The effect of ZrSiN diffusion barrier on the bonding strength of titanium porcelain

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Abstract

ZrSiN film was selected as diffusion barrier of titanium porcelain interface and sputtered on polished titanium substrate with RF reactive magnetron sputtering. XRD, XPS and TEM results revealed that the ZrSiN diffusion barrier is a nano-composite that consists of nano-crystallite ZrN and amorphous-like SiNx phase. The results also showed that after simulated porcelain sintering thermocycles the surface of Ti substrate without ZrSiN diffusion barrier appears Ti oxide, however, the surface of Ti substrate with ZrSiN diffusion barrier appears no Ti oxides and only Zr, Si N and O. This proves that ZrSiN diffusion barrier protect the Ti substrate against oxidation during porcelain sintering. The results of three-point bending test also proved that ZrSiN diffusion barrier significantly improves the bonding strength between Ti substrate and porcelain. The ZrSiN diffusion barrier with higher Si content results in higher bonding strength of the Ti/porcelain. This indicates that amorphous Si–N phase of ZrSiN diffusion barrier improves its barrier property.

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PACS: 66.30.MY; 87.15.BY
Keywords: Titanium porcelain; Diffusion barrier; Bonding strength

1. Introduction

In recent years the use of titanium (Ti) and its alloys in dental implants and prostheses has increased dramatically because of their excellent biocompatibility, desirable properties, and low cost [1–4]. However, practical problems with Ti casting, joining, and Ti porcelain bonding remain to be solved [5–10]. Failures that occur in Ti porcelain dental restorations are of concern to clinicians. One property that contributes to the excellent biocompatibility of titanium but also causes problems when bonding to porcelain is the presence of surface oxides. When dental porcelain is applied, Ti has great affinity to oxygen, and its oxidation rate increases exponentially at elevated temperatures. Oxide layer formed on Ti surfaces at porcelain sintering temperatures is porous, nonadherent and unsuitable for porcelain bonding [11,12]. It easily spills off and cracks because of its porosity and internal stresses. Conventional dental furnaces have a vacuum level of around 10−2 Torr, and it is not sufficient to prevent titanium oxidation during dental porcelain sintering to titanium surface. In order to prevent the formation of a weak interface between titanium and porcelain, an intermediate layer can be deposited on Ti prior to the application of porcelain. The intermediate layer must consist of biocompatible materials, must act as a barrier to the diffusion of oxygen, and must be strongly bonded to the Ti substrate. It also must be capable of establishing a strong bond to the porcelain [13]. The researches have proved that ZrSiN film is an excellent diffusion barrier to prevent the diffusion between Cu and Si [14]. The aims of this investigation were to study the characteristics of ZrSiN films deposited on titanium to prevent titanium oxidation and to identify the effects of ZrSiN films with different Si content on the bonding strength between dental porcelain and titanium.

2. Experimental

In this paper 1 μm ZrSiN film was selected as diffusion barrier and sputtered on polished titanium substrate (25 mm × 3 mm × 0.5 mm) with RF (radio frequency) reactive magnetron sputtering.
magnetron sputtering. Base pressure of vacuum chamber is better than $2 \times 10^{-5}$ Pa and the substrates were cleaned by bombardment of Ar ion. The ZrSiN film was deposited in gas mixture of Ar and N$_2$. The flow rate of N$_2$/Ar was 4:16 sccm. Zirconium plate with different number Si chips (10 mm × 10 mm × 0.6 mm) on top of it was used as a target. Si chips number was 1, 2, 3, and 4 respectively. The input RF power, sputtering pressure and substrate bias voltage were 300 W, 0.3 Pa and −100 V respectively. After the deposition of ZrSiN diffusion barrier, the bonding agent, opaque, dentin and glaze of Duceratin (Degussa) were brushed onto ZrSiN/Ti substrate and sintered. Table 1 lists the sintering schedule of Duceratin porcelain. The titanium plate without ZrSiN diffusion barrier was used as comparison. Each sample was washed in an ultrasonic bath in acetone for 10 min before insertion into the vacuum chamber. The silicon wafers provided control substrates on which the film could be analyzed.

X-rays diffraction (XRD), scan electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), Transmission Electron Microscope (TEM), and energy dispersive analysis of X-rays (EDS) were used to study the samples. The bonding strength of samples was evaluated with three-point bending test according to ISO9693 1999. A porcelain fracture without a resultant delamination of porcelain from the titanium substrate indicated porcelain shear bond strength is greater than the fracture strength of the porcelain alone. The maximum stress on the surface of the metal was used to calculate bonding strength with the formula: $\sigma_B = \frac{3WL}{2bd^2}$, where $W$ is the maximum load, $L$ is the distance between the supports, $b$ is the width of the specimen, and $d$ is the depth of the specimen. Seven specimens were tested for each experimental group.

### 3. Results and discussion

The effect of the silicon concentration on the X-ray diffractograms of ZrSiN films is displayed in Fig. 1. At lower silicon concentration (1.9 at.%), only the ZrN phase is detected by XRD. This result implies that Si might be present in an amorphous phase of silicon nitride. At higher silicon concentration (18 at.%), no diffraction peak is observed and the film seems to be amorphous. Whatever the silicon concentration, no diffraction peak of silicon-containing compound is detected. To obtain further information on the chemical environment of silicon atoms, XPS analyses have been performed. Fig. 2 shows the Zr3d and Si2p spectra in Zr–Si–N films. The peak binding energies of Zr–N are consistent with the standard records of stoichiometric ZrN [15,16]. This suggests that the

<table>
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<tr>
<th>Table 1</th>
<th>Firing Schedules of Duceratin (Degussa) Porcelains</th>
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<tr>
<td></td>
<td>Bond</td>
</tr>
<tr>
<td>Low temp (°C)</td>
<td>600</td>
</tr>
<tr>
<td>Pre-heat time (min)</td>
<td>5</td>
</tr>
<tr>
<td>Heat rate (°C/min)</td>
<td>55</td>
</tr>
<tr>
<td>Vacuum on (°C)</td>
<td>450</td>
</tr>
<tr>
<td>Vacuum off (°C)</td>
<td>780</td>
</tr>
<tr>
<td>Vacuum level</td>
<td>Full</td>
</tr>
<tr>
<td>High temp (°C)</td>
<td>780</td>
</tr>
<tr>
<td>Holding time (min)</td>
<td>1</td>
</tr>
<tr>
<td>Cooling procedure</td>
<td>Bench cool</td>
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</table>

![Fig. 1. XRD pattern of ZrSiN film with different Si concentration.](image1)

![Fig. 2. XPS spectra of as-deposited ZrSiN films Zr3d and Si2p.](image2)
addition of Si to ZrN does not substantially affect the bonding state between Zr and N. The Si2p core level of XPS spectra contains only 101.7 eV bond energy indicates that silicon atoms are fully nitrided in the coatings.

TEM examination and electron diffraction pattern (not shown here) of ZrSiN film with different Si concentration revealed that when Si concentration was low the ZrN grains are very fine with a length of 20 nm or less. When the Si concentration is high, the ZrSiN film becomes a wholly amorphous structure, indicating that ZrN exists as finer grain phase in the film.

As a summary, the analyses of XRD, XPS and TEM indicate that the microstructure of ZrSiN film consists of nano-crystallite ZrN and an amorphous SiNₓ phase.

Fig. 3 shows SEM micrograph of Ti samples that have undergone porcelain sintering thermocycles in a dental furnace without actual application of the porcelain layers on Ti. Fig. 3(a) shows a SEM micrograph of the oxidized surface of a thermocycled Ti sample without ZrSiN coating. Fig. 3(b) shows the micrograph of a ZrSiN coated Ti sample after thermocycle. The micrograph shows that the ZrSiN coating appears fully coherent to Ti substrate. There is no any crack or flaw. The EDS results also revealed that the surface of Ti substrate without ZrSiN diffusion barrier appears Ti oxide, however, the surface of Ti substrate with ZrSiN diffusion barrier appears no Ti oxides and only Zr, Si, N and O. It can be inferred that the ZrSiN coating layer provided protection to the titanium substrate against oxidation.

The three-point bending test results of samples with and without ZrSiN diffusion barrier are shown in Table 2. The ZrSiN diffusion barrier appears to block the oxidation of the Ti substrate and results in statistically significant increases in the bond strength of porcelain to Ti substrate. Ti samples coated with ZrSiN diffusion barrier had higher bonding strength than those of samples without the protective coating. The bonding strength of Ti/porcelain increases as the Si concentration of ZrSiN diffusion barrier increases.

Fig. 4 shows SEM micrograph of the fractured Ti surface without and with ZrSiN diffusion barrier after three-point bending tests. In Fig. 4(a), without ZrSiN diffusion barrier the Ti sample reacted with the porcelain and the fracture takes place at the interface of Ti/porcelain. In Fig. 4(b), when ZrSiN diffusion barrier was applied the Ti substrate fractures mainly occurs inside the porcelain layer or near the porcelain layer part of ZrSiN coating/porcelain interface but not at the Ti/ZrSiN coating.

Fig. 5 gives SEM micrographs of the cross-sectioned Ti/porcelain samples before three-point bending test. Fig. 5(a) reveals that there exists pre-crack in Ti/porcelain interface without ZrSiN diffusion barrier. But in Fig. 5(b), Ti adheres to porcelain well and there is no pre-crack in Ti/porcelain interface when ZrSiN diffusion barrier was applied.

Above results proved that compact bonding between porcelain and ZrSiN coating was achieved. The bonding strength values of Ti/porcelain with ZrSiN coating were significantly higher than those of samples with no ZrSiN protective coating. The bonding strength increases as Si concentration of ZrSiN diffusion barrier increases. The reason might be that the amorphous SiNₓ in ZrSiN films decreases the diffusion path of oxygen to Ti substrate and improves the bonding strength. As Si concentration increases there is more amorphous SiNₓ phase, which can prevent oxygen from diffusing into Ti substrate and the formation of porous Ti oxides.

Based on the above analyses it is obvious that for protective coating it is essential to prevent the formation of excessive, porous Ti oxides in order to maintain compact bond of Ti and porcelain. Because titanium possesses large negative Gibbs energy of oxidation, continued oxidation could occur resulting from reduction of the oxides in the porcelain via displacement reactions. Therefore porcelain-induced oxidation at elevated temperature may result in a substantial decrease in oxide adherence to titanium. Up to now there is limited information regarding the bonding strength between dental porcelain and Ti with ZrSiN diffusion barrier.

Table 2

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<tr>
<th>Si Concentration (at.%)</th>
<th>Bonding Strength (MPa)</th>
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<tr>
<td>Without ZrSiN coating</td>
<td>25.2 ± 0.86</td>
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<tr>
<td>1.9 at.% Si</td>
<td>32.7 ± 0.73</td>
</tr>
<tr>
<td>5.2 at.% Si</td>
<td>40.5 ± 0.64</td>
</tr>
<tr>
<td>9.5 at.% Si</td>
<td>48.9 ± 0.58</td>
</tr>
<tr>
<td>18 at.% Si</td>
<td>57.3 ± 0.96</td>
</tr>
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Results of the bonding strength test here indicated that the ZrSiN film applied to titanium surfaces seemed to prevent the adverse oxidation effect, resulting in the maintenance of an appropriate oxide layer for porcelain bonding. Because of the excellent biocompatibility, desirable properties, and relatively low cost of ZrSiN film deposition, its application to the surface of Ti as interlayer of Ti/porcelain system needs further investigation.

4. Conclusion

The effect of Si concentration of ZrSiN film which was deposited by RF magnetron sputtering, on bonding strength between titanium and dental porcelain was studied. Oxidation experiments that simulated thermocycles of porcelain sintering were carried out in order to characterize the ZrSiN film’s effectiveness in preventing the adverse oxidation of Ti and enabling the compact bonding of porcelain and titanium. The conclusions are as follows: (1) ZrSiN film consists of nanocrystallite ZrN and an amorphous SiNₓ phase. (2) ZrSiN diffusion barrier improved the bonding strength of titanium/porcelain 2 times over that of nonprotected titanium/porcelain. (3) ZrSiN diffusion barrier with higher Si concentration result in higher bonding strength.

References