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Role of cohesive strength, adhesive strength, and oxides thickness in the adherence of porcelain veneered on pure titanium

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Titanium and its alloys, owing to the properties of moderate modulus of elasticity, high strength, good corrosion resistance, low cost compared to precious metals, and inert biocompatibility, are becoming a category of material in metal-porcelain restorations for dental implants. During firing of porcelain veneered on titanium, however, it was observed that the oxidation of metals becomes severe at high temperature [1–4]. This marked oxidation under high temperature and longer duration time causes the metal oxides to grow [5]. With increasing firing temperature or time, the grown Ti oxide thickness appears to increase with decreasing bonding strength of porcelain coating veneered on Ti [6, 7]. This phenomenon was quite accepted and it was speculated that the degradation of oxide adherence at high temperature and longer oxidation time was due to the development of growth stresses in the oxide [5]; however, no evidence was provided.

The correlation between the oxide thickness and the bonding strength of porcelain on titanium was confirmed by a later study; however, an early study suggested that the fracture of the system could occur inside the Ti substrate rather than through the Ti oxides [8]. If the latter could be substantiated, which is part of the purpose of the present study, then the phenomenal oxides growth could only be a relevant occurrence rather than the cause of failure of the coating system subject to a bonding test. Moreover, a valid bonding test measures the bonding strength of a combination of adhesive (coating to substrate) strength and cohesive (within the coatings themselves) strength. Previous studies [5–8] assumed that the degradation of the bonding strength was caused by the sole variation and deterioration of the adhesion between porcelain and titanium as a function of firing time. During the firing procedure, however, the sintering state of the porcelain coating during prolonged firing might vary and affect the cohesive strength of porcelain coating, which then affects the bonding strength of the coating. Hence the variation of cohesive strength of the coating as a function of firing time needs to be investigated. As implied in the bonding test, however, the cohesive strength and adhesive strength of the coating system cannot be measured independently, without interference from each other. To determine the independent cohesive strength of the porcelain coating, the coating was detached freely from Ti substrate, which is explained later. The approximate cohesive strength of porcelain was estimated from the flexural strength of free porcelain coating, determined by three-point bending test. Moreover, the bonding strength of the porcelain coating on Ti was tested by four-point bending test and the fractography of the system was examined.

The pure Ti (ASTM Grade II) plates (6 mm × 8 mm × 3 mm) to be veneered with a single layer of opaque porcelain (Duceratin, Ducera Dental GmbH) were ground to 600 grit (SiC paper), sand-blasted with SiC particles (650 μm) and etched in a mixed acid solution (6 ml HF, 9 ml HNO_3, and 85 ml distilled water) for 60 s. The surface roughness of the etched Ti plates was controlled to about 5 μm (Ra), and the porcelain layer (about 300 μm) contained a dispersed crystalline SnO_2 phase in an amorphous matrix. Firing of

TABLE I Firing procedures of porcelains veneered on Ti substrate for PT-A and PT-B specimens

Procedure	PT-A	PT-B
Vacuum (torr)[a]	0.05	0.05
Start temperature (°C)	25	25
Heating rate (°C/min)	55	55
Firing temperature (°C)	800	800
Holding time (s)	286	1024
Cooling	in air	in air

[a] Vacuum was applied through the whole firing procedure until the holding time was reached.

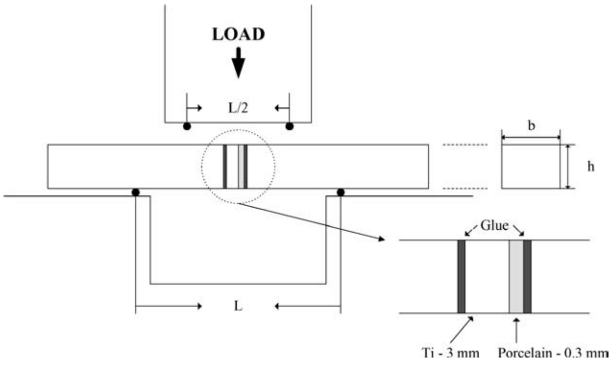

Figure 1 Schematic diagram of bonding strength measurement by four-point bending test with specimen glued to extension stainless steel bars (L is 20 mm, b is 8 mm, and h is 6 mm).

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TABLE II Structures, mechanical properties, and failure modes of porcelains veneered on titanium

Specimen	Oxides thickness (μm)	Bonding strength (MPa)[a]	Area fraction of adhesive failure (%)[b]	Flexural strength (MPa)[c]	Porosity (%)[d]
PT-A	0.3 ± 0.01	23.0 ± 2.1	55.5 ± 6.7	42.8 ± 4.3	1.1 ± 0.4
PT-B	0.6 ± 0.02	18.4 ± 1.1	74.7 ± 8.0	32.8 ± 4.0	8.1 ± 0.7

[a] Values are measured by four-point bending test; each value is the average of six tests and values are given as mean ± S.D.

[b] Each value is the average of six tests and values are given as mean ± S.D.

[c] Values are measured by three-point bending test; each value is the average of eight tests and values are given as mean ± S.D.

[d] Each value is the average of eight tests and values are given as mean ± S.D.

the porcelain coating/Ti composite specimens was carried out in a quartz tube according to the firing procedures as shown in Table I. The table also shows that the PT-A and PT-B specimens were fired for 286 s and 1024 s, respectively. The oxide thickness between porcelain and titanium was examined by scanning electron microscopy (Philips XL-40, FEG, The Netherlands). The fraction of the volumetric porosity of porcelain coating was analyzed with a computer image analyzer (OPTIMAS 6.0) by taking the continuous photographs of the porcelain surface for each of the eight tests.

The bonding strength of the porcelain on Ti was measured by four-point bending test as shown in Fig. 1 [9, 10] and the value was calculated from the formula [11]

$$\sigma_b = 3PL/4bh^2, \tag{1}$$

where σ_b is the bonding strength, P is the fracture load, L is the length of support span, b is the specimen width, and h is the specimen height. Then the fracture surfaces of delaminated porcelain and Ti substrate were observed by optical microscopy, and the photographs were transferred to the mentioned computer image analyzer for quantitative analysis of the area fraction of adhesive failure (AD failure). Afterward, the Ti substrate side and delaminated porcelain side of the fractures for

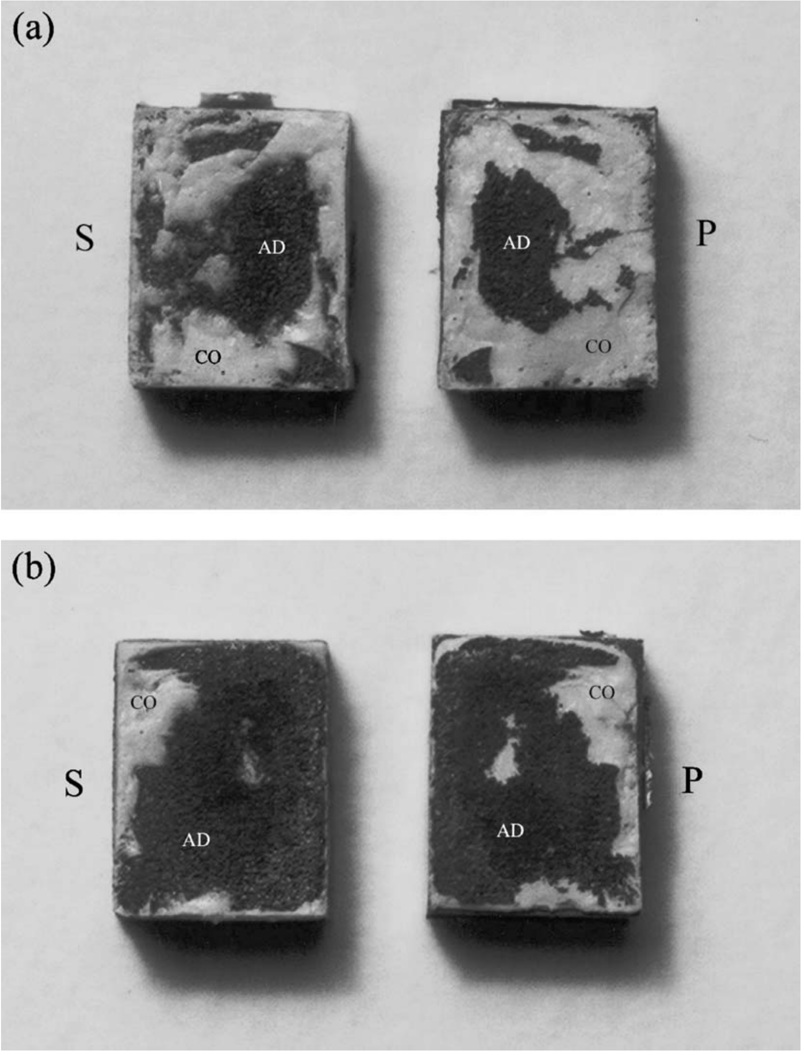

Figure 2 Fracture surfaces of (a) PT-A specimen and (b) PT-B specimen after four-point bending tests (AD is the adhesive failure, CO is the cohesive failure, P is the delaminated porcelain side, and S is the Ti substrate side).

both PT-A and PT-B were analyzed by thin-film X-ray diffractometry (Rigaku Rint 2000, Japan) with Cu K_α radiation, operated at 40 kV, 100 mA, and fixed angle of 0.5° with the scan speed of 1°/min to determine the phase ingredients. The method for measuring the flexural strength of free porcelain coating influenced by firing time was as follows. Similar to the above experimental procedures, a single opaque porcelain layer (about 300 μm) was veneered on Ti substrate (50 mm × 8 mm × 3 mm). After different firing times, the composite specimens were immersed in a corrosive solution of 10 ml Br_2 and 90 ml methanol to remove Ti and thus free the porcelain coating. Measurement of the flexural strength of free porcelain coating was carried out by three-point bending test and the value was calculated from the formula [11]

$$\sigma_f = 3PL/2bh^2, \qquad (2)$$

where σ_f is the flexural strength, P is the fracture load, L is the length of support span, b is the specimen width, and h is the specimen height.

The measured values of oxide thickness and bonding strength between porcelain and titanium for PT-A and PT-B are shown in Table II. The results agree with the literature that as the oxide thickness increases, the corresponding bonding strength decreases from 23.0 ± 2.1 MPa for PT-A specimen to 18.4 ± 1.1 MPa for PT-B specimen with increasing firing time. This table also shows the results of flexural strength and porosity fraction for both PT-A and PT-B free porcelain coatings. The value of flexural strength for PT-B, measuring approximately the cohesive strength of the coating, is lower than that for PT-A, which indicates that the cohesive strength of the porcelain coating decreases with longer firing time. The variation of cohesive strength can be attributed to the change of porosity in the coatings. With increasing firing time for PT-B specimen, its fraction of porosity increases substantially (Table II), the reason being explained in reference [12]. Increasing the fraction of porosity decreases the bonding strength of materials [13–15]. It seems likely that the increase of porosity fraction for PT-B might induce a drop of cohesive strength of porcelain, to result in the weaker bonding strength of the coating as shown in Table II.

The above argument, however, is not supported by the fractography. The fracture surfaces of PT-A and PT-B are shown in Fig. 2, where the dark contrast indicates an adhesive failure with dispersed white-contrast spots, while the white contrast indicates that the cracks have propagated through the porcelain indicating cohesive failure. This figure reveals a mixed cohesion failure and adhesive failure, i.e., the fracture propagated through the porcelain coating and the near-interface between porcelain and Ti substrate, respectively. To be specific, the adhesive fracture could propagate through the Ti oxides, the interface between porcelain and Ti oxides, and inside the Ti substrate. The higher measured area fraction of adhesive failure for PT-B specimen is inconsistent with the indication of lower cohesive strength of the same specimen. The lower cohesive strength should have resulted in a higher area fraction of cohesive failure, or the corresponding lower area fraction of adhesive failure. The experimental result infers that the adhesive strength of the coating, which can hardly be directly measured, is dominantly degraded with longer firing time. An approximate estimation can be drawn from Table II, that while the flexural strength degrades 23.4% for PT-B specimen compared with PT-A specimen, the corresponding increase of area fraction of adhesive failure is 34.6%. It can only be inferred that the adhesive strength of the coating degrades more than the degradation of cohesive strength of the coating, with increasing firing time. This result suggests that the deterioration of bonding of porcelain veneered on titanium with firing time is dominantly determined by the degradation of adhesive bonding of porcelain, and that the degradation of cohesive strength of porcelain should only play a secondary role.

The result of thin-film X-ray diffraction patterns focused on the areas of adhesive fractures (Fig. 2) is shown in Fig. 3, which indicates that the fracture has occurred inside the Ti substrate and/or the interface between porcelain and Ti rather than through the Ti oxides as evidenced by the fact that no TiO_2 was observed to

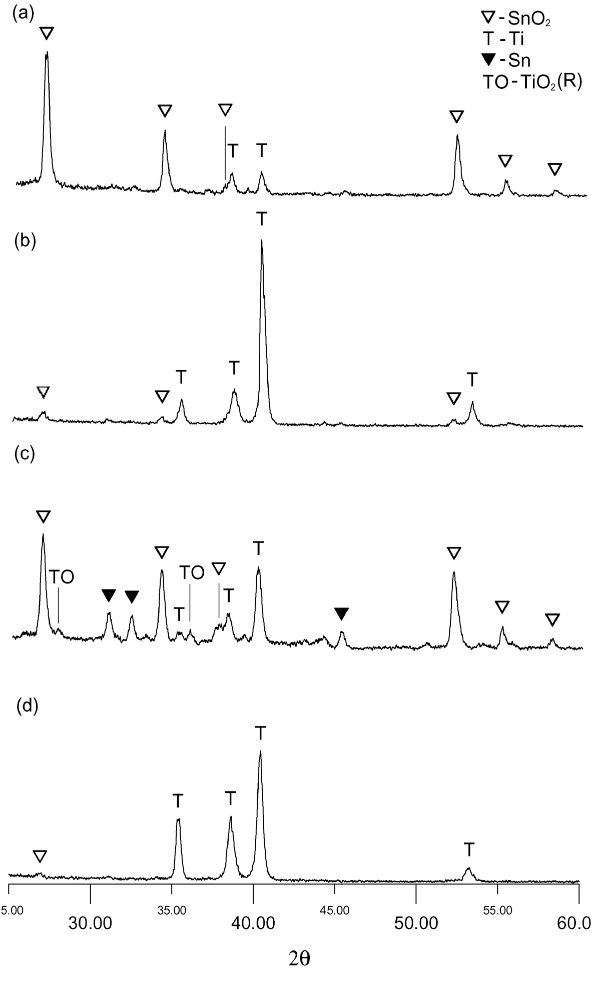

Figure 3 Thin-film X-ray diffraction pattern (Cu K_α) on the area of adhesive failure of the (a) delaminated porcelain side of PT-A, (b) Ti substrate side of PT-A, (c) delaminated porcelain side of PT-B, and (d) Ti substrate side of PT-B specimens by four-point bending test (TiO_2 has a rutile structure).

adhere to the Ti side of PT-A (Fig. 3b) or PT-B (Fig. 3d). This indicates that the fracture propagated inside the Ti substrate and/or along the interface between porcelain and Ti oxides instead of propagating through the Ti oxides. Furthermore, the intensity of Ti spectrum in Fig. 3c is higher than that in Fig. 3a, which reveals that the quantity of Ti detached to the delaminated porcelain side of PT-B is higher than PT-A. Hence, as the firing time increases, the crack could propagate deeper into the Ti substrate. The SnO_2 phase, an ingredient of porcelain, found in the X-ray diffractometry, should originate from the dispersed white-contrast spots in Fig. 2, indicating a cohesive failure. Previous arguments of the role of the growth stress of oxides on the degradation of bonding strength of the porcelain coating were not based on the observation of the fracture behavior of the coating, but on the phenomelogical correlation between the oxide thickness and the bonding strength [5–8]. The present study suggests that an increase of the thickness of oxide might play a less important role to explain the fracture of the system with longer firing time. With longer firing time, however, the Ti substrate might deteriorate significantly, enabling the crack to propagate deeper into the Ti substrate, and thus cause a loss of adhesive strength of the coating and the bonding strength of the porcelain veneered on titanium. It is likely that the diffusion of oxygen into the titanium will cause brittleness of the metal with increasing firing time [8]. This also explains why the fraction of AD failure of PT-B is higher than PT-A (Table II), with increasing firing time.

Additionally, the formation of Sn was phenomenal in the thin-film X-ray spectra of Fig. 3c. A possible explanation of this result is that the substrate metal atoms of Ti migrate into the porcelain side, thereby exchanging the Sn atoms of the $Sn0_2$ to produce the reduced Sn [16].

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