Journal of Alloys and Compounds 505 (2010) 332–336

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effects of surface treatments on bond strength of dental Ti–20Cr and Ti–10Zr alloys to porcelain

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ARTICLE INFO

Article history:
Received 6 November 2008
Received in revised form 19 May 2010
Accepted 28 May 2010
Available online 18 June 2010

Keywords:
Metals and alloys
Ceramics
Scanning electron microscopy

ABSTRACT

The purpose of this study was to investigate the effect of surface treatments, including sandblasting and grinding, on the bond strength between a low-fusing porcelain and c.p. Ti, Ti–20Cr and Ti–10Zr alloys. The surface treatments were divided into 2 groups. Grinding surface treatment was applied to the first group, which served as the control, and sandblasting was applied to the second group. After treatment, low-fusing porcelain (Titankeramik) was fired onto the surface of the specimens. A universal testing machine was used to perform a 3-point bending test. The metal–ceramic interfaces were subjected to scanning electron microscopic analysis. Of the sandblasted samples, the debonding test showed that Ti–20Cr alloy had the strongest (31.50 MPa) titanium–ceramic bond ($p < 005$), followed by c.p. Ti (29.4 MPa) and Ti–10Zr (24.3 MPa). Of the grinded samples, Ti–20Cr alloy showed 27.3 MPa titanium–ceramic bond ($p < 005$), followed by c.p. Ti (14.3 MPa) and Ti–10Zr (failure). The SEM micrographs of the metal surface after debonding showed residual porcelain retained on all samples. On the whole, sandblasting surface treatment appears to have had a more beneficial effect on the Ti–ceramic bond strength than grinding surface treatment. Furthermore, surface treatment of Ti–20Cr with either grinding or sandblasting resulted in adequate bond strength, which exceeded the lower limit value in the ISO 9693 standard (25 MPa).

1. Introduction

Porcelain-fused-metals (PFMs) are widely used for esthetic restoration. Because the success of the PFM depends on a strong bond between porcelain and metal, the appropriate choice of porcelain and metals is important for a clinically successful PFM. For adequate bonding, the coefficient of thermal expansion of the ceramic and metal should be compatible.

Given the dramatic increase in the prices of noble metals and the fact that base metals might jeopardize human health, researchers have been searching for a substitute for both noble and base metals, and titanium (Ti) has become the most popular candidate. In fact, this metal has been successfully used for dental implants and other dental applications for the last two decades. Due to its desirable physical and mechanical properties, excellent corrosion resistance and biocompatibility, the application of Ti in dentistry has increased substantially. For example, Ti is widely used for removable and fixed partial dentures and PFM restorations [1,2].

However, Ti reacts strongly with oxygen at high temperature and forms a thick TiO_2 layer which is not good for titanium–porcelain bonding. Therefore, lower temperature porcelain firing is required to prevent excessive oxide formation [3,4]. Although low temperature firing can compromise bond strength, several surface treatments could enhance the Ti ceramic bond strength. These include using acid etching and sandblasting [5–7]. Whereas acid etching has not shown positive results, sandblasting of the Ti surface has been shown to improve the adhesion of the ceramic to the Ti substrate. Sandblasting is also the most common method among many diverse surface treatments used in previous studies.

Three methods are commonly used to evaluate the bond strength between metal and porcelain, a 3-point bending test defined by ISO 9693 and area fraction of adherent porcelain (AFAP) which is used to examine the porcelain residue on the fractured metal surface [8,9]. In this study, we utilized the 3-point bending test, which is the simplest and the most similar to authentic application in the oral environment.

In previous studies of a series of Ti–Cr and Ti–Zr alloys had been investigated the results showed that all Ti–Zr alloys had better

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doi:10.1016/j.jallcom.2010.05.174

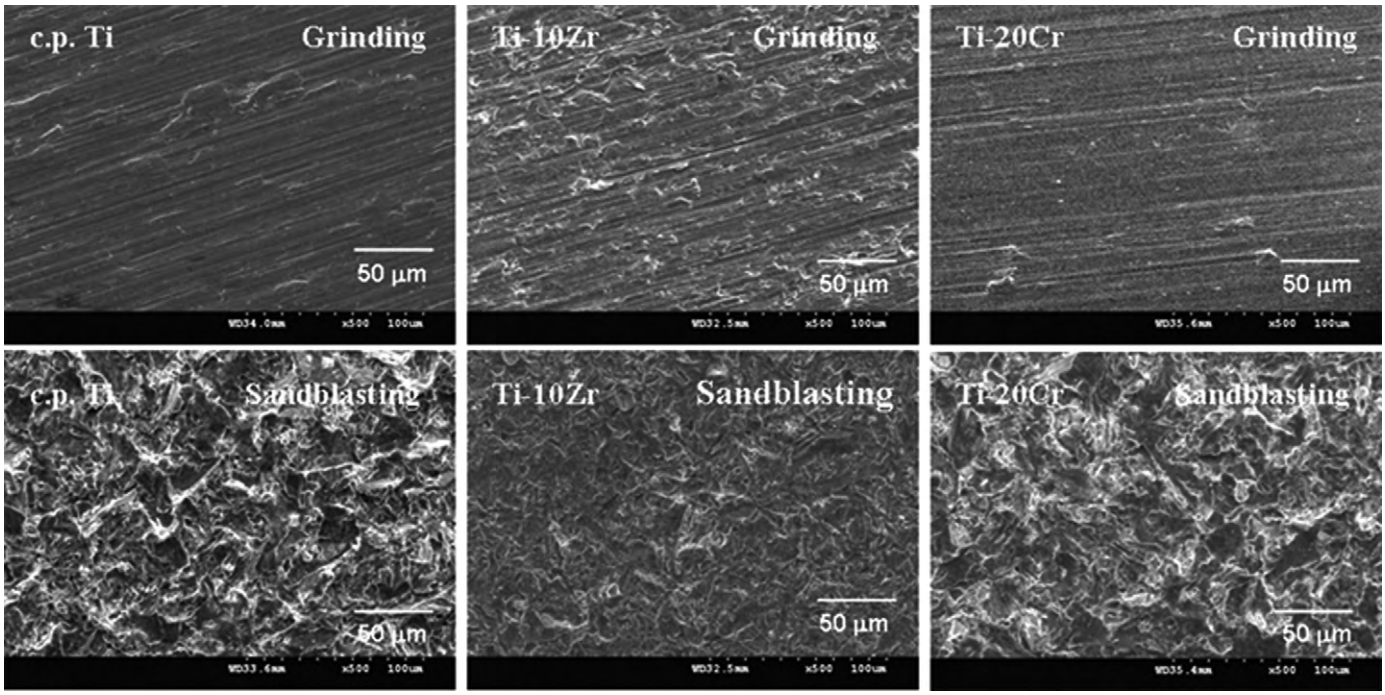

Fig. 1. SEM micrographs of grinded and sandblasted specimen surfaces.

mechanical properties than cp Ti [10,11]. Thus, the Ti–10Zr alloy was found to have the highest bond strength (25.1 MPa), which was also higher than that of c.p. Ti (21.1 MPa). In addition, the bending strength of the Ti–20Cr alloy was about 1.8 times greater than that for commercially pure titanium (c.p. Ti). Moreover, the elastic recovery capability of the Ti–20Cr alloy was greater than that of c.p. Ti by as much as 460%. The bond strength of porcelain to Ti–20Cr was 25.1 MPa.

Although the bond strengths of Ti–10Zr and Ti–20Cr alloys were above the DIN 13.927 standard (25 MPa), they were still not strong enough for dental applications. Thus, the purpose of this study was to evaluate the effect of surface treatments on the bond strength of experimental Ti–20Cr and Ti–10Zr alloys to dental porcelain and further improve their bond strengths. After a bending test, the bonding interface between metal and porcelain substrates was observed through SEM with energy dispersive spectrometry (EDS).

2. Materials and methods

2.1. Materials

Ti–10 wt%Zr (Ti–10Zr) and Ti–20 wt% (Ti–20Cr) were prepared with raw c.p. Ti, zirconium (Zr) and chromium (Cr) (99.8%, 99.95% and 99.3% respectively in purity) by a commercial arc-melting vacuum-pressure-type casting system (Castmatic, Iwatani Corp., Japan). C.p. Ti was used as the control. The alloy ingots and the c.p. Ti were cut to uniform dimensions of 25.0 mm × 3.0 mm × 0.8 mm.

2.2. Grinding and sandblasting

For grinding, SiC papers (#320 and #600) were utilized to completely remove the α-case layer, which is caused by the cutting process, and continued until achieving the dimensions 25.0 mm × 3.0 mm × 0.5 mm required by ISO 9693. In the sandblasting group, samples were sandblasted with 120 μm alumina particles at a pressure of 2-bar by holding the sample at 10 mm from the tip of the nozzle for 20 s. After surface treatment, all samples were cleaned in distilled water and then acetone in an ultrasonic cleaner for 10 min each. Surface roughness of specimens was recorded with a roughness tester (SE1700, Kosaka Laboratory Ltd., Japan) prior to porcelain firing. The cut-off value was set at 0.08 μm to characterize surface roughness. Statistical calculation of surface roughness was performed using an average of 3 surface roughness measurements parallel to the long axis at the central segment of each specimen.

2.3. Bond strength between experimental metals and porcelain

Commercial low-fusing porcelain for Ti (Titankeramik, Vita, Germany) was applied to all experimental metals according to the manufacturer's working instructions. A thin layer of bonding paste with dimensions of 8 mm × 3 mm was built up on the central part of each specimen according to ISO 9693 before two layers of opaque and then one layer of dentin porcelain were applied with a custom-made jig which controlled the thickness of each. The bond strength of each sample was measured by a universal machine (AG-1S, Shimadzu Corporation, Japan), and five specimens were used for this test. The samples were positioned with the porcelain

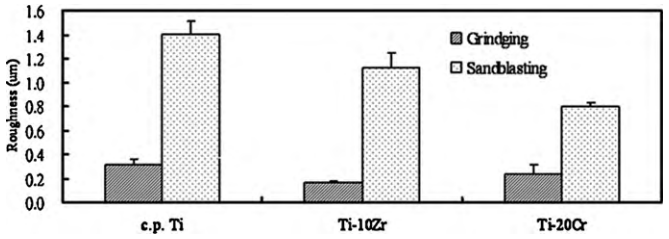

Fig. 2. Surface roughness of grinded and sandblasted specimens.

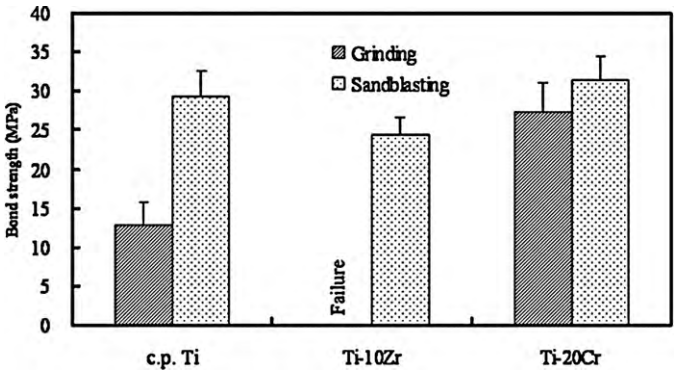

Fig. 3. Bond strength of c.p. Ti, Ti–10Zr and Ti–20Cr alloys to porcelain.

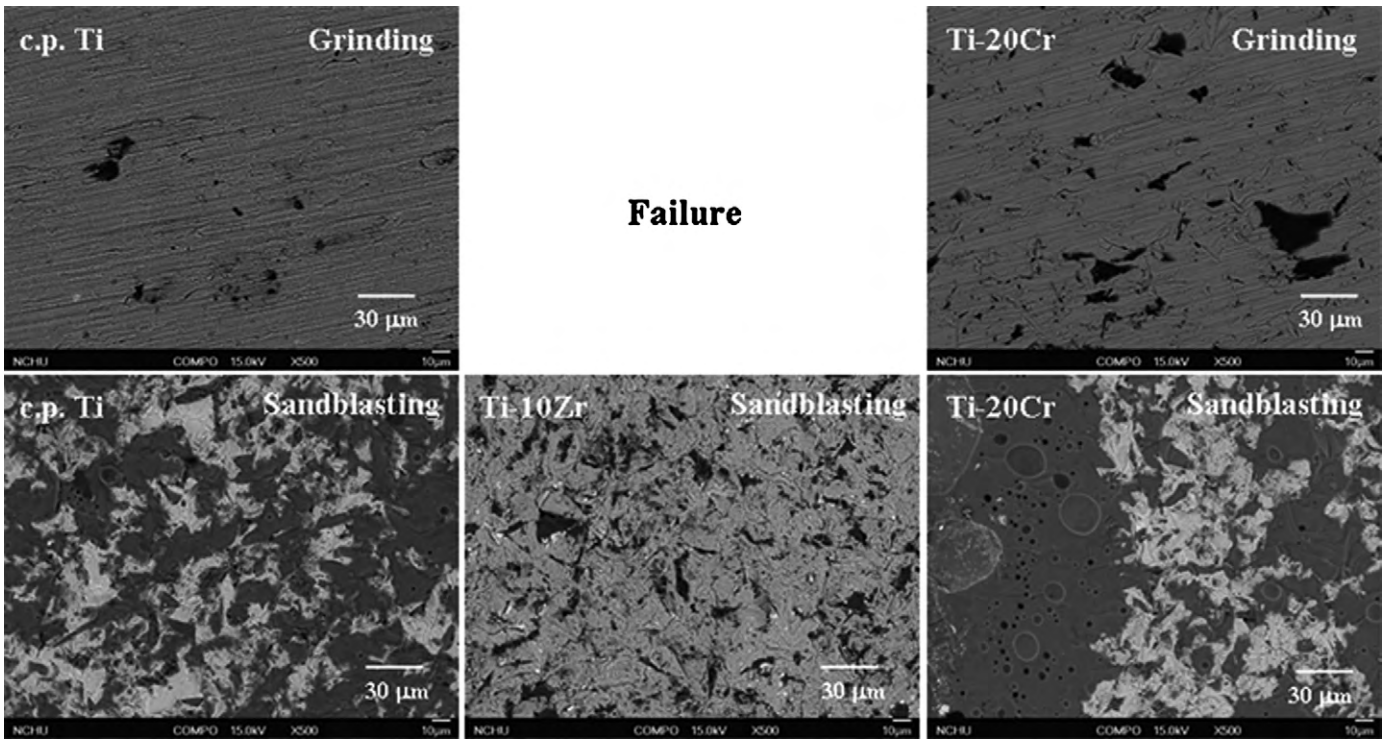

Fig. 4. SEM micrographs of c.p. Ti, Ti–10Zr and Ti–20Cr after debonding.

on the opposite side to the center support before loading with a crosshead speed of 0.5 mm/min until a drop in the stress and strain curve occurred.

2.4. Scanning electron microscopy

Scanning Electron Microscopy (SEM) (JSM-6700F, Jeol, Tokyo, Japan) was carried out to characterize the type and morphology of the fracture in representative specimens selected from each alloy 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 characterized using a scanning electron microscope equipped with an energy dispersive spectrometer.

3. Results and discussion

3.1. Surface roughness

Fig. 1 shows the morphologies of metal surfaces before porcelain application. As shown in Fig. 1, patterns on the surface of the metal substrates treated with aluminum oxide sandblasting were rough and irregular in comparison with those of the grinded surfaces. Fig. 2 shows surface roughness results of the two surface treatments. Surface roughness of all metals was significantly higher after sandblasting than after grinding ($p < 0.05$). In other words, SEM

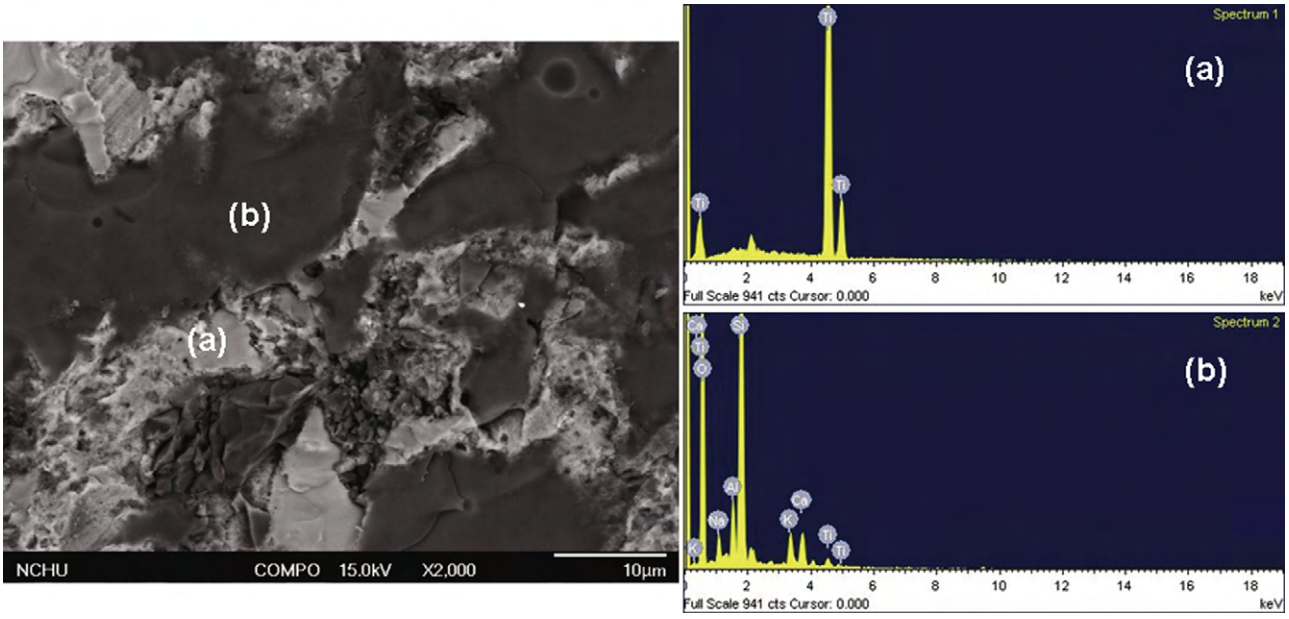

Fig. 5. SEM micrograph of c.p. Ti surface after debonding, and the accompanying EDS elemental analyses of the two areas marked (a) and (b), respectively.

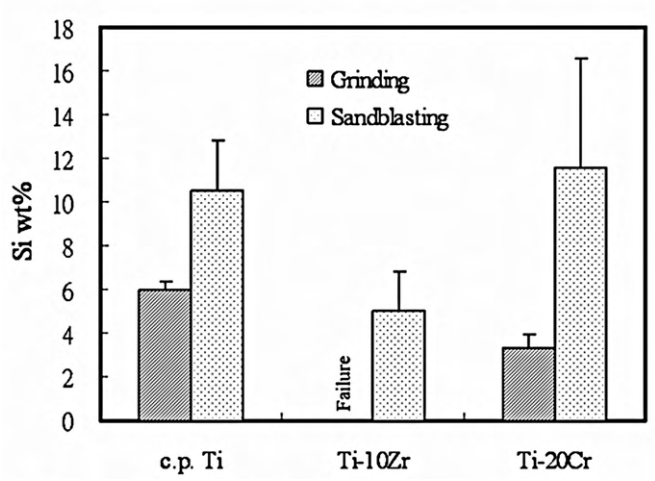

Fig. 6. Si wt% in residual porcelain after debonding.

micrographs were consistent with the measurement of the surface roughness of the specimens. Furthermore, the difference in surface treatment resulted in different surface morphology that may have affected the bond strength of porcelain to metal. Not only did results differ according to surface treatment, but different alloy types also showed significant differences ($p < 0.05$). After sandblasting, the roughness of Ti–20Cr (0.80 μm) and Ti–10Zr (1.13 μm) was significantly lower than that of c.p. Ti (1.41 μm). This implies that adding Zr or Cr to Ti can decrease the roughness of the alloy surfaces after sandblasting. This could be correlated to the hardness values of metals, with Ti–20Cr having the highest hardness (326 HV), followed by Ti–10Zr (266 HV) and c.p. Ti (186 HV). In general, higher hardness generally makes sandblasting treatment more difficult to apply. However, there was no significant difference in surface roughness of c.p. Ti, Ti–10Zr and Ti–20Cr specimens after grinding ($p > 0.05$).

3.2. Bond strength

Fig. 3 shows the bond strength of c.p. Ti, Ti–10Zr and Ti–20Cr alloys to porcelain. Significant differences were found in bond strength between the grinding group and the sandblasting group and all sandblasted specimens had greater bond strength values than grinding specimens ($p < 0.05$). For the grinding group, the porcelain layers of Ti–10Zr were broken away at either opaque or dentin layer. In contrast, for the sandblasting group, the bond strength of Ti–10Zr was elevated to 24.3 MPa. This indicates that sandblasting could be more beneficial to bonding in the titanium–porcelain system than grinding. On the other hand, the bonding strength of the Ti–20Cr grinding group (27.3 MPa) did not show a significant difference ($p > 0.05$) to the sandblasting groups of either c.p. Ti (29.4 MPa) or Ti–20Cr (31.5 MPa), which indicates that Cr can enhance the titanium–porcelain system under both conditions. For c.p. Ti, the grinding group (16.2 MPa) showed significantly lower bonding strength than the sandblasting groups (29.4 MPa).

3.3. SEM analysis

Fig. 4 shows SEM micrographs of c.p. Ti, Ti–10Zr and Ti–20Cr after debonding. The photomicrographs of the metal surfaces showed residual porcelain retained on the metal surface. Greater quantities of residual porcelain islands were found adhering to the metal surface of the substrate in the sandblasting group, attesting a better mechanical performance. Taking c.p. Ti as an example, under greater magnifications (Fig. 5), two distinct areas were found on the surface after debonding. EDS spectrums on the two areas of the c.p. Ti surface are shown in Fig. 5(a) and (b). An X-ray spectrum of the grey area marked point (a) shows the Ti substrate. EDS analysis of the black area, marked point (b) reveals Na, K, Ca, and Si (Fig. 5(b)) which indicates that these black areas represent the residual porcelain. The presence of Al and O, suggests that these areas could be produced by sandblasting with alumina particles. Since aluminum particles with a diameter of 120 μm were used for the sandblasting surface treatment, it is

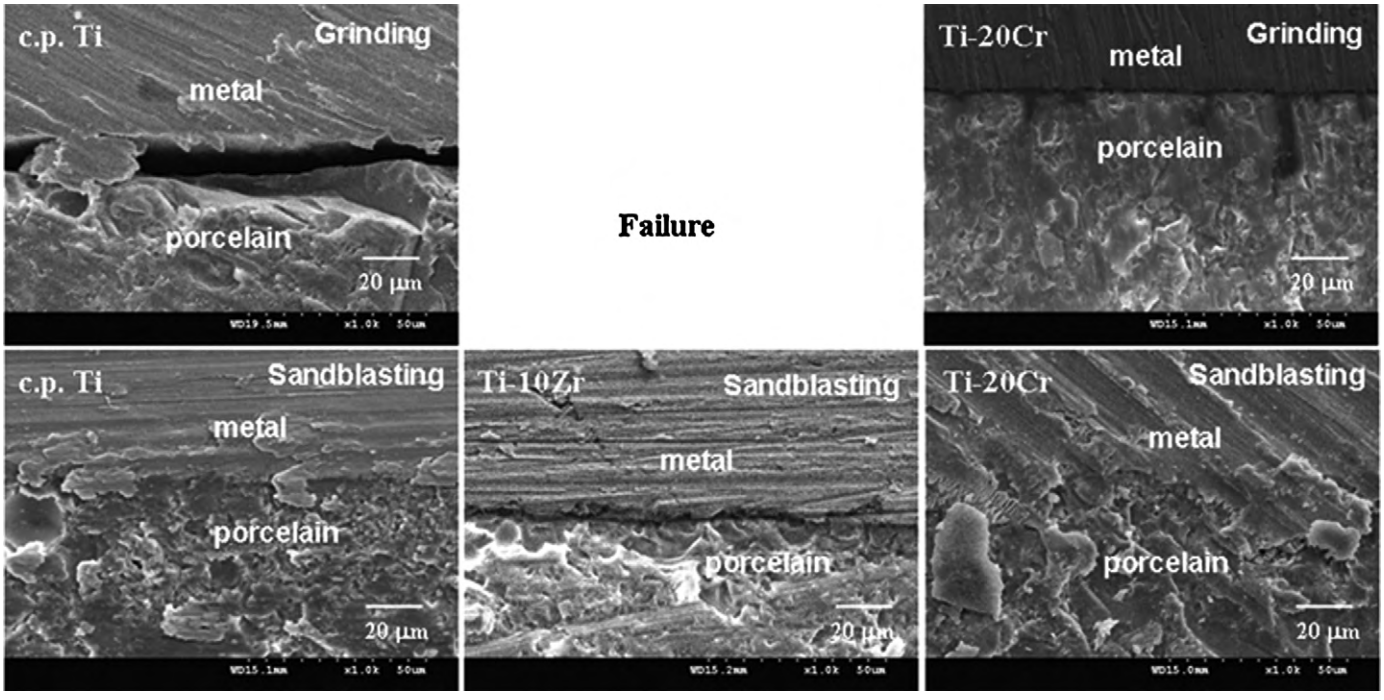

Fig. 7. SEM micrographs of cross-sections of metal–ceramic interfaces.

most likely that these small particles were embedded in the Ti surface.

EDS analyses indicating silicon weight percentage (Si wt%) for debonded specimens are shown in Fig. 6. The sandblasted group showed significantly higher Si values compared with the grinded group, which again confirms the superior ceramic adherence of sandblasted surfaces. Könönen and Kivilahti have shown that roughening the Ti surface by sandblasting changes the oxide formation at the Ti–ceramic interfaces and improves the Ti ceramic adhesion [12]. In addition, such a roughened surface also provides increased mechanical interlocking between Ti and ceramic. For all groups in the present study, sandblasting with 120 μm particles before porcelain firing yielded roughened surfaces which resulted in mechanical interlocking in the metal ceramic bonding.

3.4. Cross-section observations

Fig. 7 shows the SEM photomicrographs of cross-sections of all specimens. As shown in Fig. 7, there was no obvious gap between Ti–20Cr and porcelain for either condition. Although a previous study has shown that the thermal expansion coefficient (CTE) value of the Ti–20Cr alloys ($11.5 \times 10^{-6}\,^{\circ}C^{-1}$) was slightly higher than that of c.p. Ti ($10.1 \times 10^{-6}\,^{\circ}C^{-1}$) [10], this appears not to have affected the bond strength as was expected. On the other hand, as shown in Fig. 7, there was a visible gap between Ti–10Zr and porcelain. Again, this is contrary to predictions based on a previous study, which showed that the CTE value of the Ti–10Zr alloy ($9.9 \times 10^{-6}\,^{\circ}C^{-1}$) was lower than that of c.p. Ti [11]. In addition, the mismatch of CTE between Ti–10Zr alloy and porcelain significantly affected the bond strength of the ceramic–metal systems. In these studies by the authors, it was found that the degree of deflection depends on the difference in thermal contraction at the temperature when the porcelain begins to solidify and that a mismatch of CTE between metal and porcelain may significantly contribute to failure [13]. However, in the present study, it was found that if suitable amounts of appropriate alloying elements are added, Ti alloys have the potential to overcome the mismatch in the CTE with low-fusing porcelains. In fact, optimal bonding characteristics require metals and porcelains to be chemically, thermally, and mechanically compatible, and long-term clinical reports regarding the success of Ti–porcelain systems are still needed.

4. Conclusions

In this study, it was found that surface treatment strongly affected the bond strength of c.p. Ti, Ti–10Zr and Ti–20Cr to low-fusing porcelain. A sandblasting treatment increased surface roughness more than grinding treatment, and provided a corresponding improvement in the metal–ceramic bond strength. Furthermore, it was found that the Ti–20Cr alloy demonstrated superior bond strength to both the other metals in this study. This appears to be due to the beneficial effects of increased Cr content which mitigates the effects of a CTE mismatch between Ti–20Cr and porcelain.

Acknowledgement

The authors would like to thank the support of this research by Grant 96-2622-E-166-001-CC3 from the National Science Council, Republic of China.

References

[1] R.R. Wang, A. Fenton A, Quintessence Int. 27 (1996) 401–408.
[2] J.A. Hautaniemi, H. Hero, J.T. Juhanoja, J. Mater. Sci. 3 (1992) 186–191.
[3] H. Kimura, C.J. Horng, M. Okazaki, J. Takahashi, Dent. Mater. J. 9 (1990) 91–99.
[4] M. Adachi, J.R. Mackert Jr., E.E. Parry, C.W. Fairhurst, J. Dent. Res. 69 (1990) 1230–1235.
[5] M.J. Reyes, Y. Oshida, C.J. Andres, T. Barco, S. Hovijitra, D. Brown, Biomed. Mater. Eng. 11 (2001) 117–136.
[6] I. Al Hussaini, K. Al Wazzan, J. Prosthet. Dent. 94 (4) (2005) 350–356.
[7] R.R. Wang, G.E. Welsch, O. Monteiro, J. Biomed. Mater. Res. 46 (1999) 262–270.
[8] ISO 9693, Metal–ceramic dental restorative systems, 2nd ed., International Organization for Standardization, Switzerland, 1999.
[9] A. Sadeq, Z. Cai, R.D. Woody, A.W. Miller, J. Prosthet. Dent. 90 (2003) 10–17.
[10] W.F. Ho, T.Y. Chiang, S.C. Wu, H.C. Hsu, J. Alloys Compd. 474 (2009) 505–509.
[11] W.F. Ho, W.K. Chen, S.C. Wu, H.C. Hsu, J. Alloys Compd. 471 (2009) 185–189.
[12] M. Könönen, J. Kivilahti, J. Biomed. Mater. Res. 28 (1994) 1027–1035.
[13] R.R. Wang, G.E. Welsch, O. Monteiro, J. Biomed. Mater. Res. 46 (2) (1999) 262–270.