Surface characterization and bond strengths between Ti-20Cr-1X alloys and low-fusing porcelain

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INTRODUCTION

For reasons of mechanical strength and pure aesthetics, porcelain-fused-metal (PFM) plays an important role in the crown and bridge technique¹. Use of c.p. Ti and its alloys in dentistry and medicine has increased in recent decades due to their excellent biocompatibility, high strength to weight ratio, corrosion-resistance and low cost²,³. Although porcelain fused to a metal crown is usually used as a technique for dental restorations, titanium’s insufficient bond strength with porcelain yields inferior dental applications.

The bond of porcelain to a metal is ascribed to both a mechanical interlocking between both materials, and to chemical bonds between the porcelain and an oxide layer that is constructed during the firing process on the surface of the metal. In most cases, the failure of the titanium-porcelain bond is caused by the stress of the difference of the CTE of titanium and ceramic, thus having a negative effect on the flexural bond strength of the titanium ceramic system⁶. Additionally, the appropriate oxide thickness may increase the bond strength, but the failure may also be attributed to an excessively thick oxide layer, weakening the bond strength of c.p. Ti⁵. Many studies have paid close attention to evaluating the titanium-porcelain bond since a strong adherence is the main requirement for clinical success³,⁶,⁷,⁸,⁹,¹⁰.

At present, many efforts are focused on the development of new titanium alloys that can both improve aesthetics achieved by porcelain veneering, and increase metal-ceramic bond strength¹¹,¹². In addition, alloying additions could change the CTE of titanium¹³ either through dissolution in solid state, or the formation of new phases, with some effects on metal-ceramic bond strength¹⁴,¹⁵.

A number of test methods are used for measuring bond strength, which can be classified as shear tests, flexure tests, and tensile tests¹⁶,¹⁷. The International Organization for Standardization has recommended a three-point flexure bond test¹⁷, which is described in the revision of the standard ISO 9693¹⁸. The purpose of this study was to evaluate the bond strength of experimental ternary Ti-20Cr-1X alloys to dental porcelain, and its potential application as a superior dental restoration material. The bonding interface between metal and porcelain substrates after the bending test was observed using a SEM with energy-dispersive spectrometry (EDS). The CTE values of the Ti-20Cr-1X alloys and c.p. Ti were also evaluated.

MATERIALS AND METHODS

A series of Ti-20Cr-1X alloys (X=Nb, Mo, Fe, Zr) and c.p. Ti was used for this study. For the sake of simplicity, throughout the text “Ti-20Cr” refers to “Ti-10 wt.% Cr” and “Ti-20Cr-1X” refers to“Ti-20 wt.% Cr-1 wt.% X”, where X is a given alloying element. The Ti alloys, including Ti-20Cr-1Nb, Ti-20Cr-1Mo, Ti-20Cr-1Zr and Ti-20Cr-1Fe, were prepared using a commercial arc-melting vacuum-pressure-type casting system (Castmatic, Iwatani Corp., Japan). The ingots were melted five times to improve chemical homogeneity. The difference in pressure between the two chambers allowed the molten alloys to instantly drop into a graphite mold at room temperature. In this study, the experimental alloys were fabricated using a graphite mold instead of a dental investment mold. There were at least five
specimens tested for each test. In this study, a low-fusing porcelain named Duceratin (Ducer Dental-GmbH, Rosbach, Germany) was used. Porcelain-bonding agent powder and liquid were mixed according to the manufacturer’s instructions. According to ISO 9693\(^{18}\), standardization of the porcelain applications over the center of each metal strip was conducted by means of a die in the dimensions 8×3×1 mm. This process complied with the instructions of manufacture, and was conducted in an electric furnace (Multimat 99, Dentsply Intl., York, PA).

A three-point flexural device in a universal testing machine (AG-IS, Shimadzu, Kyoto, Japan) was used to test the specimens’ bond strength in all groups. Metal-Porcelain specimens were positioned on supports with 6.37 mm diameters and 20 mm span distances with the porcelain layer facing down. A compressive load was applied at the midline of the metal strip by a rounded loading rod at a crosshead speed of 0.5 mm/min until a sudden drop in load occurred in the load-deflection curve, indicating the bond failure. The bending strength was calculated according to the following formula\(^{18}\), indicating the bond failure. The bending strength was calculated according to the following formula\(^{18}\), $\sigma = \frac{3PL}{2bd^2}$, where $\sigma$ is the bond strength (MPa), $P$ the maximum load at the point of fracture (N), $L$ the distance between the supports (mm), $b$ the width of the porcelain-fused-to-metal specimen (mm), and $d$ the thickness of the porcelain-fused-to-metal specimen (mm).

SEM (JSM-6700F, Jeol, Tokyo, Japan) was carried out to characterize the type and morphology of the fracture in representative specimens selected from each combination in which there was complete separation between porcelain and metal after the bending test. Specimens were cleaned in an ultrasonic bath with distilled water for 10 min prior to the SEMs. The elemental analysis of the failed surfaces at the metal-porcelain interface was investigated using a scanning electron microscope equipped with an energy dispersive spectrometer (EDS).

Thermal expansion was tested using a push-rod dilatometer (Theta Dilamatic II, Port. Washington, NY) at a heating rate of 5°C/min, using a starting temperature of 25°C, and target temperature of 650°C in the air atmosphere. The linear CTE value was calculated between 25 and 500°C from the plotted curve of expansion versus temperature. One-way ANOVA was used to evaluate data and Duncan’s multiple range test was ran to determine the significance of deviations among each group. In all cases, the statistical difference was considered significant at $p<0.05$ level.

**RESULTS**

**Bond strength**

The bonding strength of the experimental Ti-20Cr-1X alloys and c.p. Ti with Duceratin porcelain are shown in Fig. 1. For the Ti-20Cr-1X alloys, the mean bonding strength values that ranged from 25.13 (Ti-20Cr-1Fe) to 30.59 (Ti-20Cr-1Mo) MPa were above the lower limit value in the ISO 9693 standard (25 MPa), and were significantly higher than those of c.p. Ti (21.1 MPa). As shown in Fig. 1, among the Ti-20Cr-1X alloys, 1 wt% element addition may cause different bond strengths. ANOVA test results showed significant overall differences among the bond strengths of the metal-porcelain for c.p. Ti and Ti-20Cr-1X alloys ($p<0.05$). Results of the Duncan’s multiple comparison test revealed that the bonding strengths of the Ti-20Cr-1Mo alloy were significantly ($p<0.05$) higher than that of c.p. Ti and the other Ti-20Cr-1X alloys.

**SEM analysis**

Fig. 2 shows the micrographs of the titanium alloy surface after the debonding test. As shown in Fig. 2, the residual porcelain was retained on the metal surface for all testing specimens in this study. The c.p. Ti surface exhibited the least amount of retained porcelain on the metal surface after debonding (Fig. 2(a)), suggesting the occurrence of mostly adhesive failure, and confirming the lower mechanical strength values obtained. These results are similar to those found by\(^{15-22}\). The observations made in the c.p. Ti covered by Duceratin porcelain showed a smaller quantity of porcelain adhering in comparison to the other specimens, confirming the data obtained by mechanical testing. More traces of retained porcelain were observed on specimens such as Ti-20Cr-1Mo alloy. The results of the metal-ceramic bond strengths also showed that the Ti-20Cr-1Mo alloy was significantly higher in this respect.

All specimens showed similar features within the interfacial area in Fig. 2. Taking Ti-20Cr-1Mo alloy as an example, under greater magnifications ($\times2,000$) in Fig. 3, four different areas were found on the surface after debonding. The four areas on the Ti-20Cr-1Mo alloy surface after debonding are summarized in Table 1 and the EDS spectrums on the four portions of the Ti-20Cr-1Mo alloy surface after debonding are shown in Fig. 3 (a)-(d). X-ray spectrum of white area reveals the presence of Ti and Cr on marked point (a) (Fig. 3(a)). Chemical compositions in the gray area, include marked point (b) from EDS analysis contain O, Na, Al, Si and K.
In the light point, O, Na, Al, Si, and Sn were observed on point (c) (Fig. 3(c)). In the black area, both Al and O were found on point (d) (Fig. 3(d)).

**Coefficient of thermal expansion (CTE)**

For the thermal expansion test, thermal expansion curves and CTEs of the tested specimens were determined, and are shown in Fig. 4 and Table 2. Fig. 4 shows the thermal expansion curves of c.p. Ti and Ti-20Cr-1X alloys. Fig. 4 shows that the thermal expansion rate in the temperature range 25–800°C was uniform. Table 2 shows the mean CTE values, standard deviation, and range of the tested specimens.

**Fig. 2** SEM morphology of metal-ceramic surface after debonding from the Duceratin porcelain. (a) c.p. Ti, (b) Ti-20Cr-1Mo, (c) Ti-20Cr-1Nb, (d) Ti-20Cr-1Zr, and (e) Ti-20Cr-1Fe.
deviations and results of the Duncan's multiple comparison test. ANOVA test results showed significant overall differences among the CTE values of metal/alloys ($p<0.05$). The CTE values of the Ti-20Cr-1X alloys were higher than that of c.p. Ti ($10.12 \times 10^{-6}/°C$), and ranged from $11.03 \times 10^{-6}/°C$ to $11.36 \times 10^{-6}/°C$, depending on the elemental composition. Results of the Duncan's multiple comparison test revealed that the Ti-20Cr-1X alloys had a significantly higher CTE than that of c.p. Ti ($p<0.05$).

The mismatch of CTE between metal and porcelain significantly affected the flexural bond strength of the ceramic-metal systems, which may contribute to bond failure. Titanium alloys have the potential to overcome the mismatch in the CTE with low-fusing porcelains if suitable amounts of appropriate alloying elements are added.

Table 1  Summary of the four areas on Ti-20Cr-1Mo alloy surface after debonding

<table>
<thead>
<tr>
<th>Area</th>
<th>Elements</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>Ti, Cr</td>
<td>Ti-20Cr-1Mo substrate</td>
</tr>
<tr>
<td>Gray</td>
<td>O, Na, Al, Si, K</td>
<td>Dentin layer</td>
</tr>
<tr>
<td>Light</td>
<td>O, Na, Al, Si, Sn</td>
<td>Bonding layer</td>
</tr>
<tr>
<td>Black</td>
<td>O, Al</td>
<td>Sandblasting particle</td>
</tr>
</tbody>
</table>

Table 2  Coefficient of thermal expansion of c.p. Ti and Ti-20Cr-1X alloys ($\times 10^{-6}/°C$)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>c.p. Ti</th>
<th>Ti-20Cr-1Mo</th>
<th>Ti-20Cr-1Nb</th>
<th>Ti-20Cr-1Zr</th>
<th>Ti-20Cr-1Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE ($\times 10^{-6}/°C$)</td>
<td>$10.12 \pm 0.29$</td>
<td>$11.36 \pm 0.09$</td>
<td>$11.03 \pm 0.10$</td>
<td>$11.20 \pm 0.10$</td>
<td>$11.14 \pm 0.44$</td>
</tr>
</tbody>
</table>

Fig. 3  SEM morphology of Ti-20Cr-1Mo alloy surface after debonding, and the accompanied EDS elemental analyses of the four portions marked (a)-(d), respectively.

Fig. 4  Thermal expansion curves of c.p. Ti and Ti-20Cr-1X alloys.
DISCUSSION

Because all of the specimens had identical dimensions, the load at bond failure could be used as a parameter to compare the bond strengths among systems. The high bond strength between porcelain and alloys with Cr content was reported by Ho et al.7, who concluded that the high bond strength of Ti-Cr alloy was due to the suitable CTE difference between porcelain and metal. Apart from the high percentage of Cr demonstrated within the oxide layer of Ti-Cr alloy, the rare Nb, Mo, Zr and Fe elements may be essential in establishing the chemical bond between porcelain and Ti-Cr alloy in this study.

A three-point bending test was adopted as a standard for ISO 969318. Anusavice23 used finite element stress analysis to show that was a suitable method. In this study, the thicknesses of metal and porcelain specified in this standard were similar to those applied in the clinical situation. The clinical performance of metal-ceramic restorations is normally estimated by bond strength tests of the combinations between the metal substrates and the porcelains19). Thus, the commercial porcelain Duceratin used in this study might be suitable for the Ti-20Cr-1X alloy system.

According to the SEM/EDS analysis, Table 1 shows the summary of the four areas of Ti-20Cr-1Mo alloy surface after debonding. As shown in Table 1, the white, gray, light and black areas represent the Ti-20Cr-1X substrate, dentin layer, bonding layer, and sandblasting particles, respectively. For Ti-20Cr-1X substrate, Ti and Cr were found in the white areas, and the amount of Mo (1wt%) was too small to be found. The black areas contain only two elements, Al and O, suggesting that these areas could have been produced by sandblasting with alumina particles. The surface treatment of metal using aluminum particles with a diameter of 120 µm provided a roughened surface in this study. It is possible that the small particles may have embedded in the titanium surface. In fact, Ho et al.7 found that sandblasting abrasion could contaminate the surface of titanium with alumina particles.

Residual stress and fractures are strictly related to the difference of thermal expansion between the metal substrate and the porcelain. The mismatch of CTE between metal and porcelain significantly affects the flexural bond strength of the ceramic-metal systems, which may contribute to failure20. In this study, the CTE of the Duceratin porcelain, according to its manufacturer, is 12.5×10⁻⁶/°C (bonding layer). Thus, the CTE of 10.12×10⁻⁶/°C for c.p.Ti exceeds the difference between them by 2.38×10⁻⁶/°C. On the other hand, the difference between Ti-20Cr-1Mo alloy and porcelain reaches the lowest value (1.4×10⁻⁶/°C). The results showed that Ti-20Cr-1Mo had the highest bond strength, which was higher than that of c.p. Ti. It was concluded that there is a smaller difference in the CTEs between Ti-20Cr-1Mo alloy and Duceratin porcelain, verifying the data obtained by bond strength testing.

The strengths of all the experimental alloys were significantly higher when compared to those of c.p. Ti, indicating that all the experimental alloys developed an acceptable bond strength when bonding to the porcelain. The minimal clinically acceptable bond strength (25 MPa) has been established in this study, but a continuing study of porcelain fused to titanium is necessary because long-term clinical reports regarding the success of the titanium-porcelain systems are still needed. Ideally, favorable bonding characteristics include mechanical, chemical and thermal compatibility between metal and porcelain19). In order for metal and porcelain to be compatible, the least difference in the CTE between the materials is best. When appropriate quantities of suitable alloying elements are added in titanium alloys, they have the possibility to overcome the mismatch in the CTE with low-fusing porcelains.

Furthermore, the mechanical properties of the experimental alloys may be one of the important factors affecting the observed values of bonding strength. Our previous work showed that when 1 wt.% Nb, Mo, Zr or Fe was added, the microstructures of the Ti-20Cr-1X alloys showed all the equi-axed β grain structures25). Our previous work showed that the mechanical properties of the Ti-20Cr-1X alloys can be changed by adding small amounts of alloying elements. The alloying elements Nb, Mo, Cr and Fe contribute significantly to increased microhardness and strength.

Though the order of the difference of CTE values was Ti-20Cr-1Mo>Ti-20Cr-1Zr>Ti-20Cr-1Fe>Ti-20Cr-1Nb, based on the comparison of Table 2 and Fig. 1, the observed order of bonding strength was Ti-20Cr-1Mo>Ti-20Cr-1Nb>Ti-20Cr-1Zr>Ti-20Cr-1Fe. This difference was explained in our previous study in which the Ti-20Cr-1Nb alloy showed the highest bending strength and Ti-20Cr-1Zr showed the highest bending modulus25). This discrepancy demonstrates that other factors such as the mechanical properties of metal substrates did affect the bonding strength. These alloys may have deflected obviously after the porcelain was debonded during the bonding test. Tuccillo studied the deflection of metals and porcelains from heating to cooling and the results of this study showed that bending was affected more by the incompatibility of the thermal expansion curves of metals and porcelain than by the difference in the CTEs20).

CONCLUSION

1. The bond strengths of all the Ti-20Cr-1X alloys ranged from 25.13 MPa (Ti-20Cr-1Fe) to 30.59 MPa (Ti-20Cr-1Mo), and were above the lowest limit value in the ISO 9693 standard (25 MPa). The Ti-20Cr-1Mo alloy had the highest bond strength, which was actually higher than that of c.p. Ti (21.1 MPa).
2. The surface of Ti-20Cr-1Mo alloy after de-bonding exhibited more retained porcelain on the metal surface. This could be related to the match of the CTE of metal and porcelain.
3. The CTE values of all the Ti-20Cr-1X alloys

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ranged from $11.03 \times 10^{-6}/°C$, and were higher than that of c.p. Ti ($10.12 \times 10^{-6}/°C$), depending on the elemental composition. Of all the Ti-20Cr-1X alloys, the CTE of the Ti-20Cr-1Mo alloy ($11.36 \times 10^{-6}/°C$) was the highest.

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