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Effect of preoxidation of titanium on the titanium–ceramic bonding

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Abstract

To improve the titanium–ceramic bonding is a challenged theme because the bonding plays an important role in long-term performance of dental prosthetic implants. This study focused on the pre-heat treatment effect on the surface characteristics of titanium and the bond strength of the porcelain–titanium system. Phase, morphology, and oxide layer thickness of the pre-heat-treated titanium were evaluated. In particular, the bond strength of porcelain fused to pre-treated titanium was measured by using three-point bending test. Statistical analyses were made using one-way analysis of variance (ANOVA). The results revealed that with an increase in treatment temperature, the intensity of diffraction peaks of rutile-type titania formed on pre-treated titanium surface increased. With regard to the thickness of the oxide layer, a monotonous change with increasing treatment temperature was observed. The bond strength of the porcelain–titanium system was 27.6 MPa for untreated titanium, which is above the minimum value of 25 MPa specified in ISO 9693 standard for the three-point bending test. When titanium subjected to pre-heat-treatment at 600–850 °C, the values became the range of 23.7–34.5 MPa, indicating significant differences ($p<0.05$). The highest value resided in the optimal pre-treatment temperature of 750 °C at which specimens also presented greater amounts of remained porcelains on the titanium side among all tested groups after bending test. On the basis of the data, the pre-heat treatment in air for titanium substrates might be a simple and effective method for strengthening the titanium–ceramic bonding.

Keywords: Titanium; Heat treatment; Bond strength; Porcelain; Dental prosthesis

1. Introduction

Commercially pure titanium is applied as a metal base in clinical fixed prosthetic dentistry because of its mechanical properties, high strength-to-weight ratio, low density, corrosion resistance, and good biocompatibility [1–8]. Metal–ceramic (MC) dental crowns have been widely used due to their esthetic appearance and good mechanical properties [6–9]. It is of importance that porcelain should be strongly bonded to titanium substrate in order to achieve successfully long-term clinical use. To pursue the high titanium–ceramic bonding is still a concerned theme although commercial porcelain systems for bonding titanium are available today. This titanium–ceramic bonding is influenced by the surface properties of the titanium substrate [7,10], in addition to porcelain firing conditions such as the addition of bonding agent [1,11] and atmosphere control [12–14]. For example, Atsü and Berksun depicted that firing in an argon atmosphere that limited the oxidation of titanium improved the titanium-porcelain bonding when using some of the porcelain products [13].

Due to highly reactive nature of titanium at high temperatures, an excessive thick and nonadherent layer of titanium oxide formed on the surface during porcelain application, which constructed the weak region of the porcelain–titanium system, may adversely affect MC bonding [1,3,6,11,15]. A number of surface modification methods to improve oxidation properties of the metal surface in an effort of enhancing porcelain–metal bonding have been introduced. They included roughening [1,8], bonding coating [12,15,17–19], etching [16,20], and preoxidation [2,11]. Roughening the titanium surface by sandblasting provided the increased mechanical interlocking between titanium and porcelain, leading to a higher bond strength. In the case of etching, the bond strength of the porcelain fused to titanium treated with hydrochloric acid was comparable to that of the

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conventional porcelain–alloy system [20]. The formation of a densely oxide layer made up of gold, chromium or silicon coating reduced oxidation rate of titanium to enable titanium–porcelain bonding to be higher bond strength [15,17–19]. Yamada et al. [11] found that significant lower interfacial toughness values occurred for pre-heating at 600 °C as compared to untreated Ti6Al7Nb specimens due to the excess of Al atoms on the titanium alloy surface. Contrary to the findings, Ito et al. found that Au-1.6 wt.% Ti alloy subjected to oxidation treatment at 1000 °C presented statistically greater three-point bending strength than those without heat treatment [21]. Their EPMA (electron probe X-ray microanalysis) observation indicated an accumulation of Ti and O contents on the alloy side at the alloy–porcelain interface, which enhanced the bond strength through the surface titanium oxide layer.

In this study, attempts have been made to create an adherent oxide layer on the titanium surface for improving the titanium–ceramic bonding. The use of pre-heat treatment following nitric acid passivation aimed at changing surface characteristics of the titanium, thereby promoting the bonding by means of prevention of titanium from sequential oxidation during porcelain firing. Evaluation of this potential method included phase composition and depth-profiling analysis, particularly the bond strength of porcelain to titanium.

2. Experimental procedure

2.1. Pre-heat treatment of titanium

ASTM grade 2 commercially pure wrought titanium (Spemet Co., Taipei, Taiwan) plates of 25 mm × 3 mm × 0.6 mm were used. All dimensions were monitored by multipoint measurements with a Mitutoyo digimatic caliper (Kanagawa, Japan). First, the titanium specimens were mechanically polished with 240 grit wet emery paper down to 0.55 nm thick, followed by air abrasion with 50 μm aluminum oxide particles (Korox 50, Bego, Bremen, Germany) on a dental air-abrasion unit (BL-24, Kimnico, Taipei, Taiwan). The roughened substrates were ultrasonically rinsed in deionized water and acetone for 30 min, respectively. After which, the clean specimens were passivated in 30% nitric acid for 30 min at room temperature, cleaned in deionized water for 30 min, and then dried under vacuum. Prior to porcelain application, the specimens were heat-treated over the temperature of 600–850 °C at 50 °C interval for 1 h at a heating rate of 10 °C/min in air, and then cooled to room temperature. The titanium specimens without heat treatment were referred to as the control.

The changes in the crystal components of the titanium specimens before and after heat treatment were detected using an Shimadzu XD-D1 X-ray diffractometer (XRD, Kyoto, Japan) with Ni-filtered CuKα (wavelength of 0.5418 nm) radiation operated at 40 kV and 40 mA at a scanning rate of 1°/min. Specimens were fixed on an aluminum sample holder. Phase identification was achieved using search match software (XRD-6000, Shimadzu, Kyoto, Japan) that utilized the International Center for Diffraction Data (ICDD) database (International Center for Diffraction Data, Newtown Square, PA, USA). The morphology of various heat-treated titanium specimens was observed under a JEOL JSM-6700F field-emission scanning electron microscope (FESEM, Tokyo, Japan). In FESEM, the electron gun is to use a field-emission cathode that provides narrower probing beams, leading to the improved spatial resolution down to 1 nm. Oxidation layer thickness of heat-treated titanium surface was analyzed by glow discharge optical spectrometer (GDOS, LECO GDS-750 QDP, Mönchengladbach, Germany) with voltage of 700 V. The use of GDOS can detect all elements including H, O, C and N in quantities ranging from trace element to main constituent. Depth profile of thickness between 100 nm and 100 μm can be measured with a resolution of approximately 5 nm.

2.2. Porcelain fused to titanium

Duceratin porcelain (Ducera Dental, Rosbach, Germany) for bonding to titanium substrates was used. The porcelain consisting of bonding (Haftbond), opaque, and dentin ceramics was fired on the titanium surface according to the manufacturer's recommendations, as listed in Table 1. Briefly, the three different ceramic layers were applied symmetrically over a length of 8 mm to achieve the final thickness of 1 mm onto the central portion of each specimen surface. A custom-made jig was used to ensure the precision of porcelain thickness. The whole firing process was carried out in air, instead of the "normal" condition — the reduced atmosphere. Before debonding test the MC specimens for cross-sectional examination under a FESEM were prepared by mounting the specimens in epoxy resin and mechanical polishing to a level of 1 μm Al_2O_3 powder, following the standard metallographic procedure. A Pt–Ag film was coated onto the specimens.

ISO 9693:1999 was adopted to evaluate the bond strengths between titanium and porcelain by means of three-point bending test [22]. The specimen was positioned on supports with a span distance of 20 mm in a universal testing machine (EZ-Test, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/min, where the porcelain side positioned was opposite to the applied loading. One-way ANOVA method was used to evaluate the statistical significance of mean bond strength. A Tukey's post-hoc multiple comparison test at 5% significance level was used to determine the significance of the deviations in strength of the test groups. After the debonding, the amount of the remained porcelain on the titanium side was examined under a light microscope associated with image analysis software (Image-Pro Plus 4.5, Media Cybemetics, Silver Spring, MD, USA).

Table 1
Firing schedules of Duceratin porcelains

	Start temperature (°C)	Pre-heat time (min)	Heat rate (°C/min)	Final temperature (°C)	Holding time (min)
Haftbond®	450	3	100	830	3
Opaque	300	3	55	755	1
Dentin	300	3	55	720	1