# Effects of various surface treatment agents on the adhesion of the thermosetting facing resin to titanium

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**Abstract** : Studies have been conducted to examine the strength of the bond between thermosetting facing resin and the surface of titanium pretreated with various primers or by other methods. The effect of titanium-based organic coupling agents were assessed in an attempt of improving the strength of adhesion between titanium and thermosetting facing resin and of searching for surface treatment agents which have a high affinity for titanium. The bonding strength was also examined for specimens treated with Silicoater or conventional primers.

The bonding strength of Silicoater-treated specimens was highest and of specimens treated with any primer was lower. Exposure to thermal cycles resulted in lower bonding strength of both Silicoater-treated specimens and primer-treated specimens. The strength of TTIP-treated specimens heated at 400℃ was higher than that of primer-treated specimens. Thus, it was suggested that TTIP would have a higher affinity for the surface of titanium than conventional primers, allowing better bonding strength and durability.

**Key words** : titanium, thermosetting facing resin, organic coupling agent, titanium alkoxide, surface treatment agent

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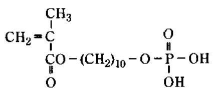
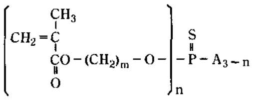
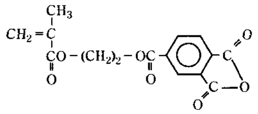
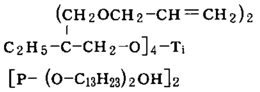
**Table 1.** Adhesive metal primers used.

| Primer | Code | Chemical name<br>(Manufacture. Lot. No.) | Formula |
|---|---|---|---|
| Phosphate | MDP | 10-Methacryloyloxydecyl dihydrogenphosphate<br>(Kurare Co. Ltd. Lot. No. 0068AF) |  |
| Thiophosphate | MEPS | 1-Thiophosphatemethacrylate<br>(GC Co. Ltd. Lot. No. 190871) |  |
| Carbonate | 4-META | 4-Methacryloxyethyl trimellitate anhydride<br>(Sun Medical Co. Ltd. Lot. 705054) |  |
| Organo-titanium compound | Titanate | Tetrakis (2.2-diallyoxymethyl-1-butoxy) titanbis (ditridecylphosphate)<br>(Ajinomoto Co. Ltd. Lot. No. 70701) |  $\overset{(CH_2OCH_2{-}CH{=}CH_2)_2}{\overset{\vert}{C_2H_5{-}C{-}CH_2{-}O]_4{-}T_i}}$<br>$[P{-}(O{-}C_{13}H_{23})_2OH]_2$ |
| Titanium alcoxide | TTIP | Titanium tetraisoproxide<br>(Kanto Chemical Co. Lnc.<br>Lot. No. 91051633) | $[(CH_3)_2CHO]_4T_i$ |

## INTRODUCTION

Crowns coated with thermosetting facing resin have often been used clinically as of obtaining an aesthetically favorable coronal restoration of anterior teeth, following recent improvements in materials (i. e., improved resin color, hardness and adhesion to metal frames). In the past, gold alloys and nickel-chromium alloys were often used for the manufacturing of metal frames. In recent years, the use of titanium, which is safer in vivo, has been recommended. When pure titanium is used to manufacture the metal frames of thermosetting facing resin-coated crowns, it is essential to ensure strong and durable bonding between the titanium and resin. Several studies have been conducted to examine the strength of the bond between thermosetting facing resin and the surface of titanium pretreated with various primers or by other methods[1-5]. Some of these methods have begun to be used clinically[6-19]. However, none of these methods has been shown to provide adequate bonding strength and durability. Further modifications of these methods are therefore needed.

The present study was undertaken to clarify the effects of surface treatment agents which might have a higher affinity for titanium than conventional primers, and to devise a technique to improve the strength of the bond between resin and titanium. Thus, we compared the effects of titanium-based organic metal coupling agents used as a primer for adhesion. Of the various titanium-based coupling agents available, we selected a kind of titanate and a kind of titanium alcoxide for this study. To perform comparisons, the bonding strength yielded by using conventional Silicoater treatment or by treatment with three kinds of coupling agents was also examined.

## METERIALS AND METHOD

### 1. Preparation of test pieces

Metal test pieces to be bonded were prepared by casting pure titanium. The castings used for the bending test were prepared as follows. First, a model plate (30 ×30 mm) was prepared with #26 sheet wax. This was followed by moulding with a phosphate-bonded investment formulated for titanium casting (Selibest CB, Lot 15609, NISSIN). Casting was conducted with an arc type centrifugal casting machine, the Silicast (KOBELCO). The JIS class 3 titanium (Lot 140641, GC) was used in this study. The cast specimens used for the shear test were prepared as follows. First, a cylinder-shaped model (5 mmØ×15 mm) was prepared with inlay wax. This was followed by moulding and casting similar to the processes mentioned above. The surface of the cast specimens were abraded with a carbide bur, followed by sand-blasting with alumina power (125 μm) for 20 seconds and ultrasonic treatment in acetone solution for 5 minutes. The test pieces were stored in a desiccator for 24 hours before further treatment.

### 2. Surface treatment

The surface of each titanium test piece was treated with one of 5 primers, or Silicoater, as shown in Table 1. Of the five primers, three (MDP, MEPS and 4-META) were applied with a brush to the test pieces, which were then dried at room temperature for 5 minutes. When titanate was used, it was diluted with methylethylketone to a concentration of 5-30 % before being applied to the test pieces. The test pieces treated with titanate were dried at room temperature for 5 minutes. When the titanium alcoxide (TTIP) was used to treat test pieces, a thin layer of this agent was brushed on the surface of the test pieces, which were then heated in an electric furnace at 200-500 ℃ and left standing in the furnace until they cooled. Treatment with Silicoater was performed according to the manufacture's instruction[17-19].

### 3. Bonding under various experimental conditions

Immediately after surface treatment of the titanium pieces, a 0.3 mm layer of a photopolymerizing type opaque resin (AXIS, Lot. 211071. GC) was brushed on the surface of the test pieces in two rounds. Light was irradiated on the test pieces for 3 minutes, after each round of resin application. Subsequently, a 2mm layer of dentin color resin (AXIS, Lot. 07081DE. GC) was created in 2 rounds, involving a 3 minutes exposure to light after each round. After polymerization, was completed, the specimens were stored in a desiccator for 24 hours. The test pieces were divided into two groups; (1) specimens stored at room temperature and (2) specimens subjecuted to 2,000 thermal cycles, with each cycle consisting of a 60 second immersion in water at 4 ℃ and a 60 second immersion in water at 60 ℃.

### 4. Bending and shear test

A three-point bending test was carried out using a universal materials testing machine (Autograph DDS-5000, SHIMADZU) at a cross head speed of 1mm/min. The resin-coated side of each plate-shaped test piece was placed facing up during this test. The minimum load causing

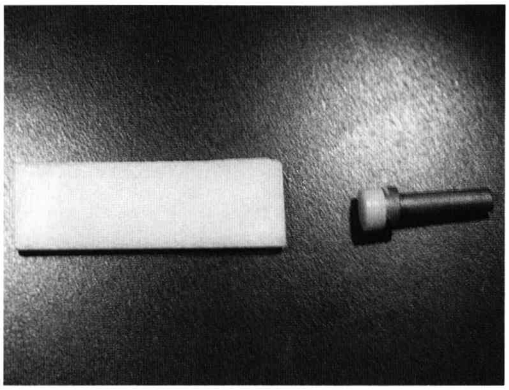


**Fig. 1.** Photograph of specimens for bending test (left) and shearing test (right).

the destruction of the resin-coated side was measured. A shear test was conducted with the same testing machine. The cylinder-shaped test piece was mounted in a special jig designed for performing shear tests, and the test was conducted at a cross head speed of 1㎜/min. The shear bond strength was determined from the minimum load causing the shear destruction of the test piece (Fig. 1).

5. Statistical analysis

Both bending and shear tests were conducted 5 times under each set of conditions. Significance of difference in bending strength and shear strength was statistically analysed using Student's *t*-test for multiple comparison between the meanes at the p=0.05 level among surface treatments and among storage conditions.

## RESULTS

1. Bonding strength with conventional treatment

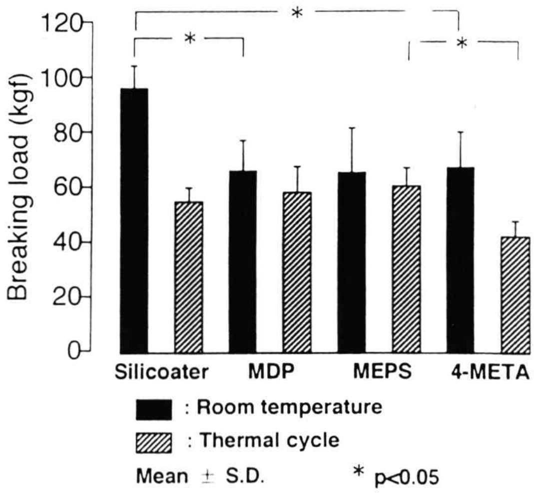


**Fig. 2.** The breaking load obtained from the bending test of resin bonded titanium plate pretreated with the conventional methods.

Fig. 2 shows the breaking load obtained from the bending test of resin bonding titanium plate pretreated with the conventional methods. When test pieces stored at room temperature were subjected to this test, the resistance was 97 kgf for Silicoater-treated specimens, 68 kgf for MDP-treated specimens, 71 kgf for MEPS-treated specimens and 70 kgf for 4-META-treated specimens. Thus, the bending resistance of specimens stored at room temperature was significantly smaller following treatment with any of the 3 primers than following treatment with Silicoater. For specimens exposed to thermal cycles, the bending resistance of Silicoater-treated specimens was 55 kgf, indicating a significantly smaller bending resistance compared to the specimens stored at room temperature. The bending resistance of MDP- or MEPS-treated specimens exposed to thermal cycles (59 kgf for MDP-treated specimens and 61 kgf for MEPS-treated specimens) was slightly smaller than the resisitance of the same specimens stored at room temperature although this difference was not significant. The resistance of 4-META-treated specimens exposed to thermal cycles (44 kgf) was significantly smaller than that of 4-

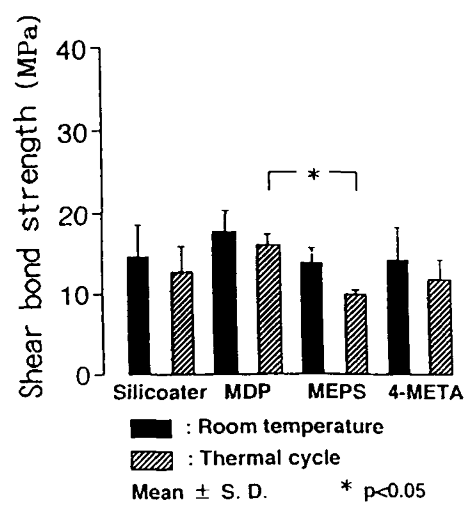


**Fig. 3.** The shear bond strength of resin bonded titanium plate pretreated with the conventional methods.

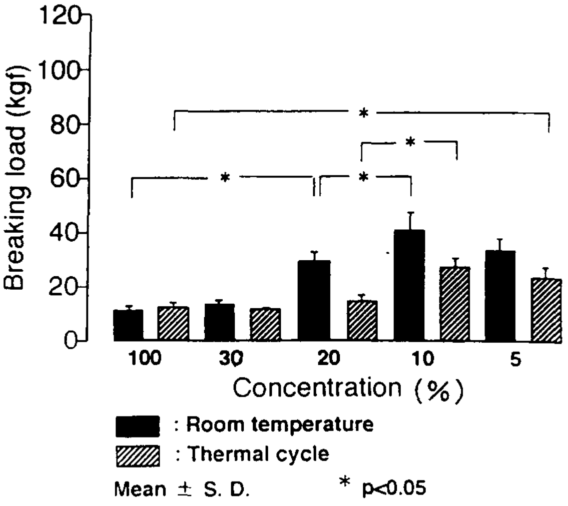


**Fig. 4.** The breaking load obtained from the bending test of resin bonded titanium plate pretreated with each concentration of the titanate solution.

META specimens stored at room temperature. It was also significantly smaller than that of specimens treated with any other primer.

Fig.3 shows shear bond strength of resin bonded titanium plate pretreated with the conventional methods. Among the specimens stored at room temperature, MDP-treated specimens had a slightly higher strength than the specimens treated with any of the primers. However, the strength was ranged between 14 and 18 MPa for all specimens stored at room temperature, without any significant difference depending on the method of treatment. Exposure of specimens to thermal cycles resulted in less shear bond strength compared to those stored at room temperature, irrespective of the method of treatment used. The strength exposed to thermal cycles was slightly higher for MDP-treated specimens (16 MPa) than for specimens treated with Silicoater (12 MPa) or 4-META (12 MPa), although the defference was not significant. The MEPS-treated specimens after exposure to thermal cycles had the lowest strength (10 MPa), which differed significantly from that of MDP-treated specimens exposed to thermal cycles. These results from the bending and shear tests indicate that treatment with Silicoater leads to relatively high bending resistance but low shear bond strength, that treatment with MEPS leads to lower shear bond strength than treatment with MDP, and that other treatment methods leads to a similar tendency of change in both bending resistance and shear bond strength.

2. Bonding strength with titanate treatment

Fig.4 shows the bending resistance of titanate-treated specimens. When stored at room temperature, the bending resistance was about 12 kgf for specimens treated with 30 or 100 % titanate. The resistance was significantly higher for specimens treated with 20 % titanate (27 kgf). It reached a peak

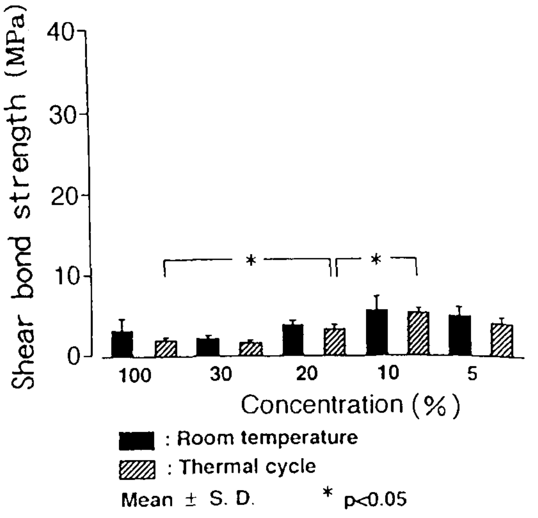


**Fig. 5.** The shear bond strength of resin bonded titanium plate pretreated with each concentration of the titanate solution.

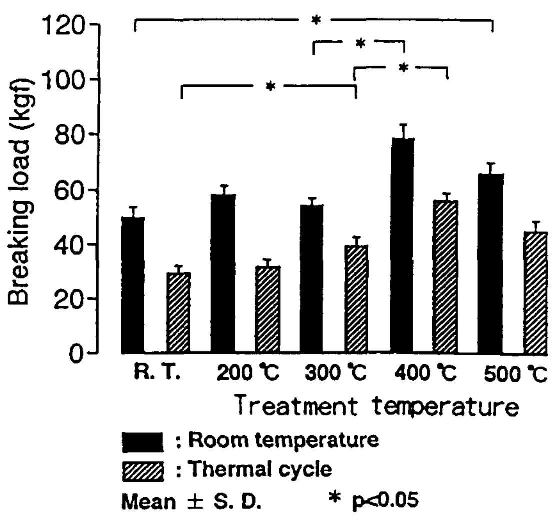


**Fig. 6.** The breaking load obtained from the bending test of resin bonded titanium plate pretreated with TTIP at 200–500 ℃.

(40 kgf) when the concentration of titanate was 10 %, and it was slightly lower (33 kgf) when the concentration further decreased to 5 %. Thus, the bending resistance of specimens treated with titanate was significantly lower than that of specimens treated with Silicoater or any of the conventional primers. When the specimens were exposed to thermal cycles, the bending resistance of specimens treated with 30 or 100 % titanate did not decrease from the strenght recorded for specimens stored at room temperature. However, the resistance of specimens treated with 20 % titanate was reduced significantly to 14 kgf by exposure to thermal cycles, compared to the specimens stored at room temperature. The bending resistance of specimens exposed to thermal cycles was 27 or 23 kgf for specimens treated with 10 % or 5 % titanate respectively. The resistance of these specimens was higher than the resistance of specimens treated with higher concentrations of titanate and exposed to thermal cycles but significantly lower than the resistance of the specimens treated with 10 % or 5 % and stored at room temperature.

Fig. 5 shows the shear bond strength of specimens treated with titanate. At each concentration of titanate, the strength was below 6 MPa, which was significantly lower than the strength of specimens treated with Silicoater or any conventional primer. The shear bond strength of titanate– treated specimens exposed to thermal cycles showed a tendency similar to that observed in the specimens stored at room temperature, irrespective of the concentration of titanate used. The relationship between the concentration of titanate and the bending resistance was retained in the relationship between the concentration of titanate and the shear bond strength.

### 3. Bonding strength with TTIP treatment

Fig. 6 shows the bending resistance of TTIP–treated specimens. Of the specimens stored at room temperature, those which

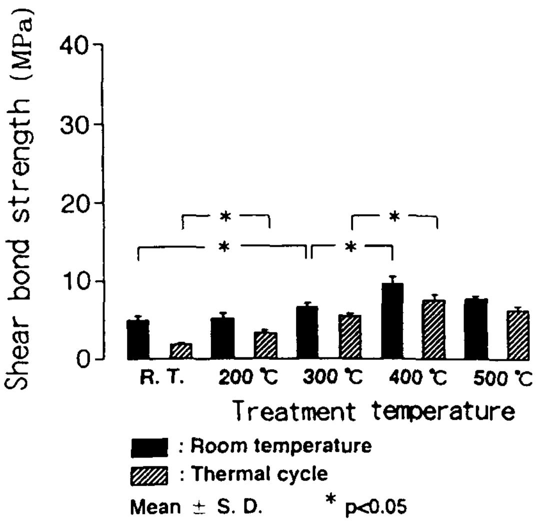


**Fig. 7.** The shear bond strength of resin bonded titanium plate pretreated with TTIP at 200–500 ℃.

were not heat-treated after TTIP treatment had a bending resistance of 50 kgf, and those which were heat-treated at 200 and 300 ℃ had a slightly higher bending resistance (54 – 58 kgf). The bending resistance reached a peak (78 kgf) when heat-treated at 400 ℃. The peak bending resistance significantly higher than the resistance recorded with specimens treated by any conventional primer (Fig. 2). When heat-treated at 500 ℃, the resistance decreased to 65 kgf, but it was still significantly higher than the resistance of specimens without heat treatment. When specimens were exposed to thermal cycles during storage, the bending resistance was lower compared to the specimens stored at room temperature. The decrease in bending resistance due to exposure to thermal cycles tended to become greater as the temperature used for heat treatment after TTIP treatment became lower. When heat-treated at 400 ℃, the bending resistance was highest (56 kgf), which was comparable to the resistance of specimens treated with Silicoater, MDP or MEPS and exposed to thermal cycles (Fig.2).

Fig. 7 shows the shear bond strength of resin bonded titanium plate pretreated with TTIP at 200–500 ℃. At any temperature used for heat treatment, the strength of TTIP-treated specimens was below 10 MPa, which was significantly lower than the strength of specimens treated with Silicoater or any conventional primer (Fig. 3). The relationship between the temperature used for heat treatment and the bending resistance was retained in the relationship between the temperature for heat treatment and the shear bond strength. Similar to the tendency in the bending resistance, the decrease in shear bond strength following exposure to thermal cycles became greater as the temperature used for heat treatment became higher.

## DISCUSSION

Titanium can be characterized by the likelihood that a strong oxidized surface layer is formed. The adhesion of titanium to adhesive material is mediated by this layer. To increase the strength of the bond between titanium and resin, it is therfore important to make the oxidized layer active and use a primer which binds strongly to the surface.

Treatment with Silicoater reinforces the adhesion of metals to resin by directly fusing silicate ($SiO_x$–C) to the metal surface and by applying a silane coupling agent[17-19]. In the present study, treatment of titanium with Silicoater resulted in a shear bond strength of 15 MPa. When the specimens were exposed to 2,000 thermal cycles after Silicoater treatment, the strength decreased to 13 MPa. The shear bond strength of other metals treated with Silicoater is reported to be 18 MPa for Ag-Pd alloys (12 MPa after exposure to thermal cycles)[18], 14 MPa for Co-Cr alloys (10 MPa after exposure to thermal cycles)[19], and 15-17 MPa for Ni-Cr alloys (11 MPa after exposure to thermal cycles)[19]. Thus, the bonding strength of titanium treated with Silicoater and its decrease following exposure to thermal cycles are similar to those reported for other metals, although experimental conditions differ slightly between different metals. This suggests that the bonding strength of silicate to the metal treated with Silicoater is similar for all these metals, or that shearing takes place in the coupling agent or resin layer rather than in the silicate-metal interface. In any event, it seems necessary to precisely identify the location where shearing occurs by analysis of the sheared, section, etc,.so that measures to reinforce the identified location can be taken. Not only Silicoater-treated titanium but also Silicoater-treated other alloys showed an approximately 30 % decrease in bonding strength when exposed to thermal cycles. This indicates the necessity of improving the durability of Silicoater-treated metals.

When primers were applied directly, the shear bond stress was highest (18 MPa) for the specimens treated with MDP (a phosphate ester primer). The strength of these MDP-treated specimens decreased to 16 MPa after exposure to thermal cycles. These results suggested that when MDP was used as a primer, the hydrophilic phosphoric acid group elevates the bonding strength by forming hydrogen or coordinate bonds with the surface layer of titanium. When MEPS (with the thiophosphoric acid group serving as an adhesive functional group) or 4-META (with the carboxylic acid group serving as an adhesive functional group) was used, the shear bond strength was 14 MPa, which was lower than that for MDP-treated specimens. The thiophosphoric acid group and the carboxylic acid group seem to have less affinity for the titanium surface than the phosphoric acid group. The strength of specimens treated with MEPS decreased to 10-12 MPa after exposure to thermal cycles, indicating that these specimens are not highly durable. The shear bond strength of 4-META-treated specimens also decreased to 12 MPa after exposure to thermal cycles. This is probably because the thiophosphoric acid group does not strongly bind to the surface layer of titanium, and because MEPS is not so water proof as 4-META.

Titanate primers have both a moiety binding to inorganic substances and a moiety binding to organic substances in their molecules. This type of primer binds chemically to the surface of inorganic substances to form an organic layer which improves the bonding strength[20-21]. We attemped to improve the affinity for titanium by making use of this action mechanism. However, the bonding strength thus obtained was much lower than that yielded by treatment with conventional primer such as MDP, MEPS or 4-META, and the bonding strength decreased greatly after exposure to thermal cycles. As shown in Table 1, a titanate primer is composed of titanium bound to surrounding hydrophilic hydrolyzable groups and long chains of phosphoric acid group. On the hydrophilic surface of titanium, the long chains of phosphoric acid group do not exhibiting a strong binding capacity. The hydrophilic hydrolyzable group undergoes hydrolysis if heated at relatively low temperatures and this can also cause a low bonding strength.

When the surface of titanium was coated with TTIP (a titanium-based organic metal compound) and it was then heat-treated, the bonding strength was higher than titanium treated with conventional primers and was comparable to the strength of Silicoater-treated titanium. TTIP is likely to undergo hydrolysis in the presence of water at room temperature. If heated at over 350 ℃, it undegoes thermal decomposition to yield a transparent titanium oxide layer. When titanium was coated with TTIP and heated, the bonding strength increased probably due to the formation of titanium oxide layer on the surface. The bonding strength of these titanium specimens decreased only slightly after exposure to thermal cycles, probably due to the effects of the titanium oxide layer. The structure of the interface between titanium and TTIP needs to be further examined to clarify the effects of the titanium oxide layer. To establish the clinical usefulness of TTIP treatment, it is necessary to find out appropriate condition for concentration of primers and the heating time.

## CONCLUSION

The effects titanium-based organic coupling agents were assessed. To make comparisons, the bonding strength was also examined for specimens treated with Silicoater or conventional primer. The following results were obtained :

1. When Silicoater and conventional primers were used, the bonding strength of specimens stored at room temperature was highest for Silicoater-treated specimens and lower in specimens treated with any primer.
2. Exposure to thermal cycles resulted in lower bonding strength of both Silicoater-treated specimens and primer-treated specimens, compared to the strength of these specimens stored at room temperature.
3. The bonding strength of TTIP-treated specimens was higher for specimens heated at 400 ℃ after TTIP treatment than for specimens kept at room temperature after TTIP treatment. The strength of TTIP-treated specimens heated at 400 ℃ was higher than that of primer-treated specimens.
4. TTIP was found to have a higher affinity for the surface of titanium than coventional primers, allowing better bonding strength and durability.

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# チタンと硬質レジンの接着における各種表面処理剤の効果

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（受理：1998年10月29日）

**抄録**：チタンと歯冠用硬質レジンの接着強度を改善することを目的として，チタンと親和性の高い表面処理剤を検索するために，有機チタン系カップリング剤の効果を検討した。*Silicoater* 処理および従来のプライマー処理による接着強度と有機チタン系カップリング剤による接着強度と比較を行ない，以下の結果が得られた。

1. *Silicoater* 処理およびプライマー処理における接着強度は，室温保存では *Silicoater* 処理が最も高く，プライマー処理は低かった。
2. サーマルサイクル後の接着強度は，*Silicoater* 処理およびプライマー処理でも室温保存と比較して低下した。
3. *TTIP* 処理における接着強度は，400℃ 加熱すると室温より高く，プライマー処理より高かった。
4. チタンの表面処理剤として，*TTIP* 処理法は従来のプライマー処理より親和性が高く，接着強度は高い。