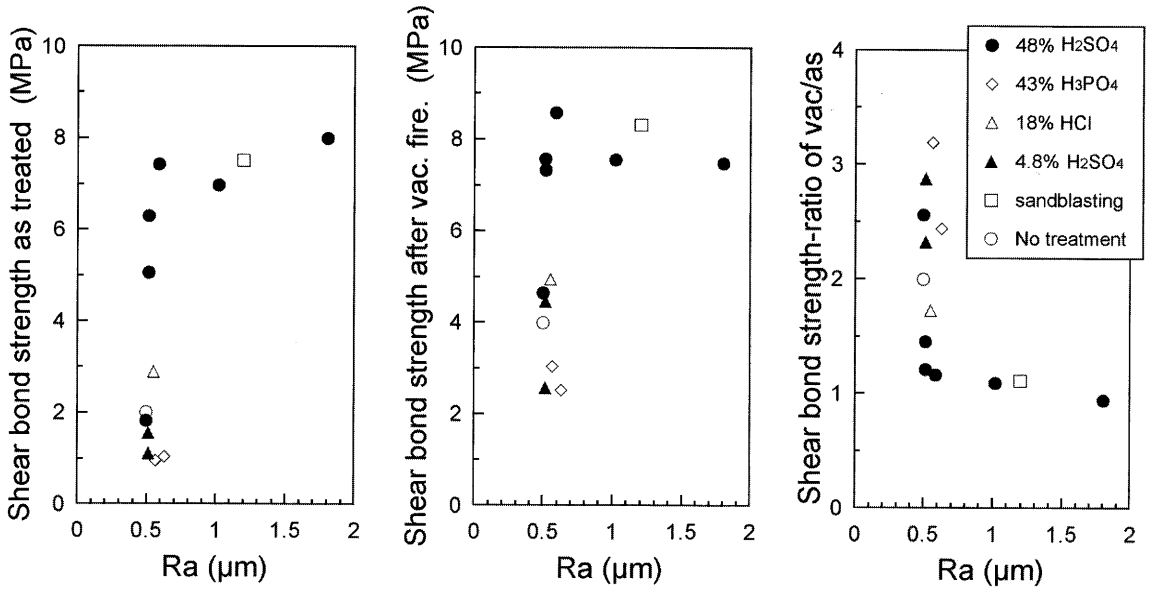

Fig. 5 Relationship between surface roughness (Ra) and average shear bond strength of as-treated cpTi (left) and vacuum-fired cpTi (center), and the ratio of the strengths of vacuum-fired to as-treated cpTi (right).

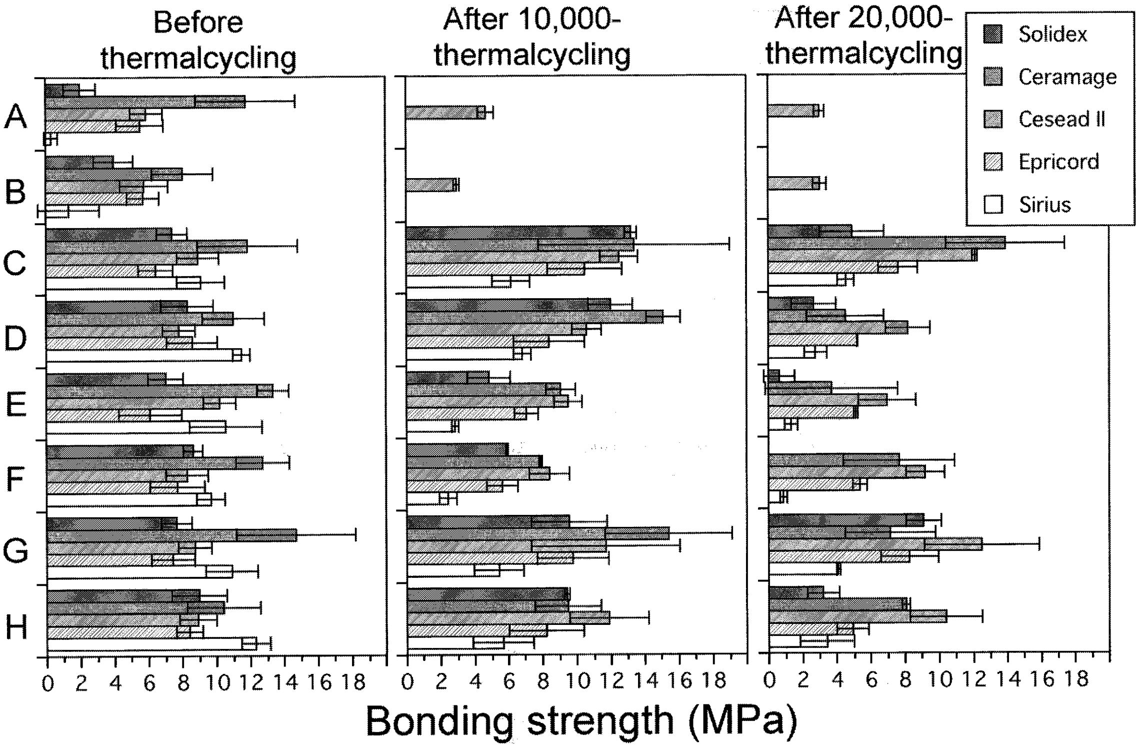

Fig. 6 Shear bond strengths of cpTi treated using eight conditions for five veneering resins before and after 10,000 and 20,000 thermal cycles.

DISCUSSION

Effect of acid etching on surface roughness and bond strength

Bond strength between resin and cpTi was independent of surface roughness and vacuum firing for Ra exceeding 0.6 μm (Fig. 5). But below this Ra range, vacuum firing was efficacious in increasing bond strength. Results of the present study led to the following three conclusions. First, TiH_2 had no effect on bond strength, although it was formed on the acid-etched surface and disappeared with vacuum firing as reported previously[11]. Hydrogen embrittlement of titanium can occur and that it depends on the hydrogen content. Judging from the SEM micrographs of the surface and cross-sections (data not shown), the thickness of the titanium hydride layer after etching in concentrated H_2SO_4 was less than 1 μm. After etching in HCl, it was reported that the calculated average thickness of TiH_2 in the steady state (after 5 hours) was approximately 600 nm in 29% HCl at 50℃[14]. After sandblasting and etching in a mixture of 10.6% H_2SO_4 and 63.6% HCl at 60 to 80℃ for three to 10 minutes[15], hydrogen was located in a layer approximately 150 nm thick[16]. Therefore, due to low hydrogen content, titanium hydride layer on the titanium surface did not reduce the bond strength between the resin and etched titanium.

Second, there was no linear relationship between the surface roughness of cpTi and the bond strength to resin. At Ra of about 0.6 μm, bond strength became independent of surface roughness. Indeed, above a critical surface roughness, bond strength between the resin and cpTi exceeded the strength of the resin itself. Therefore, adhesive fracture that occurred at the titanium-resin interface occurred below the critical value, whereas fractures that occurred above the critical value were a mixture of cohesive failure within the resin and adhesive failure at the interface. This meant that mechanical bonding contributed most to the bonding between the resin and cpTi.

Third, oxide formation might influence the efficacy of vacuum firing on increasing bond strength at low surface roughness. Previously, the authors had demonstrated that a small amount of oxide was effective in increasing bond strength due to micro-mechanical bonding[8]. However, macro-mechanical bond strength due to surface roughness would have a greater effect on bond strength in a substrate with a large surface roughness, as mentioned above.

Bonding durability

After thermal cycling the five resins veneered to cpTi treated under eight conditions, it was found that the factors of sandblasting, acid etching, resin type, and thermal cycling had significant effects on bond strength ($p<0.01$), whereas vacuum firing had no effect on bond strength ($p>0.05$; Fig. 6 and Table 3).

Table 3 Five-way analysis of variance of the bond strength of five veneering resins to cpTi treated using eight conditions involving sandblasting, acid etching, and vacuum firing

Source	d.f.	Sum of squares	Mean square	F-value	Contribution (%)
Sandblasting	1	267.96	267.96	67.78^{**}	4.63
Acid	1	1484.92	1484.92	375.59^{**}	25.63
Vacuum firing	1	12.81	12.81	3.24	0.22
Resin	4	768.29	192.07	48.58^{**}	13.27
Thermal cycling	2	750.73	375.37	94.94^{**}	12.96
Sandblasting* Acid	1	344.87	344.87	87.23^{**}	5.95
Acid* Thermal cycling	2	268.22	134.11	33.92^{**}	4.63
Resin* Thermal cycling	8	419.61	52.45	13.27^{**}	7.24
Sandblasting* Resin* Thermal cycling	8	202.78	25.35	6.41^{**}	3.50
Acid* Resin* Thermal cycling	8	153.98	19.25	4.87^{**}	2.66
Error	283	1118.57	3.95		
Total	319	5792.75			

$^{**}p<0.01$

Group information of main source

Source	Level	Data number	Mean	Standard deviation
Sandblasting	without	160	6.13	4.80
	with	160	8.01	3.26
Acid	without	160	5.08	4.17
	with	160	9.07	3.18
Vacuum firing	without	160	7.16 │	4.36
	with	160	6.98 │	4.06
Resin	Sirius	64	5.56 │	4.52
	Solidex	64	5.73 │	3.86
	Epricord	64	6.25	2.94
	Cesead II	64	8.34 │	2.87
	Ceramage	64	9.47 │	5.01
Thermal cycles	0	160	8.36	3.36
	10,000	80	6.96	4.80
	20,000	80	4.61	4.03

Common vertical lines indicate no statistically significant differences at $\alpha=0.05$.

Table 4 Composition of the primers used in this study

Product	Primer name	Composition
Solidex	Primer paste	4-AET, UDMA, aluminum-silicate glass
Ceramage	Metal Link	10-MDDT, 6-MHPA, acetone
Cesead II Epricord	Alloy primer	VBATDT, MDP, acetone
Sirius	Retention flow	Polyfunctional methacrylate, SiO_2 microfiller, pigment

4-AET: 4-acryloyloxyethyl trimellitate
10-MDDT: 10-metacryroxydecyl-6,8-dithioctanate
6-MHPA: 6-metacryloxyhexyl phosphonoacetate
VBATDT: 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithione
MDP: 10-methacryloyloxydecyl dihydrogen phosphate
UDMA: urethane dimethacrylate

Acid etching made the greatest contribution, whereas sandblasting contributed the least. In other words, H_2SO_4 etching alone was an adequate treatment to increase bonding to resins. Although vacuum firing eliminated all traces of titanium hydride and led to the formation of titanium oxide (Fig. 2), this had no effect on the bond strength to any resin.

Table 4 shows the composition of the primers used in this study. Sirius had a relatively high bond strength before thermal cycling, but its bond strength decreased dramatically with thermal cycling. This appeared to be caused by the absence of an adhesive agent in the "Retention flow" that was painted on before the body resin[17]. All the other primers contained some adhesive agent. The "Primer Paste" of Solidex had 4-AET as an adhesion-promoting monomer[18]. "Metal Link" of Ceramage contained 10-MDDT and 6-MHPA[19,20]. "Alloy Primer" of both Cesead II and Epricord contained VBATDT and MDP[18]. It was reported that the carboxylic acid derivative 4-AET and the phosphoric acid derivative MDP interact with metallic oxide films created on base metals[3,19–23], whereas VBATDT and 10-MDDT have affinities to noble metal elements, such as Au, Pd, Pt, and Ag, instead of base metals[19,24,25]. As for the carboxylic acid derivative 4-methacryloyloxyethyl trimellitate anhydride (4-META), its carboxylate groups are thought to interact with metallic oxide films created on base metals via hydrogen bonds[26]. When the carboxylate groups of 4-AET and the phosphoric groups of MDP and 6-MHPA bonded to the oxide on the titanium surface via hydrogen bonds, as with 4-META, the presence of OH seemed to play an important role. Results of the present study implied that a greater amount of OH in the surface layer would result in a stronger bonding due to hydrogen bonding between the surface and the resin. However, in our previous study, OH amount had no significant effect on the bond strength of resin to alkaline-treated titanium[9]. Furthermore, Cesead II and Epricord used the same primer but showed different results for bonding durability. It was possible that the difference in bonding durability stemmed from the difference in mechanical properties of individual opaque and body resins, thereby leading to differing results.

Concerning substrate pretreatment, we concluded that the contribution of micro-mechanical interlocking to the bond between titanium and resin was much greater than that of chemical bonding, although the adhesion between a polymer and a metal cannot be explained only by chemical interaction or solely by micro-mechanical linkage[27]. Both are responsible, and both do contribute to bonding strength and durability. Results of the present study suggested that acid treatment is a simple and effective way to modify the titanium surface for adhesion to resin, chiefly because this treatment produced a rough, active surface.

CONCLUSIONS

CpTi was etched using concentrated acids, and the bonding strength of acid-etched cpTi to veneering resins was determined by means of a pull-shear bonding method before and after thermal cycling. Etching in 48% H_2SO_4 resulted in increased surface roughness and increased bond strength compared to etching in 18% HCl or 43% H_3PO_4. Specimens etched in 48% H_2SO_4 at 60℃ for 60 minutes had the greatest bond strength to the five types of composite resin evaluated, before and after 10,000 and 20,000 thermal cycles. Sandblasting had little effect on bonding durability, while vacuum firing had no significant effect on the bond strength to any resin. Therefore, acid etching with concentrated H_2SO_4 is a simple and effective surface modification method of titanium for bonding to veneering composite resins.

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