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Effect of ZrN coating by magnetron sputtering and sol–gel processed silica coating on titanium/porcelain interface bond strength

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Abstract In this study, a coating technique was applied to improve the bond strength of titanium (Ti) porcelain. ZrN coating was prepared by magnetron sputtering, and silica coating was processed by a sol–gel method. The treated surfaces of the specimens were analyzed by X-ray diffraction, and the Ti/porcelain interface was investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy. The coated specimens appeared fully coherent to the Ti substrate. The fractured bonding surface was also investigated by SEM. The residual porcelain on the metal surface could be observed in the ZrN group and silica group, but there was no obvious porcelain remaining in the control group. A three-point-bending test showed that the bonding strength of the ZrN group (45.99 ± 0.65 MPa) was higher than the silica group (37.77 ± 0.78 MPa) ($P < 0.001$) and control group (29.48 ± 1.01 MPa) ($P < 0.001$), while that of the silica group was significantly higher than the control group ($P < 0.001$). In conclusion, conditioning the ceramic surface with ZrN and silica coatings resulted in a stronger Ti/porcelain bond. ZrN coating by magnetron sputtering was a more effective way to improve the bond strength between Ti and porcelain compared with sol–gel processed silica coating in this study.

1 Introduction

Bonding porcelain to titanium (Ti) for porcelain-fused-to-metal (PFM) crowns remains a clinical problem in dentistry. Not only is Ti more expensive than the common base metals such as nickel and chromium for the patient, but its use is also problematic for dentists. The highly oxidative nature of the surface of Ti has been postulated as the cause of the weak bond between porcelain and Ti [1, 2]. To circumvent the high firing temperatures (>950°C) required for conventional dental ceramics that produce a thick weakly bonding oxidation layer, manufacturers have developed low-fusing porcelains (<850°C) with favorable thermal expansion coefficients [1, 3]. While some studies have reported that bonding of low-fusion porcelains to Ti is acceptable, methods such as sandblasting, acid treatments, and silicone nitriding have been pursued to enhance bonding [4–6]. However, these methods cannot effectively prevent Ti from oxidation. The bonding of Ti and porcelain is still of concern to dentists, and Ti/porcelain restorations are still not the first choice for dentists compared with other restorations at the same price. Optimum adherence between the porcelain and metal is the main prerequisite for clinical success. Therefore, increasing the Ti bonding strength could allow it to be an alternative for noble metals in developing countries while achieving acceptable biocompatibility.

Coating the Ti substrate with another layer can prevent the formation of an excessive and non-adherent Ti oxide layer during porcelain firing and improve the bond between the ceramic and Ti by controlled oxidation [7]. In dental

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applications, this intermediate layer could affect the aesthetics of the final restorations, but for clinical use, it is a simple low cost method.

Reports on the use of coatings in the literature have been contradictory [2, 7–9]. It was advocated by Oshida and Hashem [7] that nitridation of the Ti surface could control the film thickness that might ensure satisfactory bonding with porcelain. However, the mechanical test results in the latter part of that same study failed to support their hypothesis. No statistically significant difference could be demonstrated between bond strengths of fired porcelain on nitrided pure Ti and non-coated Ti [8]. On the other hand, the results presented for silicon nitride (Si_3N_4) coating were encouraging. It was reported by Wang et al. [6] that Si_3N_4 coatings were effective in preventing the oxidation of Ti and also provided a significant improvement in ceramic bonding.

More recently, ZrN films have been gaining considerable attention because of their superior mechanical properties, golden color, and various applications such as providing diffusion barriers in the microelectronic industry and a protection layer used in fission reactors. Thin films are deposited by various methods: evaporation, spray pyrolysis, chemical vapor deposition, and magnetron sputtering. A fast and uniform deposition can be achieved by magnetron sputtering. Until now, there has been little research on the use of ZrN coatings in the dental field. However, Zhang et al. [10] had reported on depositing an intermediate layer of ZrSiN on Ti prior to the application of porcelain to prevent oxidation of the metal.

Silica coatings are used in many dental applications. It is a popular method of surface conditioning for ceramics, especially alumina ceramics. Related investigations have demonstrated that this surface conditioning improves the bond strength to alumina ceramics [11] and results in a durable resin bond for 5 or more years [12].

The solution–gelation (sol–gel) method offers a relatively simple coating method with many applications. The coatings obtained using the sol–gel process are characterized by low thickness, high homogeneity, satisfactory mechanical, and chemical stability, good bonding to the substrate, high biocompatibility, and corrosion resistance. Thus, these properties render the sol–gel coatings very attractive for use in the dentistry field. We previously successfully prepared silica coatings by the sol–gel method and found that the prepared silica coating can improve the resin bond strength of glass-infiltrated alumina ceramics [13].

In this study, we prepared the ZrN coating by sputtering of a zirconium target in a mixture of Ar/N_2 direct current magnetron discharges and silica coating by the sol–gel method in order to improve the bond strength between Ti and porcelain. Magnetron sputtering is a powerful and flexible technique which can be used to coat virtually any work piece with a wide range of materials—any solid metal or alloy and a variety of compounds. The sol–gel process has also many advantages: low processing temperature, homogeneity of the coatings, easy control of coating thickness, as well as the possibility of obtaining both mono- and multi-components, which can be multi-layered, and the possibility of producing coatings for implants with complex geometries [14]. Both methods are suitable for the diversified surfaces of dental restorations and have potential for applications in dental labs. Therefore, the coatings were prepared by these two methods to investigate their effect on the bond strength of specific low-fusing Ti porcelain bonded to Ti. The bond strength was determined according to a three point-bending configuration. Furthermore, SEM analysis was also utilized to observe the characteristics of the bond interface and bond failure. Our results showed that porcelain bonded to Ti after surface modifications were improved compared to the control group and demonstrate the potential of these methods for application in the dental field.

2 Materials and methods

2.1 Materials

Commercially cast pure Ti (CP Ti) was purchased from Shanghai Rijin Dental Material Co., Ltd. Low-fusing Dental Porcelain was purchased from Vita Titankeramik (Vita, Germany). Zr disk was purchased from ZhongBang Rare Metal Co., Ltd. (BaoJi, China). Nano silica sol (30% wt, pH 8.5–10, density 1.12–1.30 g/cm^3, and average diameter 10–20 nm) was purchased from HengShengDa Chemical Co., Ltd. (QingDao, China).

2.2 CP Ti specimens

Twenty-seven blocks of CP Ti specimens with dimensions of 25 mm × 3 mm × 0.5 mm were fabricated following the process described by Troia et al. [15]. These blocks were radiographically examined to verify their quality, and no air bubbles were found. The testing surface of every block (25 mm × 3 mm) was polished with carbide tungsten. The polished surface of each block was air-abraded with 120-μm alumina using an airborne-particle abrasion standardization device (Jianian Futong Medical Equipment; Tianjin, China) set at 45°, and 10 mm from the air-abrasion tip to the middle of the metal strip. The pressure during air-abrasion was 0.2 MPa, applied for a period of 20s. The metal samples were left in the open air at room temperature for 5 min and then rinsed in acetone for 15 min. The samples were finally cleaned with hot steam and then dried with pure N_2. The final sample is presented in Fig. 1a. The above procedure was performed in a dental lab immediately after the CP Ti specimen was molded.

2.3 Surface modification

The metal strips were divided into three groups of 9 samples each and subsequently subjected to one of the following three surface modification procedures (Table 1): silica group, silica coating prepared using a 30% silica sol; ZrN group, ZrN coating by magnetron sputtering; control group, no surface treatment.

Silica coating was processed following the steps shown in Table 1. The photo of the specimen with the silica coating was not taken because no visible change was observed compared with the control.

In the ZrN group, the target, a Zr disk of 99.9% purity with a diameter of 78 mm and 3 mm in thickness was pre-sputtered in an atmosphere of argon for about an hour in order to remove the surface oxide formed during air exposure before deposition. The distance between target and substrate holder was fixed at 60 mm. The pumping system was a turbomolecular pump–rotary pump combination, capable of giving a background pressure on the order of 6.0×10^{-6} Pa. A system pressure of 0.3 Pa was achieved prior to the film deposition. Two mass flow controllers were utilized to regulate the relative amount of Ar and N_2 supplied into the chamber during the deposition (30:2). Initially, the Ar pressure was set at 0.26 Pa and then N_2 was added to obtain the desired N_2 to Ar ratio. The bias voltage was −100 V. The sputtering was done at room temperature for 1 h. The specimen after sputtering is presented in Fig. 1b. The deposited ZrN films were golden in color with metallic highlights.

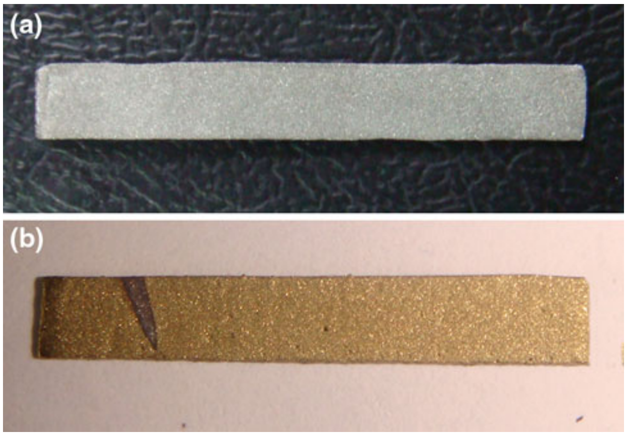

Fig. 1 CP Ti specimen. **a** CP Ti specimen. **b** CP Ti specimen with ZrN coating

Table 1 Surface modifications for commercially pure titanium

Group	Descriptions
Silica	(1) The silica sol coatings were formed by dip-coating (2) The coated blocks were stored in an obturated condition at constant humidity for 24 h to complete the conversion of sol to gel (3) The blocks were heated under vacuum to 400°C, incubated for 30 min at 400°C, and slowly cooled to room temperature
ZrN	Deposition of ZrN coating by magnetron sputtering
Control	No surface treatment

2.4 Preparation and ceramic application

Low-fusing dental porcelain (Vita Titankeramik, Vita, Germany, shade A2) was built up to dimensions of 8 mm in length, 3 mm in width, and 1 mm in thickness in the central portion of each metal strip. A thin, uniform layer of bonder (thickness: 0.2 mm) was brushed onto the central portion of each metal strip. Then, the first and second coat of opaque porcelain (thickness: 0.2 mm) was applied to each specimen. The porcelain body (thickness: 0.6 mm) was subsequently formed using a metal alignment jig and a vibrator. Firing shrinkage was compensated by a second application of porcelain for a final thickness of 1 mm. Finally, glaze firing was processed. The low fusing porcelain for Ti was fired according to the manufacturer's recommendations (Table 2). Porcelain applications for all the specimens were performed by a single investigator.

2.5 Characterization

2.5.1 *Microstructural and morphological characterization*

The crystal structures of the silica and ZrN coatings were identified by X-ray diffraction (XRD, D/max2500/PC, Rigaku Corporation, Japan), and the untreated surface was examined as a control. All the spectra were taken with an accelerating voltage of 40 kV, and a current of 110 mA. The Cu Kα radiation was used as the X-ray source. The scan rate was 2°/min for the $\theta/2\theta$ scans, where the 2θ angles ranged from 20° to 80°. The diffraction angle was 6°.

One specimen from each group was selected for examination of the metal–ceramic interface under a scanning electric microscope and energy dispersive X-ray spectroscope (SEM/EDS, JSW-5610LV-VANTAGE, Thermo Noran, USA). The operating conditions for SEM/EDS analysis were: 15 kV accelerating voltage in vacuum (3×10^{-4} Pa), 21 mm work distance. These specimens were embedded in clear autopolymerizing acrylic resin (Orthoresin, Dentsply) and cross-sectioned with a low-speed saw (Isomet 2000 precision saw; Buehler Ltd, Lake

Table 2 Procedural steps and firing schemes of the Vita Titankeramik porcelain

	Paste Bonder	First and Second Opaque	Dentin	Glaze
Low temp (°)	400	400	400	400
Drying time (min)	6	2	6	–
Pre-heat time (min)	6	4	7	4
Heat rate (°C/min)	67	98	53	93
Vacuum on (°C)	400	400	400	400
Vacuum off (°C)	800	790	770	770
Vacuum level	Full	Full	Full	Full
High temp (°C)	800	790	770	770
Holding time (min)	1	1	1	1
Cooling procedure	Bench cool	Bench cool	Bench cool	Bench cool

Bluff, Ill) for examination. The sectioned specimens were ultrasonically cleaned for 15 min and manually polished with 400-, 600-, 800-, and 1000-grit silicon carbide papers. Final polishing of the specimens was accomplished with a rotary polisher (Automata, Jean-Wirtz) with 0.05 μm aluminum-oxide polishing paste (Micropolish II, Buehler Ltd). Subsequently, they were ultrasonically cleaned in acetone each for 15 min and dried for use.

2.5.2 *Flexural test*

A three-point flexural device in a MTS synergic Universal Testing Machine (MTS, USA) was used to test specimen bond strength in the three groups ($n = 8$). Porcelain-metal specimens were positioned on supports with 2 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 2 mm metal rod at the crosshead speed of 1.0 mm/min. The load was applied until disruption of the load–deflection curve occurred, which indicated bond failure. The bond strength (τ) was calculated by the following equation given in ISO 9693:30 [16]

$$\tau = k \times F_{fail} \quad (\mathrm{N/mm^2})$$

where F_{fail} is the maximum force applied in Newtons before debonding (failure load), and k is a constant determined from a graph in ISO 9693 with units of mm^{-2}. The value of k depends on the thickness of the metal substrate and the elastic modulus of the metallic material, and the tested CP Ti was determined to be 4.7 mm^{-2}.

Bond strength mean values were compared by an analysis of variance (ANOVA), and a Tukey's multiple comparisons (SPSS 13.0) were used to determine the statistical significance of the mean differences between groups. Statistical significance was set at the 0.05 probability level.

For more in-depth study of the bond interface, representative specimens were selected from each combination in which porcelain was cracked from the metal during the flexural test to evaluate the delaminated surfaces by SEM. Specimens were cleaned in an ultrasonic bath with distilled water for 10 min.

3 Results and discussion

Numerous methods have been introduced for conditioning alloy surfaces. However, they work differently on various alloys. Among those methods, electro etching has been suggested widely, but it is not effective on Ti and noble alloys. For this reason, in this study the coating technique was employed as a good way to change the surface property of the substrate.

The elimination of the superficial layer was performed by the use of a carbide bur at low speed in order to eliminate the α-case layer, and all the groups were submitted to air-abrasion with alumina prior to porcelain firing to provide uniform surface roughness and better standardization for the bond strength of the Ti-ceramic interface. Modifications in the surface roughness could be expected after coating.

3.1 XRD spectra

The XRD spectra showed peaks corresponding to the (100), (002), (101), (102), (110), (103), (112), and (201) orientations of Ti (Fig. 2a, c). The control group (Fig. 2c) also showed peaks of Al_2O_3 from sandblasting. Heat treatment caused agglomeration of Ti particles, resulting in the increased Ti peak intensities in Fig. 2a compared with the control group (Fig. 2c). There were no peaks corresponding to SiO_2, indicating SiO_2 was in an amorphous phase (Fig. 2a). Figure 2b shows the diffraction peaks of the ZrN crystal, orientated at (111), (200), (220), (311), and (222). It was assigned to the cubic ZrN phase (JCPDS 35-0753), and the specimens showed a strong (111) preferred orientation. Our results demonstrated that ZrN was in good crystal form in the coating. The peaks of the substrate were not detected due to the diffraction angle chosen.

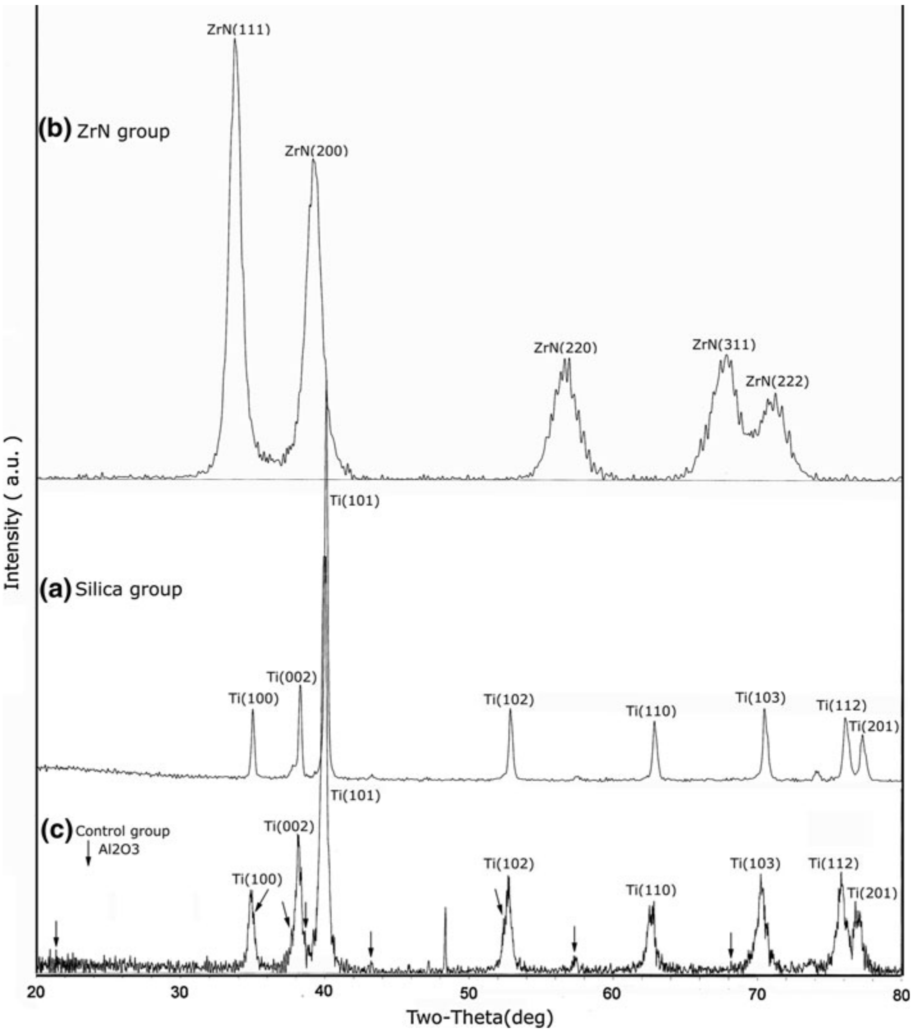

Fig. 2 XRD spectra of the tested Ti surfaces. **a** Silicon-coated Ti specimens. **b** ZrN-coated Ti specimens. **c** Uncoated Ti specimens

The surface microstructure of the three groups showed the following: silica group, Ti and amorphous SiO_2, ZrN group, ZrN crystal, control group: Ti. Previous studies have shown that some of the nanostructured silica particles can agglomerate, and numerous micro fractures are formed during the thermal treatment in silica films [17]. Additionally, small portions of the silica coating contain particles larger than 100 nm. These larger particles and micro fractures may be considered defects in the coating, but the micro fractures may also provide a type of mechanical interlocking that could lead to the increase in the bond strength of metal-porcelain systems [17]. Compared with silica, the magnetron sputtering method can achieve a more even distribution and result in a homogeneous coating. However, both of these films are helpful in improving the bond, as demonstrated by the three-point-bend test below.

However, increasing surface roughness does not necessarily result in an increase in bond strength. Reyes et al. [5] used 50-μm abrasive particles, while 120-μm particles were used in this study. Derand and Hero [18] observed that the use of 250-μm alumina particles, compared with 50-μm particles, significantly improved the bond between Ti and ceramic. Gilbert et al. [19] found that airborne-particle abrasion could contaminate the surface of Ti with alumina particles, which could weaken the mechanical interlocking of the porcelain and Ti.

N_2 partial pressure is a key parameter that determines the nature of the ZrN phases [20]. ZrN_x $(x > 1)$ could also co-exist with the stoichiometric ZrN phase [20]. ZrN is a stable phase, while Zr_3N_4 and ZrN_2 are metastable phases. Basically, the deposition methods mostly aim at obtaining the thermodynamically stable ZrN phase, and the metastable phases are often ignored. Thus, the coating color can turn golden, dark red, brown, and gray in sequence and finally becomes black with the increase in nitrogen flow [20]. However, the hardness values of the ZrN films are not related to film thickness, film texture or residual stress [21]. Differences in the chemical composition of ZrN films may lead to differences in the effect of film deposition on the Ti-porcelain bonding strength. According to Fragiel et al. [22], a N_2 partial pressure of 1×10^{-4} Torr ensures adequate conditions to obtain appropriate mechanical properties for the composite ZrN-based coating. In this study, the N_2 partial pressure was set at 1×10^{-4} Torr, and ZrN films were about 1 μm according to the deposition rate (1 μm/h).

3.2 SEM/EDS analysis of the bond surfaces

Scanning electron microscopy is a valuable and necessary method to investigate metal–ceramic bonds and was performed in this study to evaluate the interface before and after the bending test. SEM micrographs of the cross-sectioned Ti-porcelain samples before the three-point-bending test are shown in Fig. 3. Microscopic observations of the interface, which directly influences the quality of bonding, indicated that in both cases quite good bonding between porcelain coatings and the metal substrate was obtained. The Ti oxide layer was not observed either at the interface or on the surface of either component, including the control group. This could explain why the bond strength in the control group was acceptable. The coated groups (ZrN coating and silica coating) appeared fully coherent to the Ti substrate with no cracks or flaws. Meanwhile, cracks and flaws could be observed in the control group, as indicated by arrows in Fig. 3c. An average thickness of 4 μm was obtained for the silica coating as observed by SEM. The porcelain used, TitanKeramik, displayed excessive porosity with a random distribution that is in agreement with previous studies [23].

The chemical bonding of the coatings would favor the enhancement of the bond strength between the metal substrate and the porcelain. For the ZrN coating, Zr preferentially reacts with O rather than Ti at high temperature, e.g., 800°C. This prevents the formation of non-adherent oxide on the Ti surface. Elemental N in the coating can react with the alkali metal oxides in the porcelain. Thus, the coating and porcelain can form chemical bonds. It has been reported that the bond strength between a ZrN coating by magnetron sputtering and stainless steel substrate is 26 N [24], indicating that the bond between ZrN coating and the substrate is also of sufficient strength.

A brush coating technique was employed in the study to obtain the silica coating from silica sol. We previously found that when the coating gel was thermally treated in air, Si–OH groups reacted together to form Si–O–Si (siloxane) bonds, which lead to the silica network formation. Si is the main element in the porcelain and therefore chemical bonding can also occur between the silica coating and porcelain. Bieniaś et al. also demonstrated that a SiO_2 coating produced by the sol–gel method can form chemical bonds between CP Ti and porcelain [17]. Therefore, a silica coating can provide a homogeneous interface between Ti and porcelain.

The coatings formed by hand brushing were not as uniform as the ones formed by magnetron sputtering, which could also be observed from SEM images of the interface. The difference in the processing methods may be one of the reasons why the ZrN coating was superior to the silica coating. Other reasons may include the nature of the bonding itself and mismatch of coefficients of thermal expansion, which can also influence the achievement of suitable metal-ceramic bonding. All of these methods will require further studies to improve on the procedures. For example, withdrawing the specimens from the sol solution at a constant rate could be tested to determine if it will form a better silica coating.

Energy dispersive spectroscopy analysis was performed to detect the elements at the interface. The results revealed that such elements as Ti, C, Si, O, Al, K coming from the Ti as well as the porcelain was present at the bond surface of the control group, indicating an interaction at the interface. However, the elements Zr and N were also detected at the bond surface of the ZrN group, confirming the presence of the ZrN coating. Si was detected in high amounts in all three groups since the porcelain used (Vita Titankeramik) contains a high percentage of Si in its bonder [25]. In the silica group, the Si detected was significantly increased after application of the silica coating.

According to the literature [26], it is supposed that during the heat treatment of ceramic layer, diffusion of the components and possibly a chemical reaction at the interface between the metal substrate–intermediate coatings–porcelain occurs. Ti-ceramic adhesion involves a chemical reaction between Ti and silica (porcelain) and the formation of a new Ti_5Si_3O phase, which can be responsible for the fracture of the metal-porcelain bond [27]. Si, Al and K are the major elemental ingredients in porcelain. The diffusion of the element in the porcelain into Ti was also indicated in this study. This finding concurs with those of Suansuwan and Swain [28]. However, the nature of the interface needs further investigation in this study.

3.3 Flexural test results

The mean bond strength and SD values are presented in Fig. 4. Results of the one-way ANOVA showed significant differences among the Ti-ceramic bond strengths with different surface treatments: that of the ZrN group (45.99 ± 0.65 MPa) was significantly higher than the control group (29.48 ± 1.01 MPa) ($P < 0.001$). Statistical analyses also showed that surface treatment of the silica coating (37.77 ± 0.78 MPa) enhanced the Ti-ceramic bond strength ($P < 0.001$). The difference between the ZrN group and silica group was also significant ($P < 0.001$), indicating that the ZrN coating provided a better Ti-ceramic bond in this study.

From a mechanical viewpoint, differences in surface roughness caused by different substrate treatments may

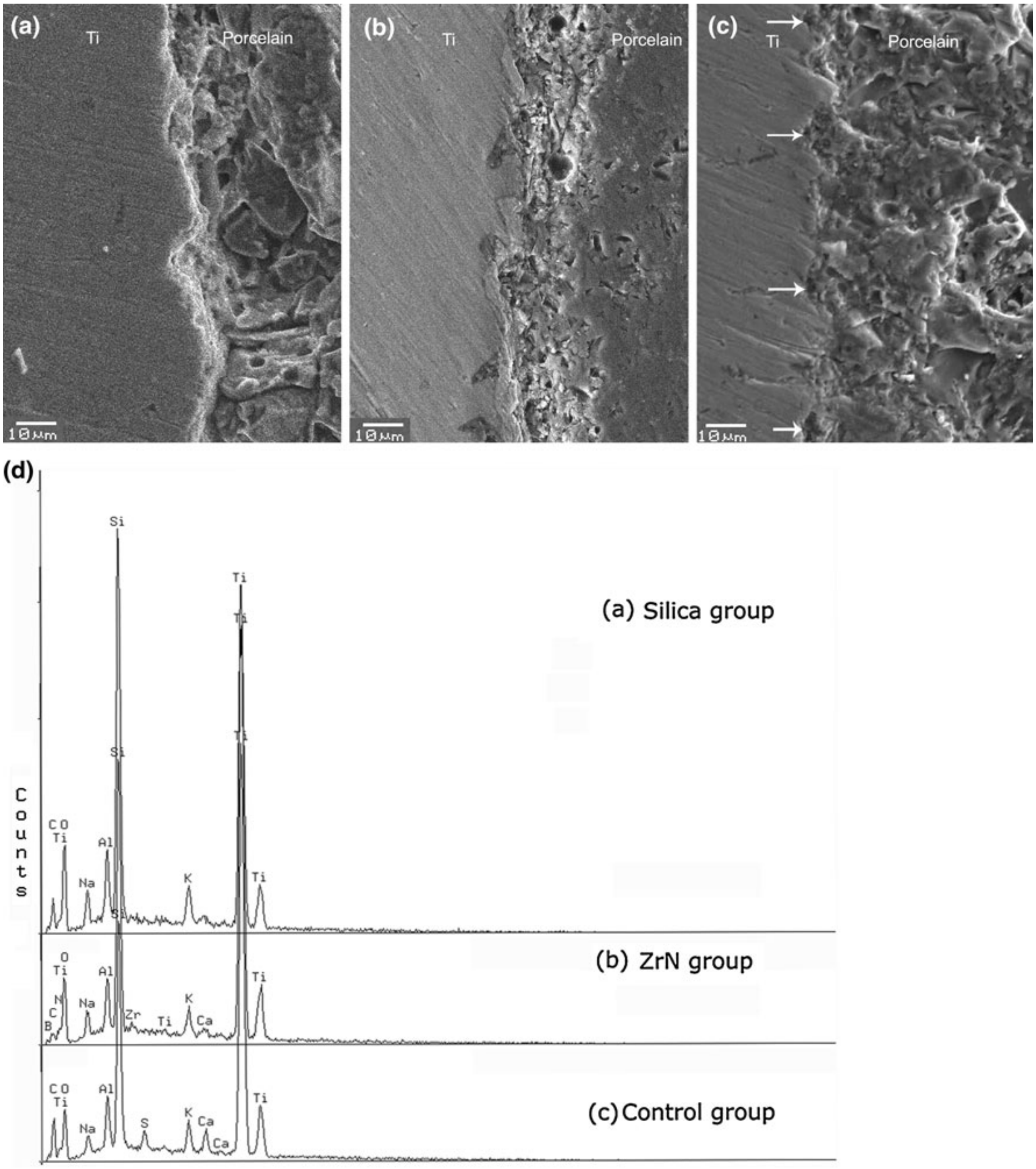

Fig. 3 SEM photographs (×1000 magnification) of cross-sections of Ti–ceramic systems and EDS analysis. **A** Silicon-coated Ti–ceramic specimens. **B** ZrN-coated Ti–ceramic specimens. **C** Uncoated Ti–ceramic specimens. The Ti oxide layer was not observed either at the interface or on the surface of either component, including the control group. **A** and **B** appear fully coherent to the Ti substrate with no fractures or flaws. However, in **C**, fractures and flaws can be seen (marked by *arrows*). **D** Panels (*a*) EDS, (*b*) EDS, and (*c*) EDS show the EDS results for the silica group, ZrN group and control group, respectively

alter the bond strength. Metal surface roughness provides mechanical interlocking between CP Ti and porcelain, an important factor that may affect bond strength observed by the three-point flexure test.

Although the three-point-flexure is widely accepted and used by several investigators to evaluate the metal-ceramic bond strength, the mode of failure may not directly correspond to the clinical situation [3, 5, 19, 29]. According to Probster et al. [29], compared to other tests such as shear, torsion and pull through tests, the three-point-flexure test has the advantage of providing complex tensions on the samples during the tests for measuring bond strength of ceramo-metal samples. However, differences in bond strengths resulting from PFM samples tested by the three-point-flexure tests have been previously reported. Lack of uniformity of sample thickness could explain the disparity in values. In this study,

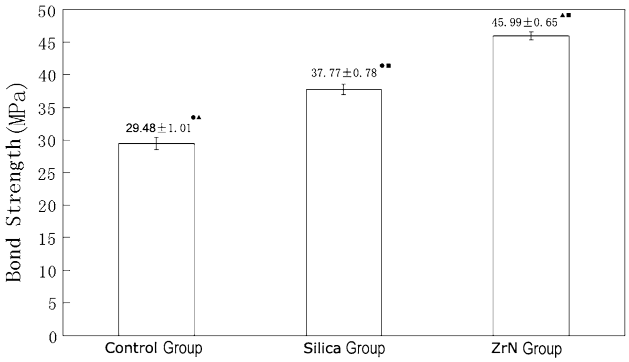

Fig. 4 Bond strength (MPa) for CP Ti surfaces modified with different methods ($n = 8$). There were statistically significant differences between any two of the three groups, as marked by the *symbols* ($P < 0.001$)

the results of the three-point-flexure test showed significant improvements in the bonds strengths of uncoated versus coated groups.

The minimum debonding/fracture initiation strength for porcelain/metal combinations set by ISO 9693 is 25 MPa [16]. The lab procedure we use now ensures that a clean surface of proper roughness is obtained as shown in Fig. 1a, which is beneficial for the bonding between CP Ti and porcelain. Hence, the control group whose surfaces only received airborne-particle abrasion had an acceptable Ti-ceramic bond. This may be due to two reasons. First, the porcelain used is a special type of low-fusing porcelain designed for Ti, and its processing temperature is not beyond 800°C, The airborne-particle abrasion likely improves the bond strength by removing loosely attached furrows, overlaps, and flakes of metal created by grinding procedures, providing mechanical interlocking, increasing surface area, and increasing wettability [5, 30].

Results from this study showed that the improvement of the ZrN coating and silica coating on Ti-ceramic adhesion was significant on CP Ti. The coating may act as a diffusion barrier to control the formation of non-adherent oxide on the Ti surface [31], since control of non-adherent Ti oxide formation is an essential step in achieving high bond strength. As observed by many researchers [18], the fracture line was located at the interface between the metal substrate and porcelain. The penetration of oxygen from the ambient atmosphere and from the porcelain should be prevented; thereby the formation of thick oxidation layer on the Ti surface which is the main cause of poor adherence can also be prevented.

The evenness of the coating also contributed to the relatively low standard deviations in the bond strength values of the coated groups compared to the uncoated ones. The variation in bond strength within the ZrN group was lower than that of the silica group, indicating a more uniform distribution of the former one. However, the thickness of the ZrN coating and silica coating were different in the study, and the precise effect of the coating thickness on bonding will require further investigation.

3.4 SEM analysis of the delaminated surfaces

Scanning electron microscopy analysis at 150 × magnification (Fig. 5) of the CP Ti surface after debonding demonstrated several dark areas on the CP Ti surface for the coated groups. An EDS test proved that those areas corresponded to the residual porcelain, while the gray ones were interlayer or exposed Ti surfaces. Consistent with the flexural strength tests, this observation indicated a combination of cohesive and adhesive bond failures. However, only trace amounts of porcelain were observed on specimens in the control group, indicating that the failure was primarily due to the adhesive.

Results from this study showed significantly higher bond strength values of the experimental groups compared with the control group, which confirmed the superiority of ceramic adherence to the coated surfaces of CP Ti. The excellent metal-ceramic adherence was exhibited by the presence of remnant porcelain on the specimen surface after the three-point-flexure test. This was only observed in the experimental groups, a clear indication of cohesive failure rather than adhesive failure.

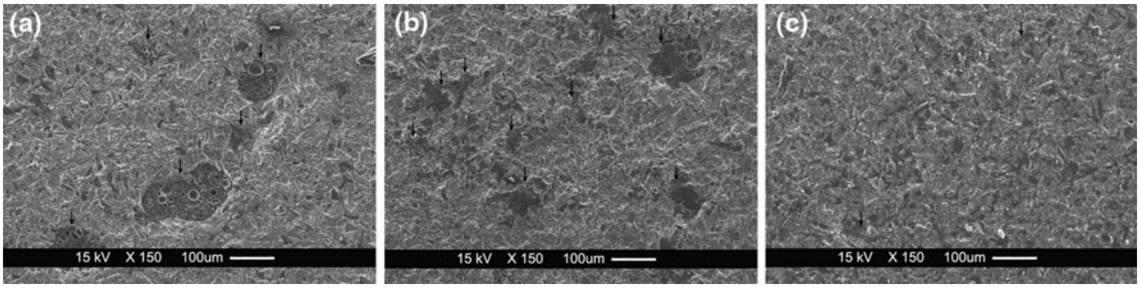

Fig. 5 SEM photomicrograph (150 × magnification) of Silica-coated (**a**) and ZrN-coated (**b**) and Uncoated (**c**) Ti surface after debonding. Ceramic remnants could be identified on metal as *dark* areas marked by *arrows*. *Gray* ones were interlayer or exposed Ti surfaces. (**a**) and (**b**) both show the ceramic remnants on the surface. (**c**) shows little residual ceramic retained on the metal surface

Meanwhile, the uncoated CP Ti surfaces were found to be free of ceramic remnants. Kimura et al. [1] stated that the formation of a metallic oxide layer on CP Ti does not adhere to the substrate and thus fracture is regarded as adhesive between the metal or metallic oxide layer and the ceramic. Although aggressive testing conditions were not performed, the absence or small amounts of residual ceramic on the CP Ti have also been observed in previous studies [30].

The ZrN coating we obtained was golden in color as shown in Fig. 1b, making it a potential alternative for gold at a lower price in the dental clinic to achieve a satisfactory aesthetic restoration. The application of ZrN coating and silica coating to the surface of Ti as an interlayer of the Ti/porcelain system will still require further work to determine the conditions to obtain the best biocompatibility and desirable properties.

4 Conclusions

Based on the results of this study, the following conclusions can be drawn:

1. The application of coatings significantly improved the bond strength of CP Ti/porcelain systems in comparison to CP Ti substrate after sandblasting only. The bond strength of both groups with intermediate coatings was at an acceptable standard level.
2. CP Ti-intermediate coating-porcelain could form chemical bonding in addition to mechanical bonding. The failure in the coated groups was both cohesive and adhesive.
3. ZrN coating by magnetron sputtering resulted in better improvement of Ti porcelain bonding strength than the sol–gel processed silica coating.

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