INTRODUCTION

Porcelain-fused-to-metal restorations (PFMRs) are a bilayered structure consisting of a metallic substructure and veneering porcelain. Due to their good mechanical properties and adaptability of casting alloys and esthetic appearance of porcelain, these dental prostheses are utilized to reconstruct patients’ oral function. Even though the patient demand for all-ceramic restorations (ACRs) has recently increased, PFMRs remain an effective option. PFMRs using precious metal or Co-Cr alloy substructures have shown similar or higher survival rates than ACRs, even in recent years1-3). Especially, PFMRs exhibited a low risk of porcelain fracture incidents for fixed partial dentures (FPDs) than zirconia-based ACRs1,3).

Titanium (Ti) has good biocompatibility and corrosion resistance, adequate mechanical properties, and a lower risk of metal hypersensitivity4,5). Thus, the clinical use of Ti and its alloys has steadily increased for dental restorations4-6). However, PFMRs using machined Ti substructures showed poor clinical performance due to a high frequency of porcelain fractures7,8). These conflicting results between Ti and other metals in PFMRs are due to differences in the manufacturing process of the metallic substructure and excessive oxidation of Ti surface during porcelain firing, which may weaken the bond strength between the metallic substructure and veneering porcelain7-11).

Although good corrosion resistance is generally achieved on the Ti surface by thin metal oxides film, Ti is as corrosive as many other base metals when the unpredictable conditions occur in the oral cavity, which is subjected to the multiple chemical, biological, mechanical, electrical, and thermal factors4,12,13). Indeed, the discoloration and dissolution of Ti and its alloys were clinically reported14,15).

To overcome these detrimental effects, previous studies have developed an experimental cast Ti alloy containing 20 mass% chromium (Ti-Cr)16-18). Adding chromium (Cr) to Ti forms a Cr oxide-rich surface film, imparting increased corrosion resistance against attack from either fluoride and peroxide compared to commercially pure Ti (cp-Ti)16,17). Moreover, the Ti-Cr alloy reduced surface damage against simultaneous mechanical wear and electrochemical corrosion19). From these advantageous characteristics, the Ti-Cr alloy would be expected as a preferred substructure material for PFMRs.

This study evaluated bond strengths of three commercial veneering porcelains to experimental cast titanium-chromium (Ti-Cr) alloy and commercially pure titanium (cp-Ti) via three-point bending test. After the bending test, the fractured specimens were analyzed using an electron probe microanalyzer (EPMA). The Ti-Cr specimens showed lower bond strengths than the cp-Ti specimens, irrespective of the layering porcelain material; however, all the strengths exceeded the minimum requirement of ISO 9693-1:2012 (>25 MPa). EPMA revealed that titanium and/or chromium elements were detected on the debonded porcelain surface of the Ti-Cr and cp-Ti specimens in the case of the higher bond strength. Contrastingly, the residual porcelain was retained on the metallic surface in the case of the lower bond strength. Although porcelain bonding to the titanium alloy is influenced by porcelain type, the Ti-Cr alloy could be feasible for porcelain-fused-to-metal restorations.

Keywords: Titanium alloy, Chromium, Porcelain, Bond strength, Metal-ceramic restorations
strengths of three different commercial low-fusing porcelains to the Ti-Cr alloy via three-point bending test in compliance with ISO 9693-1:2012 (Schwickerath crack initiation test)\textsuperscript{24}. Additionally, the thermal and mechanical properties of the Ti-Cr alloy were evaluated because these could be influenced by different manufacturing methods. The null hypothesis was that the Ti-Cr alloy would improve the porcelain bond strength compared to cp-Ti, irrespective of the porcelain.

MATERIALS AND METHODS

Preparation of the metallic specimens

Experimental cast Ti alloy containing 20 mass% Cr (denoted as Ti-Cr) was used to prepare metallic specimens. Ti-Cr ingots were made by melting sponge Ti (Ti: >99.8 mass%; Fe: <0.03 mass%, Osaka Titanium Technologies, Amagasaki, Japan) and pure Cr (>99.99 mass%, Japan Metals & Chemicals, Tokyo, Japan) by an argon-arc melting furnace (ACM-01, Diavac, Chiba, Japan) as previously reported\textsuperscript{18}). A cp-Ti (Tritan, Dentaurum, Ispringen, Germany) was used as the experimental control.

Three different shapes of metallic specimens were prepared according to ISO 22674:2016 for the thermal and mechanical properties of metallic substrates and ISO 9693-1:2012 for metal-ceramic interface characterization\textsuperscript{24,25}. Briefly, the specimens were either cylindrical rods (25 mm in length and 5 mm in diameter), single dumbbells (52 mm in length and 3 mm in diameter), and strips (25×3×0.5 mm). For casting, specific wax patterns of the respective specimens were prepared, attached to the sprue former, and invested with silica-, magnesia-, and alumina-based phosphate-bonded investment (rematitan Plus Speed, Dentaurum). Ti-Cr alloy or cp-Ti ingots were arc-melted and cast into the mold using an argon-arc melting/pressure casting machine (rematitan autocast, Dentaurum). After cooling, the castings were blasted with 250 µm Al₂O₃ particles (Blasting abrasive, Dentaurum) to remove any adhering investment and polished. Finally, the dimensions of the respective specimens were verified using an electronic digital caliper.

Thermal and mechanical properties of the metallic specimens

According to ISO 22674\textsuperscript{25}, the thermal expansions of both the Ti-Cr and cp-Ti cylinder-shaped specimens (n=2) were measured with a dilatometer (DIL 402 C, NETZSCH-Gerätebau, Selb, Germany) at a heating rate of 5°C/min from 25°C to the target temperature of 550°C in the air atmosphere. The linear CTE value of each specimen was determined between 25°C and 500°C from the plotted curve of expansion versus temperature. Tensile tests for both the Ti-Cr and cp-Ti single dumbbell-shaped specimens (n=6) were performed. The applied loading was conducted at a crosshead speed of 0.5 mm/min at room temperature using a universal testing machine (INSTRON 5569, Instron Japan, Kawasaki, Japan) according to ISO 22674\textsuperscript{25}. The proof stress from the resultant stress-strain curves at the 0.2% offset level (yield strength), tensile strength, and percentage elongation values of the specimens were measured. Young’s modulus was also evaluated using a non-contacting video extensometer (AVE 2, Instron Japan).

Preparation of the metal-ceramic specimens for bond characterization

In compliance with ISO 9693-1\textsuperscript{24}, test specimens were prepared by layering the porcelain on both the Ti-Cr and cp-Ti strip-shaped specimens (n=10 per group). Three commercial products of low-fusing porcelain (CM: ceraMotion Ti, Dentaurum; IT: GC initialTi, GC Germany, Bad Homburg, Germany; TK: VITA TITANKERAMIK, VITA Zahnfabrik H. Reuter, Bad Sackingen, Germany) were used, and fired in a dental furnace (VITA VACUMAT 40, VITA Zahnfabrik) (Table 1). The center of each strip, porcelain bond area, was blasted with 125 µm Al₂O₃ particles (Cobra, Renfert, Hilzingen, Germany) with 0.2 MPa at a 45 degree incident angle, and then cleaned by a steam cleaner. The strip was put on the jig standardized at the porcelain bond area (8×3×1.1 mm). The appropriate bonder porcelain was applied to the porcelain bond area of specimens and fired according to the manufacturer’s instructions. The porcelain layering procedure comprised five steps: opaque (twice), dentin (twice), and self-glazing. Each slurry mixture, containing porcelain powder mixed with an appropriate amount of the respective liquid, was filled into the jig. The excess liquid was blotted with tissue paper, and the specimen was carefully picked up to the jig. Finally, each porcelain was fired in a dental furnace. After firing, the bond area was examined and corrected if necessary.

Metal-ceramic bond characterization (Schwickerath crack initiation test)

The debonding/crack-initiation strength (bond strength) of the specimens was evaluated by three-point bending tests using a universal testing machine (Z010, Zwick, Ulm, Germany) with the porcelain layer positioned on the side opposite to the applied load. Each specimen was placed on supports with a 20 mm span distance in the bending apparatus. A compressive load using a rounded loading rod was applied at the middle of each specimen at a crosshead speed of 1.5 mm/min until failure. The failure force (F\textsubscript{fail}) was measured when a debonding crack occurring at one end of the porcelain layer. The bond strength (τ\textsubscript{b}) was calculated using the following formula according to ISO 9693-1\textsuperscript{24}:

\[
τ_b = k \times F_{\text{fail}}
\]

where F\textsubscript{fail} is the maximum failure force, and k is a coefficient calculated from the thickness of and the elastic modulus of the metallic substrate used, which were obtained from the tensile test as described above.
Table 1 Porcelain materials used in this study

| Product name (Code) Manufacturer | Content       | CTE (×10⁻⁶/ºC)* | Preheating temperature (ºC) | Temperature increase (ºC/min) | Firing temperature (ºC) | T_g (ºC) | Lot No.        |
|---------------------------------|---------------|------------------|-----------------------------|-------------------------------|-------------------------|----------|----------------|
| ceraMotion Ti (CM) Dentaurum    | Paste bonder  | 9.4              | 500                         | 65                            | 795                     | 575      | 1703070B      |
|                                 | Opaque        | 8.9              | 500                         | 65                            | 790                     | 565      | Powder: 1607077B Liquid: 1701149B |
|                                 | Dentin        | 8.5              | 500                         | 55                            | 750                     | 545      | Powder: 1610103D Liquid: 1611141B |
| Initial Ti (IT) GC              | Bonder        | N.P.             | 450                         | 55                            | 810                     | N.P.     | Powder: 1505191 Liquid: 15061111 |
|                                 | Opaque        | 8.9              | 450                         | 55                            | 810                     | 575      | Powder: 1410231 Liquid: 1607121 |
|                                 | Dentin        | 8.6              | 400                         | 45                            | 780 (1st) 775 (2nd)     | 575      | Powder: 1506231 Liquid: 1502251 |
| Titankeramik (TK) VITA          | Paste bonder  | 9.1–9.4          | 400                         | 67                            | 830                     | 570      | 58850          |
|                                 | Opaque        | 9.1–9.4          | 400                         | 98                            | 790                     | 570      | Powder: 26950 Liquid: 54430      |
|                                 | Dentin        | 8.2–8.9          | 400                         | 53                            | 770                     | 583      | Powder: 12430 Liquid: 54430      |

*As disclosed by manufactures. CTE: coefficient of thermal expansion, T_g: glass transition temperature, N.P.: not published.

Fracture analysis of the porcelain-debonded specimens
After the bending tests, the debonded porcelain at one end of the layer was carefully removed from all specimens. The fracture surfaces of the metallic substrate and porcelain were observed using a digital microscope (ViTiny UM12, MicroLinks Technology, Kaohsiung, Taiwan). Typical fractured surfaces of the specimens were then analyzed using a field emission electron probe microanalyzer (FE-EPMA; JXA-8530F, JEOL, Tokyo, Japan) and X-ray diffraction (XRD; Ultima IV, Rigaku, Tokyo, Japan). XRD analyses were performed with an accelerating voltage of 40 kV, a beam current of 40 mA, a 2θ angle scan range between 20° and 80°, and a scanning rate at 5°/min.

Statistical analysis
The data were analyzed for normal distributions by Shapiro-Wilk test and for variance equality by Levene test. The descriptive analysis of the mechanical properties data was performed by the Student’s or Welch’s t-tests. The bond strengths were statistically analyzed with two-way analysis of variance (ANOVA) followed by Tukey’s post-hoc multiple comparison test, considering two independent factors (metallic substrate and porcelain type). One-way ANOVA followed by the multiple comparison test were also performed to compare each independent factor. Statistical analyses were carried out using the software (BellCurve for excel, Social Survey Research Information, Tokyo, Japan) at a level of significance of α=0.05.

RESULTS
Thermal and mechanical properties of the metallic specimens
The CTE values for Ti-Cr and cp-Ti specimens were 10.67±0.11×10⁻⁶/ºC and 9.55±0.04×10⁻⁶/ºC, respectively.

The mechanical properties of the metallic specimens are shown in Table 2. The results of the elongation and Young’s modulus showed normal distribution (p=0.2032 and 0.4808, respectively) and homogeneity of variance (p=0.9688 and 0.0556, respectively), but the results of the yield and tensile strengths did not show normal distribution (p=0.0078 and 0.0023, respectively) and homogeneity of variance (p=0.0189 and 0.0047, respectively). The yield and tensile strengths were significantly higher in the Ti-Cr specimens (592 and 928 MPa) than the cp-Ti specimens (394 and 462 MPa), whereas no significant differences were observed in the elongation and Young’s modulus (p>0.05).

Bond strength
During the bending tests, one Ti-Cr specimen of the TK group failed by cracking in the middle of the porcelain layer, being excluded for the calculation of bond strength according to ISO 9693-1.
Table 2  Mean and standard deviations of mechanical property parameters of the metallic specimens

| Material | Yield strength (MPa) | Tensile strength (MPa) | Elongation (%) | Young’s modulus (GPa) |
|----------|----------------------|------------------------|----------------|----------------------|
| Ti-Cr    | 592.1±31.0\text{A}   | 928.4±45.7\text{A}    | 26.2±7.7\text{A} | 105.8±4.7\text{A}    |
| cp-Ti    | 393.7±9.2\text{B}    | 461.6±10.0\text{B}    | 21.5±7.1\text{A} | 113.9±12.2\text{A}   |

Results of statistical analysis are represented by upper case letters. Different uppercase letters in the same column mean that the groups are significant different (\(p<0.05\)).

Table 3 Two-way ANOVA of bond strengths of the specimens

| Source                | DF | Sum of squares | Mean square | F      | \(p\)    |
|-----------------------|----|----------------|-------------|--------|----------|
| Metallic material (A) | 1  | 843.615        | 843.615     | 49.398 | <0.001   |
| Porcelain type (B)    | 2  | 866.850        | 433.425     | 25.378 | <0.001   |
| (A)×(B)               | 2  | 186.419        | 93.209      | 5.458  | 0.007    |
| Error                 | 53 | 905.125        | 17.078      | —      | —        |
| Total                 | 58 | 2,778.780      | —           | —      | —        |

The bond strength of the specimens ranged between 26.3 and 43.0 MPa (Fig. 1). The results were performed by Shapiro-Wilk test and Levene test showed that the bond strength data had normal distribution and homogeneity of variance (\(p=0.1003\) and 0.1608, respectively). Descriptive statistics of the bond strength results are shown in Table 3. Two-way ANOVA revealed significant differences in the respective independent factors (metallic substrates; \(p<0.001\) and porcelain types; \(p<0.001\)), and an interaction effect between these factors was noted (\(p=0.007\)).

In the comparison within the Ti-Cr specimens, the CM group exhibited the highest bond strengths (\(p<0.05\)), whereas no significant differences were observed between the IT and TK groups (Fig. 1). Moreover, in the comparison within the cp-Ti specimens, the CM group exhibited the highest bond strengths followed by the IT group and the TK group (\(p<0.001\)).

Additionally, in a comparison between the substrates, the Ti-Cr specimens showed significantly lower bond strengths than the cp-Ti specimens (\(p<0.001\)), but no difference was observed in the TK groups.

Fracture analysis of the porcelain-debonded specimens

Figure 2 presents digital microscopic images of the debonded specimens. Irrespective of the substrates, the CM group showed a brighter gray metallic colored surface on both the metallic and porcelain sides of both specimens than the IT and TK groups. On the porcelain side, the area of the metallic color decreased in the order of the CM, IT, and TK groups.

The back-scattered electron (BSE) images and the elemental mapping images of the metallic side of the Ti-Cr specimens are shown in Figs. 3–5. Three different areas were observed in the CM group in the BSE image (Fig. 3); a high intensity of Ti was observed in the light gray area which predominated throughout the entire surface. A high intensity of Si was detected in areas of small white particle accumulation (white arrows:
Fig. 3  The BSE image and element mapping (Ti, Si, and Al) of the metallic side in the CM group of the Ti-Cr specimen.

Fig. 4  The BSE image and element mapping (Ti, Si, and Al) of the metallic side in the IT group of the Ti-Cr specimen.

Table 4  Detected cation elements on the surface of the debonded Ti-Cr specimens

| Materials | Detected cation elements |
|-----------|--------------------------|
| CM        | Metal side: Ti, Cr, Si, Al, Sn, Ba<br>Porcelain side: Ti, Cr, Si, Al, Sn, Ba |
| IT        | Metal side: Ti, Cr, Si, Al, Sn, B, La<br>Porcelain side: Ti, Cr, Si, Al, Sn, B, La |
| TK        | Metal side: Ti, Cr, Si, Al, Sn, B<br>Porcelain side: Ti, Si, Al, Sn, B |

a), and a low intensity of Al was detected in the black areas (white arrows: b). These findings indicated that the substrate elements were exposed and the airborne abrasion particles had remained, resulting in cohesive failure within the metallic surface.

In contrast, the IT and TK groups of the Ti-Cr specimens exhibited different features in the metallic side, indicating a low intensity of Ti (Figs. 4 and 5). In the BSE images, the major dark (white arrows: c, Fig. 4) and bright (Fig. 5) areas indicated a high intensity of Si and low intensities of Al in the IT and TK groups, respectively. Notably, B and/or La, originating from either the IT bonder or the TK opaque material were detected in the rest area (Table 4). These findings indicated that residual porcelain was retained on the metallic surface in the IT and TK groups, resulting in cohesive failure into the porcelain layer.

The mapping images of the porcelain side in the Ti-Cr specimens are shown in Fig. 6. Ti was observed in the CM group, whereas the IT and TK groups were slightly detected. The elements detected on the metallic side were almost similar to that of the porcelain side in the Ti-Cr specimens (Table 4), but their intensities differed. Similar elements in the cp-Ti specimens, corresponding to the respective porcelain, were detected as in the Ti-Cr specimens, except for Cr.

The typical XRD patterns of the metallic substrate and debonded porcelain specimens are presented in Fig. 7. The α-Ti peaks (Powder Diffraction File: PDF #44-1294) were detected on the substrates of both Ti-Cr and cp-Ti specimens mainly before firing porcelain, whereas the α’-Ti peaks were only observed on the substrate of the Ti-Cr specimen (Fig. 7a). Additionally, a comparison of the substrates between the Ti-Cr and cp-Ti specimens revealed only slight differences within the same porcelain materials on both the metallic and porcelain sides.

The detected peaks on both metal and porcelain sides in the CM group of the Ti-Cr specimen were similar, and assigned to α-Ti, β-Ti (PDF #44-1288), rutile TiO₂ (PDF #21-1276) and leucite (PDF #38-1423) (Fig. 7a). In contrast, the detected peaks on the metal side in the TK group of the cp-Ti specimen were assigned to α-Ti and rutile TiO₂, whereas the porcelain side was shown to unknown peaks and rutile TiO₂ originating from porcelain (Fig. 7b).
DISCUSSION

The Ti-Cr alloy is a candidate for the substructure of PFMRs due to a greater corrosion resistance against chemical and mechanical attacks\textsuperscript{16,19}. Superior mechanical properties of the substructure and adequate bond strength between the substructure and porcelain are prerequisite for PFMRs\textsuperscript{26}. However, evidence concerning these characteristics for the Ti-Cr alloy is inadequate. This study focused on the thermal and mechanical properties of the Ti-Cr alloy and its metal-ceramic bond. The results demonstrated that the Ti-Cr specimens exhibited superior tensile strength but lower bond strengths with commercial veneering porcelains than the cp-Ti specimens, thus rejecting the null hypothesis.

The thermal properties of cast Ti alloys are influenced by adding the Cr content because the CTE value of them was increased by alloying depending on the elemental composition\textsuperscript{27,28}. The CTE of the cp-Ti specimens was almost equal to the manufacturer’s technical data \((9.60\times10^{-6}/^\circ\text{C})\), indicating that the casting process was successfully performed. Moreover, the CTE of the Ti-Cr specimens was \(1.12\times10^{-6}/^\circ\text{C}\), higher CTE value than that of the cp-Ti specimens. This finding was consistent with previous studies, which reported that increasing Cr content increased the CTE values in Ti-Cr alloy by \(1.4\text{–}1.5\times10^{-6}/^\circ\text{C}\) higher than cp-Ti\textsuperscript{21,27}. Thereby, the Ti-Cr alloy might affect the metal-ceramic bond strength due to a larger CTE mismatch between the substructure and porcelain than cp-Ti.

The mechanical properties of Ti alloys are also influenced by adding Cr content because alloying improves the properties depending on their microstructures and phase compositions\textsuperscript{29,30}. Both the yield and tensile strengths of the Ti-Cr specimens were approximately twice as high as those of the cp-Ti specimens. These results were similar trends of previous studies, which reported that adding 20 mass\% Cr content to Ti increased the yield and tensile strengths than cp-Ti\textsuperscript{14,29}. 
The strength differences between the specimens might be caused by the phase transition of the Ti-Cr alloy. Generally, β-type Ti alloy, which is developed by adding the alloy elements, possesses higher strength and lower modulus compared to α-type or α+β-type Ti alloy. In binary Ti-Cr alloy, the eutectoid composition is approximately 13.5 mass% Cr content to Ti. Adding the Cr content more than 20 mass% to Ti caused the phase transition from α-phase of cp-Ti to β-phase. However, the phase composition, detecting on the α-Ti, α′-Ti and unknown peaks of the Ti-Cr substrate in this study (Fig. 7a), were inconsistent with a previous study due to a different casting procedure using the alumina-magnesia based investment. Interestingly, the ductility of both the Ti-Cr and cp-Ti specimens were different between the present study and a previous report by Hattori et al., even though the yield and tensile strengths were similar. Compared to the present study, the differences were due to variations in the casting process, including different investment materials, casting machines, and testing methods. Especially, the type of the investment materials affected the microstructure and mechanical properties of titanium surface due to the formation of the alpha-case layer (α-case layer) between molten metal and investment materials.

This study conducted three-point bending tests to evaluate bond strengths between the Ti-Cr substrate and veneering porcelains according to ISO 9693-1. Even though a variety of testing methods exist, this standard is most commonly used and comparable with the previous publications concerning PFMRs including a Ti-ceramic system. There were two main bond strength findings in this study: (1) the bond strength for the Ti-Cr specimens were lower than that of the cp-Ti specimens, irrespective of the porcelain material, and (2) the porcelain material type affected bond strengths within the respective Ti-Cr or cp-Ti specimens.

The strength differences between the Ti-Cr and cp-Ti specimens can be explained by the CTE difference between the substrate and porcelain. Metal-ceramic bond is influenced by a combination of chemical bond, mechanical interlocking, van der Waals forces, and compressive stress to the porcelain. No correlation between the bond strength and CTE differences was observed for PFMRs using Ni-Cr and Pd-Ag alloys. However, metallic substrates generally exhibit slightly higher CTE values (a positive CTE mismatch) in the range of (+0.5−1.0)×10⁻⁶°C more than porcelain due to the compressive stress in the porcelain layer when cooling after porcelain firing. Porcelain manufacturers recommend to apply the bonder material as the first layer to prevent a thick oxide layer formation on the Ti surface. The CTE mismatches between the substrate and bonder material in this study are (+1.30−1.57)×10⁻⁶°C and (+0.15−0.45)×10⁻⁶°C for the Ti-Cr and cp-Ti specimens, respectively. Although the exact range of a CTE mismatch suitable for PFMRs cannot be discussed within this study, it appeared that the CTE mismatches exceeded the acceptable range (critical level) in the Ti-Cr specimens, creating thermal incompatibility and resulting in lower bond strengths than the cp-Ti specimens. In contrast, a CTE mismatch resulted in a positive value for the Ti-Cr alloy (+1.20×10⁻⁶°C) using one bonder, leading to higher bond strengths than cp-Ti, which had a negative CTE mismatch (−0.20×10⁻⁶°C). These differences from the present study can be explained by the bonder materials possessing with different CTE values. In a previous study, another bonder (12.5×10⁻⁶°C) that had negative CTE mismatches for both the Ti-Cr and cp-Ti specimens resulted in lower bond strengths compared to the present study. In this case, the smaller CTE mismatch for the Ti-Cr alloy (−2.40×10⁻⁶°C) showed a higher bond strength than the larger mismatch for cp-Ti (−2.00×10⁻⁶°C). Additionally, a Ti-based PFMR with a higher positive CTE mismatch demonstrated a lower fracture load than that with a lower positive mismatch. Therefore, it appears that the porcelain system, including the bonder materials, also affected the bond strengths mentioned above.

In a comparison of porcelain materials within the respective substrate, the highest bond strength was observed in the CM group followed by the IT and/ or TK groups, which demonstrated different fracture behavior. These differences might be caused by the CTE value, chemical composition, and firing procedure of the porcelain used. The difficulties in Ti casting are due to its high melting point and chemical reactivity with gaseous elements, such as oxygen at high temperatures, which creates a hard, brittle reaction layer (α-case layer). The temperature of the porcelain firing for Ti alloy is preferred as low as possible because only slight oxidation occurs below 750−800°C, but it becomes remarkable above 850−900°C, creating a porous, weak, and excessively thick titanium oxide layer. Hence, low-fusing porcelains are typically used below 850°C for a Ti-based PFMR. The conventional oxidation procedure before porcelain layering was unsuited to a Ti-based PFMR because the excessively thick oxide layer formation weakened the bond strength. Thus, a combination of airborne abrasion and bonder application, as used in this study, is recommended for a Ti-based PFMR to improve the bond strength since non-bonder application has been shown to create a large gap between cp-Ti and porcelain, resulting in poor bond strength. However, attention should be paid to the large differences in the composition of bonding materials that exist among the different brands in the dental market. The highest bond strengths and different fracture behavior of the CM groups might be influenced by the firing temperature and time of the bonder material, which is below 800°C, lower and shorter than of the IT and TK groups. In contrast, the lower bond strengths of the TK groups appear associated with a higher firing temperature, a longer firing time and the non-effect of the bonder application. This assumption was consistent with a previous study, which showed that the TK bonder did not improve the porcelain bond strength to Ti. Accordingly, the high temperature of the firing might progress the excessive oxidation on the Ti surface by the longer firing time.
To clarify the bond characteristic between the substrate and porcelain, the metal-ceramic interface of the specimen was observed (Fig. 8). Unfortunately, the differences in the oxide layer thickness between the Ti-Cr and cp-Ti specimens at the interface were difficult to define and cannot be discussed within this study. Although the conventional porcelain firing temperatures for cp-Ti obtained adequate bond strengths, the Ti-Cr specimens exhibited lower bond strengths than the cp-Ti specimens. These bond strength differences might be caused by a larger CTE mismatch between the substrate and porcelain of the Ti-Cr specimens due to the Cr addition. A temperature gradient during cooling after porcelain firing in the Ti-Cr specimens was larger than that in the cp-Ti specimens. Additionally, the firing temperature might be high for the Ti-Cr alloy because the melting temperature of the Ti-Cr alloy is lower than that in the cp-Ti specimens. Furthermore, the firing temperature might be high for the Ti-Cr alloy because the melting temperature of the Ti-Cr alloy is lower than that in the cp-Ti due to Cr addition. Consequently, it is essential to develop a novel porcelain material that has a suitable CTE value, composition, and firing temperature for optimal bond strength to the Ti-Cr alloy.

Finally, although the Ti-Cr alloy could be feasible for PFMRs so as to fulfill the ISO 9693-1 requirement of the bond strengths of the porcelains to the metallic substrates in this study, it should be mentioned that the strengths vary by the manufacturing methods and the metallic composition of the substrate. Thus, further studies are necessary to clarify the influence of these factors to establish the reliability of the findings.

CONCLUSIONS

Within the limitations of this study, the conclusions are as follows:

1. Compared to cp-Ti, the Ti-Cr alloy showed a higher CTE value, superior tensile strengths, ductility and pliability than cp-Ti.
2. Although Ti-Cr specimens showed lower bond strengths of commercial veneering porcelains than cp-Ti specimens, all the strengths exceeded the minimum requirement of ISO 9693-1:2012 (>25 MPa).

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