Bonding Strength and Durability of Alkaline-Treated Titanium to Veneering Resin

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The shear bonding strengths of a veneering resin to polished, sandblasted, and retention bead-cast commercially pure titanium (cpTi) plates with and without alkaline treatment were measured before and after thermal cycling. The bonding strengths to polished cpTi with and without alkaline treatment decreased remarkably with thermal cycling (p<0.01). The bonding strength to sandblasted cpTi with alkaline treatment at 5,000 thermal cycles showed no significant differences from those before thermal cycling (p>0.05), and those at 20,000 thermal cycles showed values which were quite small (p<0.01). On the other hand, there were no significant differences in the bonding strengths of veneering resin to retention bead-cast cpTi in all conditions (p>0.05). These results suggested that although alkaline treatment is a simple and effective surface modification technique for titanium improving adhesion to resin due to formation of tight-fine rutile particles, it does not provide sufficient bonding durability for long-period restorations.

Key words: Bonding strength, Titanium, Alkaline treatment

INTRODUCTION

Commercially pure titanium (cpTi) and its alloys are frequently used as dental restoratives\textsuperscript{1)}, largely because casting techniques have been improved by various fields and disciplines\textsuperscript{2-5).} When these metals are used as restoratives for anterior teeth, the metal prostheses are generally covered with esthetic materials such as porcelain or resin\textsuperscript{6,7).} For good retention between metal core and porcelain or resin, mechanical retentions are usually prepared on the metal surface by casting of retention beads. This is because mechanical retentions have shown the highest survival rate in clinical prostheses\textsuperscript{8,6).} However, the non-retention surface of metal core is equally desirable as it helps to minimize the amount of sound enamel and dentin being unwillingly removed while preparing tooth for cementation. Removal of sound enamel and dentin occurs because retention beads are relatively large in size, about 200-750\textmu m in diameter. Therefore, many efforts have been devoted to developing new adhesive systems with consideration due to both development of adhesion promoting monomers and improvement of pretreatment methods of substrate\textsuperscript{9-16).} On the other hand, it is known that alkaline treatment increases amount of OH groups and roughness on the surface of titanium metals\textsuperscript{17-19). Our previous study demonstrated that the bonding strength between these metals and veneering resins was significantly improved by alkaline treatment\textsuperscript{20).} It seemed that the improvement depended on the formation of a tight layer of fine rutile particles containing adequate amounts of OH. It also suggested that micromechanical interlocking contributed to the bond between titanium and resin, and that its influence was greater than that of chemical bonding, although neither chemical interaction nor micromechanical linking can fully explain the adhesion between a polymer and a metal\textsuperscript{21). The purpose of the present study was to investigate the bonding strength durability of alkaline-treated cpTi to veneering resin.

MATERIALS AND METHODS

Three types of cpTi plate, with dimensions of 20 \times 15 \times 1 \text{mm}, were prepared. Type 1 was polished with alumina powder (0.3\textmu m); Type 2 was sandblasted (50\textmu m alumina) using Hi-Blaster II (Shofu Inc., Kyoto, Japan); Type 3 was prepared by casting of retention beads. The substrate plates of Types 1 and 2 were prepared by cutting the cpTi plate (KS-50, Kobelco, Kobe, Japan) as received. As for Type 3, the casting pattern was prepared as follows. Retention beads (SS, GC Corp., Tokyo, Japan), about 200\textmu m in diameter, were scattered within a circle, 8-10 mm in diameter, at the center of an acrylic plate, 20 \times 15 \times 1 \text{mm}. The casting pattern was then invested in Selevest CB (Selec Inc., Osaka, Japan), and cpTi ingot (JS-3) was cast using Ticast Super R (Selec Inc., Osaka, Japan). These plates were cleaned in distilled water by supersonic cleaning and dried in air at room temperature. All the above pretreated cpTi plates were soaked in 1M NaOH at 60\textdegree C for 1 hour, heated in vacuum up to 700\textdegree C at 50\textdegree C/min and held for 5 minutes using a porcelain furnace. The treated surfaces were characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). For comparison with standard NaOH...
treatment, some polished cpTi plates were soaked in 5M NaOH at 60°C for 24 hours and heated in air at 600°C for 1 hour.

Solidex (A3B, Shofu Inc., Kyoto, Japan) was filled into an acrylic plate with a hole, 6 mm in diameter and 2 mm in thickness, on opaque-treated metal plates and polymerized for 3 minutes by a visible light-curing unit. The specimens were immersed in water at 37°C for 24 hours. This state was defined as thermal cycle 0. Next, the specimens were immersed in 4°C and 60°C water alternatively for 1-minute periods for 5,000 and 20,000 cycles by a thermal-cycling machine. The resin disc was pulled with a stainless orthodontic wire which had a rectangular section, using a universal testing machine at a crosshead speed of 5 mm/min. More details of the bonding test method were described in our previous study. Shear bonding strengths were calculated from the fracture force and the contact area between resin and substrate (0.283 cm²). Each test was repeated five times for each condition. Bonding strength data were analyzed by Student’s t-test for multiple comparisons at p=0.05 level.

RESULTS

Fig. 1 shows the bonding strengths of veneering resin to polished, sandblasted, and retention bead-cast cpTi with and without alkaline treatment, and before and after thermal-cycling. The bonding strength of veneering resin to polished cpTi with alkaline treatment (9.74 MPa) was significantly higher than that without it (2.29 MPa) (p<0.01) at 0 cycle. However, after 5,000 and 20,000 thermal cycles, the strengths of polished cpTi both with and without alkaline treatment showed extremely low values—almost close to or zero.

The bonding strength of veneering resin to sandblasted cpTi with alkaline treatment (10.76 MPa) was significantly higher than that without it (7.54 MPa) (p<0.05) at 0 cycle. There were no significant strength differences in the sandblasted cpTi with alkaline treatment between 0 and 5,000 thermal cycles (p>0.05). On the other hand, the bonding strength of sandblasted cpTi without alkaline treatment at 5,000 thermal cycles (1.90 MPa) was significantly lower than that at 0 cycle (7.54 MPa) (p<0.01). Moreover, the bonding strengths of sandblasted cpTi with and without alkaline treatment exhibited low values at 20,000 thermal cycles, which were 0.77 and 0.22 MPa respectively.

With retention bead-cast cpTi, there were no significant differences in the bonding strength of veneering resin in all conditions (p>0.05).

Fig. 2 shows the SEM images of polished and sandblasted cpTi before and after the alkaline treatment, and after 20,000-time thermal cycling. Granular particles, less than 0.2 μm in size, were observed on the smooth surface of polished cpTi with alkaline treatment. These particles were also observed on the rough surface of sandblasted cpTi with alkaline treatment. However, these particles were not observed after 20,000-time thermal cycling. Observations on the surface of retention bead-cast cpTi showed similar results. Although all images were the surface of the plates without veneering resin, similar dissolution may occur in the interface between resin and cpTi substrate due to soaking in water.

Fig. 3 shows the XRD patterns of cpTi before and after two kinds of alkaline treatment. The XRD pattern of the standard alkaline-treated cpTi (soaked in 5M NaOH for 24 hours and fired at 600°C for 1 hour) showed the peaks assigned to substrate: α-Ti, rutile-type TiO₂, and Na₂Ti₅O₁₁. Whereas that of cpTi (soaked in 1M NaOH for 1 hour and vacuum firing up to 700°C) used in the bonding test showed smaller peaks of rutile and peaks of Na₂Ti₅O₁₁ that were quite small, as compared to that of the standard alkaline treatment.

![Fig. 1] Bonding strengths of veneering resin to polished, sandblasted, and retention bead-cast cpTi with and without alkaline treatment, and before and after thermal cycling. Common vertical lines indicate no significant statistical differences at α=0.05.
DISCUSSION

Kim et al. reported that a sodium titanate hydrogel layer was formed on the surface of titanium when it was treated with NaOH solutions at concentrations exceeding 0.5 M at 60°C for periods longer than 24 hours\textsuperscript{18}. They also reported that rutile (TiO\textsubscript{2}) and Na\textsubscript{2}Ti\textsubscript{5}O\textsubscript{11} formed at around 600°C and fully crystallized at above 700°C\textsuperscript{19}. The sodium titanate layer formed Ti-OH groups, which induced apatite nucleation, on its surface by exchanging Na\textsuperscript{+} ions for H\textsubscript{3}O\textsuperscript{+} ions in body fluids\textsuperscript{17}.

On the contrary, the purpose of the treatments in the present study was to enhance the bonding strength of titanium to veneering resin. Furthermore, short procedure time, safe manner, and ease of use are prerequisites for clinical applications in dentistry. Therefore, the optimal conditions in the alkaline treatment of titanium for bonding to resin differ from those for apatite-forming ability.

Our previous study demonstrated that NaOH concentration, soaking time, and soaking temperature had no significant effects on the bonding strength between cpTi and resin, although the amounts of sodium titanate and rutile were different\textsuperscript{20}. This suggests that the amount of sodium titanate and rutile in the surface layer has no significant effects on the bonding of alkaline-treated cpTi to resin. Therefore, the alkaline treatment employed in this study was different from that for apatite formation.

The bonding strength of sandblasted cpTi with alkaline treatment to resin demonstrated insufficient endurance against thermal cycling. Although there were no significant differences in bonding strength...
before and after the 5,000-time cycling (p>0.05), the strength at 20,000 cycles showed a value that was quite small. It seemed that the dissolution of Na2Ti5O11 resulted in decrease of bonding strength, although diffraction peaks due to Na2Ti5O11 were quite small, as shown in Fig. 3. Kim et al.25 also reported that Na2Ti5O11 disappeared, rutile remained, and apatite formed with soaking in a simulated body fluid for three days. The 5,000-time and 20,000-time thermal cycles corresponded to seven days' and 27.8 days' soaking in water respectively. It implied that Na2Ti5O11 formation should be further reduced to improve bonding durability between alkaline-treated cpTi and resin.

Adhesion between a polymer and a metal cannot be explained only by chemical interaction or micromechanical linking21. Both aspects are jointly responsible. Furthermore, many factors contribute to the bonding between resin and substrate metal, such as mismatch of thermal expansion coefficients. From the perspective of substrate pretreatment, it can be concluded that micromechanical interlocking has a greater influence on the bonding between titanium and resin than chemical bonding. The results obtained in the present study suggest that alkaline treatment is a simple and effective surface modification technique for titanium, as it improves adhesion to resin due to formation of tight-fine rutile particles. This is because simple oxidation of cpTi in air results in formation of large rutile particles which have weak adhesive strength to cpTi substrate, as reported previously11. However, its bonding durability was not sufficient to maintain a long-period restoration, as shown in the present study. Further investigations are required to evaluate bonding durability and to elucidate the optimal and practical treatment conditions that enhance bonding strength durability between titanium and resin.

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REFERENCES


