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On the bonding of porcelain on titanium

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The interface structure and bond strength between Ti and porcelain were studied using various firing times and vacuum levels. During firing an interfacial oxide layer was formed between Ti and porcelain. Fracture occurred between this oxide layer and Ti. A correlation was observed between the thickness of the interfacial layer and the bond strength: the thicker the layer, the weaker was bonding. An improved vacuum was found to increase the bond strength. Oxygen was observed by ESCA to dissolve into Ti, causing brittleness in the uppermost Ti layer with prolonged firing time.

1. Introduction

Pure titanium has been successfully used for biomedical applications during the last three decades. The main reasons for its popularity are good corrosion resistance, excellent biocompatibility, high strength/weight ratio and low cost compared with Au alloys. These properties are also beneficial if titanium is considered as a material for dental crowns and bridges. However, the high melting point of Ti [1] (1660 °C) and the high reactivity of molten titanium with oxygen and investment materials make the casting process difficult. Apart from difficulties in casting, the lack of a well documented and successful veneering of Ti with porcelain is another obstacle for application of Ti to crowns and bridges. Because of titanium's high reactivity with oxygen, especially at higher temperatures [2–4], porcelain firing should take place at temperatures below 800 °C in order to prevent an excessive oxide formation. Furthermore, titanium's thermal expansion coefficient (TEC) ($8.5 \times 10^{-6}\,°C^{-1}$) [1] is much lower than those for conventional dental alloys (ca. $13–14 \times 10^{-6}\,°C^{-1}$). Thermal expansion plays an important role in veneering because small or no residual stresses due to thermal mismatch are required for the final restoration. Thus, porcelains prepared for conventional alloys cannot be used for Ti because of their large TEC and fusing temperatures of approximately 1000 °C. For these reasons special porcelain with a lower fusing temperature and lower TEC is required for Ti.

A limited number of studies have been reported [4–9] on the bonding of porcelain to Ti. Bond strengths are reported [6] to be comparable with the bonding of commercial porcelains to Ni–Cr alloys. Oxide adherence and porcelain to Ti and Ti–6Al–4V were studied by Adachi *et al.* [5]. The porcelain was found to delaminate completely from the metal substrate. The oxide adherence was good for specimens oxidized at 750 °C but much lower for specimens oxidized at 1000 °C.

High-temperature oxidation of titanium and oxide adherence have been studied previously and are reported in the corrosion literature [10–13]. The oxide scale is known [12] to consists of periodical stacking of layers parallel to the reaction interface. According to Bertrand *et al.* [12] the oxide scale delaminates from the substrate when the oxide layer reaches a thickness of about 1 μm. However, in these studies very long oxidation times were used, whereas only very brief exposure times are applied for dental restorations to be veneered with porcelain.

In the present work the aim was to study the relationship between the interface structure and bond strength between Ti and porcelain using a variety of techniques. Firing times and vacuum levels were the main process variables.

2. Experimental procedure

Pure titanium and experimental porcelain (Table I) were used for porcelain firing experiments. The impurity content of Ti was given by the manufacturer, while the composition of porcelain powder was measured by energy-dispersive X-ray analysis (EDX). Titanium plates were cut from Ti rod and metallographically ground to 1000 grit by SiC paper, rinsed in ethanol and dried prior to porcelain firing.

A Cambridge Stereoscan 200 scanning electron microscope equipped with a Link (AN) 10000 EDX system was used for analyses of the composition of porcelain and the cross-sections of the veneered Ti plates. The composition of porcelain was measured assuming that elements Si, Al, K, Na and Ti appeared as following oxides: SiO_2, Al_2O_3, K_2O, Na_2O and

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TABLE I The composition of Ti and porcelain (porcelain composition by EDX)

Material	Composition (wt % unless stated)	Manufacturer
Ti	C 0.02, N 0.012, Fe 0.06, O 0.13, H 10 p.p.m, Ti balance	Titanium International Ltd.
Experimental porcelain	SiO_2 43.2, Al_2O_3 7.6, K_2O 3.6, Na_2O 5.6, TiO_2 35.9	DeTray

TiO_2, which are the oxides normally found in dental porcelains.

Fractured Ti and porcelain surfaces were studied with a Perkin-Elmer PHI 5400 electron spectroscopy for chemical analysis (ESCA) system. The X-ray photoelectron spectroscopy (XPS) spectra were taken using MgK_α radiation (1253.6 eV). The measured binding energies (B.E.) were calibrated by using as a reference the B.E. of the Cls line of hydrocarbon contamination (285.0 ± 0.2 eV). The vertical concentration profiles were measured by alternating Ar^+ ion sputtering and ESCA analysis. The quantitative ESCA analyses were carried out using sensitivity factors given by the manufacturer of the instrument.

Firing schedules for porcelain firing are given in Table II. Programme A was according to the recommendation of the manufacturer of the experimental porcelain, with 3 min at the maximum temperature of 800 °C. Programme B was similar to A, but porcelain veneering was repeated four times in order to simulate normal porcelain firing procedures used in dental laboratory work. In firing schedules C and D the holding time at the final temperature of 800 °C was increased to 15 and 30 min, respectively. In all these programmes (A–D) a Flagship VPF (Jelenko Co.) commercial dental porcelain firing furnace was used for veneering. In the last programme E, Ti specimens to be fired were placed inside a quartz tube which was pumped to a vacuum of 5×10^{-2} torr. The tube was then inserted into the furnace (Accu-therm II 2000, Jelenko Co.) at 600 °C and heating was started. Finally the tube, which was under pumping throughout the firing cycle, was removed from the furnace and allowed to cool to room temperature.

Porcelain-veneered Ti plates were mounted in resin and subsequently ground and polished ($\rightarrow$ 1000 grit SiC + petrodisk + OP-S (suspension liquid)/30% H_2O_2(2/1)) perpendicularly to the veneered surface.

For the measurement of bond strength between titanium and porcelain, titanium plates were cut into 6 cm × 8 mm × 1 mm test pieces and veneered with a thin (0.1–0.2 mm) porcelain layer. The specimens were glued with epoxy at 150 °C for 10 min to rectangular steel bars both on the ceramic and the metal side. Four parallel specimens were made for each firing programme. Four-point bending was carried out at a crosshead speed of 1 mm min^{-1} using a standard machine for mechanical testing (Instron).

For fracture surface analyses Ti strips (10 mm × 25 mm × 1 mm) were veneered by porcelain and bent by three-point bending.

The coefficient of linear thermal expansion (α) for Ti and porcelain was measured from 100 °C temperature to 500 °C at a heating rate of 5 °C min^{-1} (Mettler TA 300 instrument).

3. Results

The XPS Ti2p emission line as measured for Ti plates prior to porcelain firing is presented in Fig. 1. One can see that Ti appears mainly as quadrivalent TiO_2, but metallic Ti can also be seen at B.E. 454 eV. The contribution of metallic Ti is likely to originate from the underlying metal substrate. The mean free path of Ti2p photoelectrons is approximately 1.0–1.5 nm [14], which means that the thickness of TiO_2 layer can be evaluated to be a few nanometres.

The backscattering images of cross-sections of porcelain-veneered Ti with two different firing schedules (A and B in Table II) are shown in Fig. 2. In both cases a rather uniform interface layer can be seen between titanium and porcelain. The thickness of this interfacial layer, as measured from back scattering images, is given for all studied samples in Table III. It varies from 0.1–0.2 μm for vacuum-fired specimens (E, Table II) to 1.1–1.3 μm for a firing time of 30 min (D, Table II).

The results of four-point bending tests are also given in Table III. The calculation of fracture stress has been described elsewhere [15]. The maximum bond strength was obtained for vacuum-fired

TABLE II Porcelain firing programmes

Index	Firing schedule[a]
A	$550\,^\circ C \xrightarrow{42\,^\circ C\,min^{-1}} 800\,^\circ C/3\,min^{b}$ + air cooling
B	Programme A repeated four times
C	$550\,^\circ C \xrightarrow{42\,^\circ C\,min^{-1}} 800\,^\circ C/15\,min$ + air cooling
D	As C but 800 °C/30 min + air cooling
E	$600\,^\circ C \xrightarrow{15\,min} 800\,^\circ C/1\,min$ + cooling[c]

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[a] Vacuum 50 torr (6.7 kPa) applied at 675 °C for A–D.

[b] Vacuum off after 2 min.

[c] Whole firing cycle at 5×10^{-2} torr (6.7 Pa).

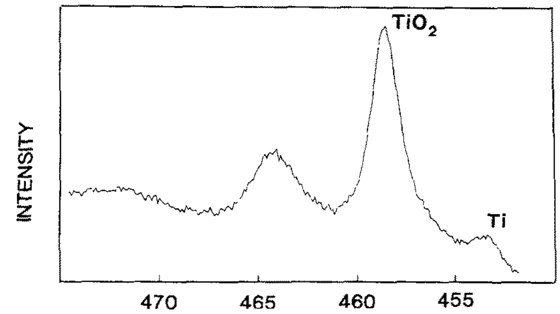

Figure 1 XPS Ti2p emission line for Ti plate prior to porcelain firing.

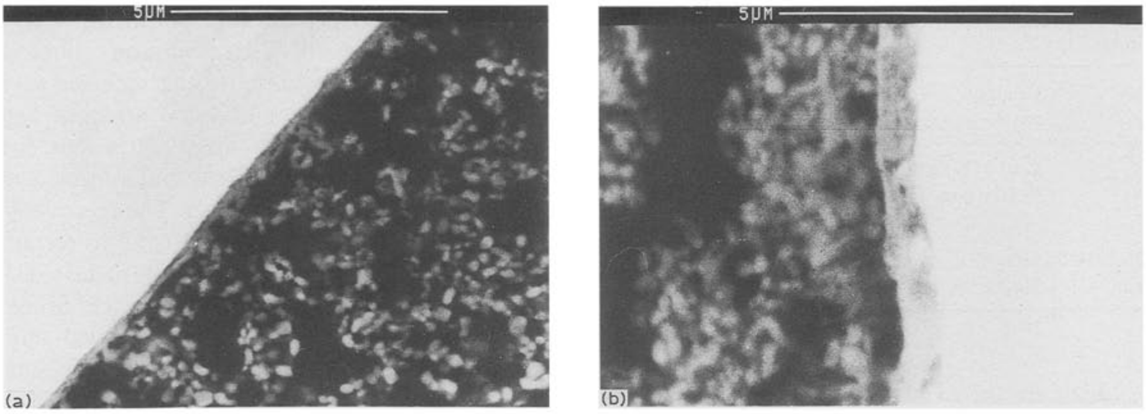

Figure 2 Backscattering images of porcelain-veneered Ti with two different firing schedules: (a) A, Table II; (b) B, Table II.

TABLE III Results from four-point bending tests and thickness of intermediate oxide layer measured from backscattering images

Firing schedule (see Table II)	Bond strength (MPa) ± SD	Thickness of oxide layer (μm)
A	18.3 ± 6.5	0.1–0.2
B	15.1 ± 5.0	0.6–0.7
C	10.0 ± 1.0	0.7–0.8
D	7.0 ± 3.7	1.1–1.3
E	30.6 + 9.7	0.1–0.2

(5×10^{-2} torr) specimens, whereas a long firing time resulted in the weakest bond.

Fractured surfaces of specimens fired for 3 and 30 min (programmes A and D, Table II) were studied with ESCA. For fractured Ti surfaces only metallic Ti could be seen after sputtering for 5 min for both specimens. The sputtering rate was evaluated to be less than 1 nm min^{-1} by using a standard reference Ta_2O_5/Ta sample. Thus, the depth removed can be estimated to be a few nanometres. These results therefore rule out the existence of a thick oxide layer, as seen in Fig. 2a and b, remaining on Ti after porcelain delamination. The oxygen profiles for these specimens and for an air-passivated Ti reference sample are presented in Fig. 3. For air-passivated Ti the amount of oxygen decreases more rapidly than for the fractured surfaces, where a relatively high oxygen concentration can be seen even after sputtering for 60 min.

The composition profiles of the delaminated porcelain fragments (firing time 3 min, programme A in Table II) facing Ti are presented in Fig. 4. The amount of oxygen decreases somewhat with the depth below the surface, while the Ti concentration increases. Otherwise there are no major changes during sputtering for 30 min. The initial change is probably caused by reduction of TiO_2 to lower oxides under sputtering. The oxide layer was too thick to be analysed by the depth profile technique employed, but the result is a quite clear indication of the existence of a thick, intermediate Ti oxide layer firmly attached to the inside of the porcelain fragment. Small amounts of silicon (a few at %) are already seen for the unsputtered surface. The Si concentration slightly increases during sputtering.

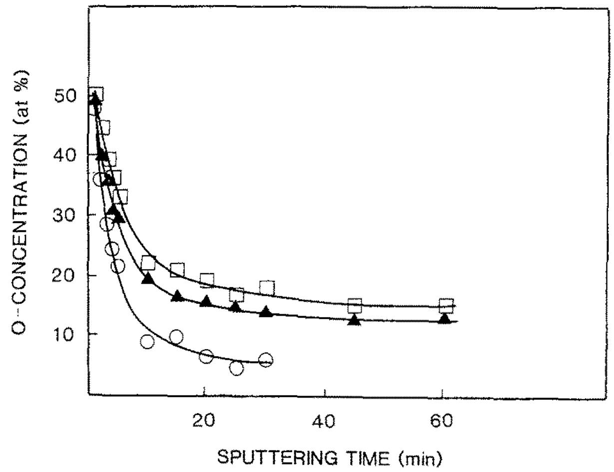

Figure 3 Oxygen profiles (ESCA) of Ti substrate subsequent to delamination of the porcelain ((▲) A and (□) D, Table II) and (○) air-passivated Ti.

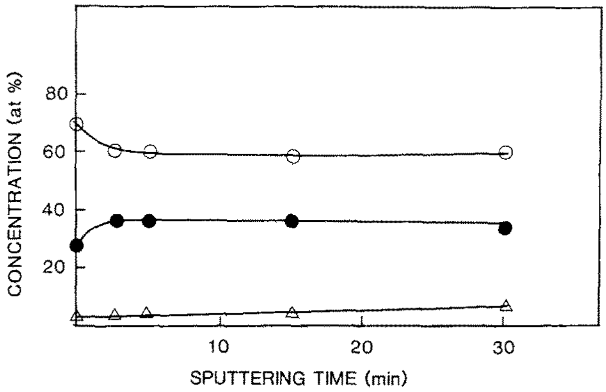

Figure 4 Composition profiles (ESCA) for delaminated porcelain (A in Table II): (●) Ti, (○) O, (△) Si.

The XPS Ti2p emission line obtained from the inside of this porcelain fragment is presented with respect to sputtering time in Fig. 5. Initial sputtering (2.5 min, curve A) was carried out in order to remove the layer exposed to air after fracture. Wide spectra can be seen after sputtering for both 2.5 and 30 min, indicating that Ti appears in several chemical states. Similar wide spectra were obtained for a TiO_2 (rutile) reference sample which was sputtered up to 30 min.

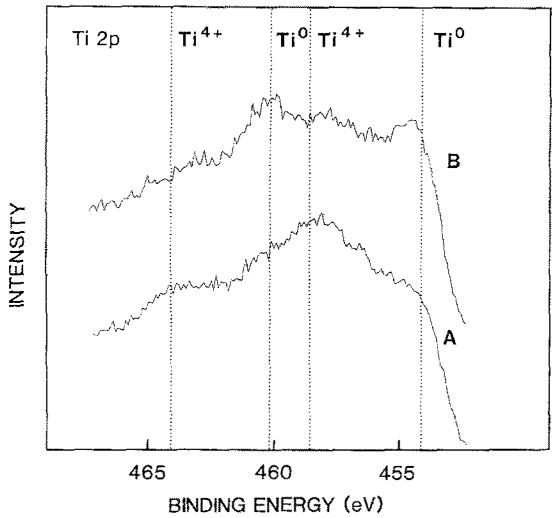

Figure 5 XPS Ti2p emission line for delaminated porcelain (A in Table II) with two different sputtering times: (A) 2.5 min, (B) 30 min.

The XPS Si2p emission line with different sputtering times for the porcelain fragment is presented in Fig. 6. In spectrum A one can see that silicon appears in two different chemical states: the higher B.E. corresponds to Si^{4+} and the lower one to Si^0. After sputtering for 30 min, mostly oxidized silicon can be seen. Whether the lower B.E. corresponds to metallic silicon or some Ti silicide cannot be distinguished on the basis of XPS measurements. The B.E. values of Si2p for Si and $TiSi_2$ have been reported to be approximately the same (98.6 and 98.8 eV) [16].

Concentration profiles for the porcelain fragment (firing time 30 min, programme D in Table II) are presented in Fig. 7. During sputtering for 5 min the amount of oxygen decreases significantly and that of Ti increases. After that no major concentration changes can be seen. The amount of Ti is clearly higher than that of oxygen. The XPS Ti2p spectrum with two different sputtering times is presented in Fig. 8. Ti appears metallic all through the sputtering cycle. This rules out the existence of a thicker TiO_2 layer adjacent to the fracture surface on the inside of the porcelain. If a TiO_2 layer is present, spectra containing Ti^{4+} peaks similar to those seen in Fig. 5 should be seen. This was not the case and it is apparent that there is metallic Ti on the inside of the porcelain indicating that fracture has occurred inside Ti. The B.E. of silicon seen in Fig. 7 corresponded to Si^0 all through the sputtering cycle.

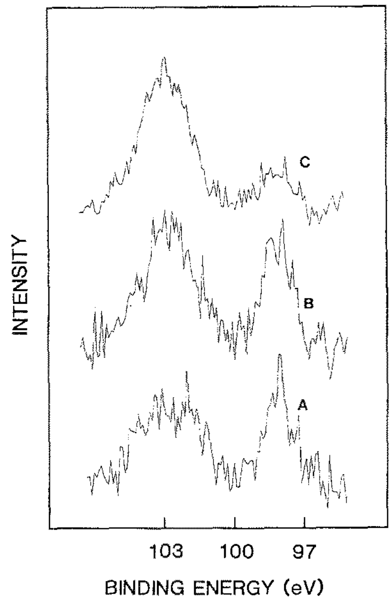

Figure 6 XPS Si2p emission line for delaminated porcelain (A in Table II) with different sputtering times: (A) 2.5 min, (B) 15 min, (C) 30 min.

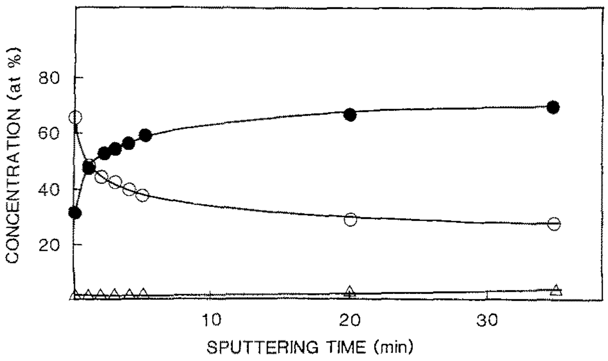

Figure 7 Composition profiles (ESCA) for a delaminated porcelain fragment (D in Table II): (●) Ti, (○) O, (△) Si.

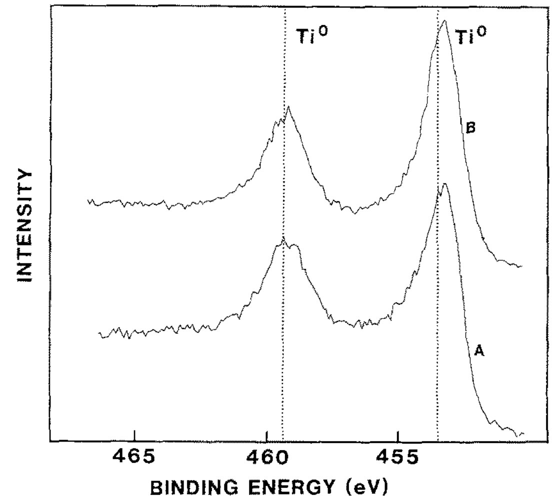

Figure 8 XPS Ti2p emission line for fractured porcelain (D in Table II) with two different sputtering times: (A) 2 min, (B) 35 min.

The composition of the delaminated porcelain fragment facing Ti (programme A, Table 2) was also analysed by EDX. The following composition (wt %) was obtained: SiO_2 31.4, Al_2O_3 4.5, K_2O 2.9, Na_2O 1.7, TiO_2 55.8. Comparing this composition with that of the porcelain powder (Table I), the amount of TiO_2 (55.8 wt %) is much higher whereas the amounts of other constituents are lower. In the EDX technique the emitted X-rays originate from a surface layer of roughly 1 μm thickness. The composition difference is most likely due to the 0.1–0.2 μm thick Ti oxide layer (Fig. 2a), sitting on the porcelain side facing the Ti substrate. The result is attenuated signals from the underlying porcelain substrate.

The coefficient of linear thermal expansion (Fig. 9) was found to be 8.6×10^{-6} and $6.4 \times 10^{-6}\,°C^{-1}$ for Ti and porcelain, respectively.

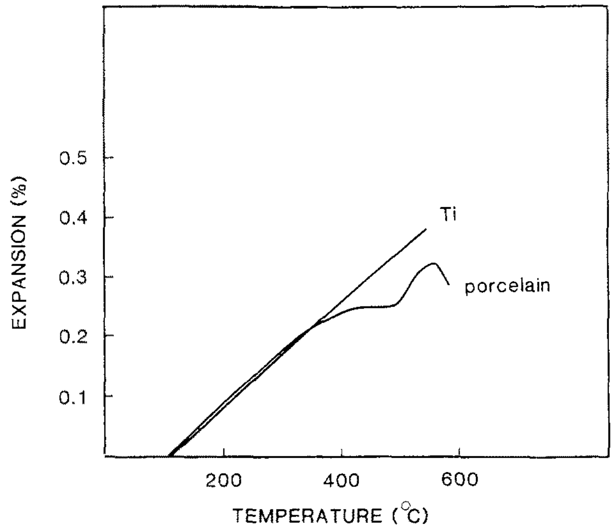

Figure 9 Thermal expansion of Ti and porcelain and thermal expansion coefficients as measured from 100 to 500 °C. TEC ($\times 10^{-6}$ °C^{-1}): Ti 8.6, porcelain 6.4.

4. Discussion

The fracture has been found to occur predominantly between the metal substrate and the oxide layer underneath the porcelain veneer or slightly into the metal substrate itself. Furthermore, the bond strength has been found to decrease with increasing oxide film thickness. This indicates that an understanding of the mechanisms of oxidation during porcelain veneering and of the fracture process is crucial for optimizing the bond strength of the porcelain veneer to the Ti substrate.

The oxidation mechanism of Ti consists of two separate mechanisms [17, 18]: (i) formation of an oxygen–metal solid solution and (ii) growth of the external oxide layer. Oxygen solubility may arise of up to or over 30 at % in interstitial sites of Ti [19]. The proportion of reacting oxygen which goes into solution has been questioned [17].

The oxide which forms on Ti under 1000 °C in air is known [17] to have a rutile structure. Generally rutile is found [17] to be an n-type semiconductor with oxygen deficiency (TiO_{2-x}). Most researchers have concluded [17] that oxygen diffusion predominates below about 900 °C, while titanium ion diffusion is also important at higher temperatures. In the first case oxide formation takes place at the metal–oxide interface because of inward diffusion of oxygen ions. Oxygen atoms necessary for further oxide formation must be obtained either by reduction of oxides in porcelain or by oxygen diffusion from the surrounding atmosphere through the porcelain layer and the thin intermediate oxide film. Ti is known [20] to have a high affinity for oxygen which is expressed as a high negative Gibbs free energy of oxidation. When Ti is in contact with a less stable oxide than TiO_2 such as SiO_2, Ti has a tendency to oxidize causing a reduction of the less stable oxide. XPS measurements made on the fracture surface of the porcelain support this assumption. Silicon near the interface (see Fig. 6) appears only partly in the oxidized state (2.5 min sputtering), whereas further away from the interface it appears mostly in the oxidized state (15 and 30 min sputtering).

The firing atmosphere significantly affected porcelain bonding (Table III), which indicates that oxygen diffusion from the surrounding atmosphere may also play an important role in oxide formation. Programmes A–D were run under a reduced air pressure of 50 torr and produced a bonding of only moderate strength. Programme E took place at the lowest pressure (5×10^{-2} torr) in these experiments, but at a different heating rate and time because another furnace had to be applied for this vacuum level (Table II). Yet an improved bond strength was achieved compared with programme A, although a possible reduced oxide film could not be detected by means of SEM. On the basis of the present experiments, therefore, both sources for the supply of oxygen are plausible.

These oxidation processes may induce stresses in the oxide scale as well as in the metal and thus cause a reduction or loss of adherence [13, 18, 21, 22]. The most common explanation for the generation of stresses is a large volume difference between oxide and metal, known as the Pilling–Bedtworth ratio (1.73 for TiO_2/Ti [21]). Compression stresses in the oxide and tensile stresses in the metal develop at the interface and increase with increasing oxide film thickness. The present results support such a mechanism, as the bond strength was reduced with increasing oxide film thickness. Epitaxial stresses may also arise, especially for very thin oxide scales. However, after the scale starts to thicken the stresses due to epitaxy are usually small. The third possibility is that the difference in the coefficient of thermal expansion between metal and porcelain (see Fig. 9) can cause residual stresses at the interface during cooling. Finally, composition changes in oxide or metal during firing can cause stresses.

This latter mechanism is relevant for Ti because large quantities of oxygen can dissolve in interstitial sites of Ti. The longer the oxidation continues, the more oxygen dissolves and the more stresses develop at the interface due to lattice parameter changes in Ti. The results obtained for the fractured specimens indicate that oxygen is dissolved into Ti (Fig. 3). If one compares two firing times (3 and 30 min, programmes A and D in Table II) one can see that the oxygen profiles are similar. However, at the short firing time (3 min) fracture took place between Ti and the oxide scale, which can be seen from ESCA analyses (Figs 3 and 4) for fractured surfaces, whereas at the long firing time metallic Ti with high oxygen solubility can be seen on the back side of the porcelain (Fig. 7). This means that the real oxygen profiles in Ti next to the oxide–metal interface are not similar. For the specimen fired for 30 min more oxygen has dissolved into the Ti lattice during prolonged firing, causing brittleness and fracture of Ti.

The thickness of the interface layer and/or the content of oxygen in solid solution in Ti have been found to affect the bond strength (Table III). For specimens fired at different air pressures (programmes A and E in Table II) the thickness is the same but the bond strength for vacuum-veneered Ti (programme E) is much better. A possible explanation for this difference in bond strength is that for vacuum-fired specimens the oxygen solubility is lower, resulting in smaller lattice parameter changes and smaller stresses and consequently better bonding.

5. Conclusions

Some concluding remarks can be made:

1. During porcelain firing a titanium oxide layer is formed between metal and porcelain.
2. The thickness of this layer depends on the firing time and oxidizing atmosphere.
3. Porcelain fracture with normal firing time occurs between oxide scale and Ti.
4. Oxygen solubility in Ti is likely to vary with respect to firing time.
5. An excessive oxygen dissolution into Ti can cause fracture inside Ti.

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