ORIGINAL ARTICLE

Interfacial analysis of porcelain fused to high-palladium alloy with different observation methods

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KEYWORDS
electron probe microanalysis; palladium—silver alloy; scanning electron microscopy combined with energy dispersive X-ray analysis; X-ray photoelectron spectroscopy

Abstract Background/purpose: In a previous fractural study of implant-supported crowns, it was found that the palladium—silver crowns possessed the highest fracture force. The ceramic—metal interface was examined to explain its high resistance to fracture.

Materials and methods: Palladium—silver crowns with the morphology of a maxillary second premolar were prepared following standard dental laboratory procedures. Crown specimens were compressed vertically in the center of the occlusal surface until fracture, using a universal testing machine. The fractured surfaces were examined using scanning electron microscopy combined with energy dispersive X-ray spectroscopy to determine the failure mode. The ceramic—metal interface of the crown was examined with electron probe microanalysis. Additionally, sheet specimens with a dimension of 10 × 9 × 4 mm³ were prepared to examine the surface morphology and composition of palladium—silver alloy after oxidation and porcelain-fused-to-metal firing cycles.

Results: The average fracture force was 1425 ± 392N. Analyses with scanning electron microscopy combined with energy dispersive X-ray spectroscopy revealed that the failure mode was cohesive within the ceramic layer. Electron probe microanalysis micrographs indicated that Sn and In were found to distribute only on the alloy side of the ceramometal crown. Energy dispersive X-ray spectroscopy analysis and electron probe microanalysis micrographs confirmed that ZnO had diffused into the ceramic phase.

Conclusion: In2O3, SnO2, and ZnO were found along the interface; the presence of these oxides at the boundary promotes ceramic—metal adhesion, and this resulted in cohesive failure of the
Introduction

Palladium—silver (Pd—Ag) alloys were first introduced for dental restorations in the 1970s as an alternative to costly gold-based dental alloys.1–2 Commercially relevant Pd—Ag alloys typically have compositions of approximately 50–60% Pd and 30–40% Ag, and contain small amounts of low-melting-point metals, such as Zn, In, and Sn, to improve castability by increasing the fluidity of the molten alloy.3 Adherence of porcelain to noble alloys is usually improved by adding easily oxidized alloy components, such as In, Sn, and Ga.4–6 Accumulation of these elements at the metal—ceramic interface has been reported in several studies.7–10 The bonding mechanism is believed to result from suitable oxidation of the metal11–14 and diffusion of the oxides into the opaque porcelain during firing.

Porcelain fracture related to an implant-supported porcelain-fused-to-metal (PFM) crown or bridge was found to have a significantly higher risk than that of tooth-supported restorations.15 It was previously thought that biological or mechanical factors were the dominant causes of failure after PFM crown restoration.16 Studies using three or four points, and double bending tests to measure bonding strength between porcelain and metal coping were unable to accurately imitate the failure mode of a PFM crown under actual oral conditions.17,18 Many PFM crown restoration casts were developed, and the Instron testing machine was introduced to determine PFM crown fracture resistance.19,20 In a recent fractural study of implant-supported crowns that were porcelain-fused to five different commercial alloys,21 it was determined that the Pd—Ag alloy had the highest fracture force. Still more detailed information is required on such a high Pd—Ag alloy commercial product in PFM crown restoration. The aim of this study is to find out the interface characteristics after PFM firing cycles, using multitechnique analysis methods, including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy combined with energy dispersive X-ray analysis (SEM/EDX), and electron probe microanalysis (EPMA), for characterizing the alloy surface after oxidation and the ceramic—metal interface after PFM firing cycles. Failure modes of fractured surfaces were determined using SEM/EDX and EPMA.

Materials and methods

Specimen preparation

The materials used in this study were Pd—Ag dental casting alloys (Argelite 50; Argen Corporation, San Diego, CA, USA) with compositions shown in column 2 of Table 1. Au and Ru were present as trace elements (each < 1 wt%). Uniform ceramic layer. ZnO was found to diffuse into the ceramic phase, and it is suggested to be beneficial for high fracture resistance in the present study.

| Alloy       | EDX   | XPS   | Upper | Middle | Lower |
|-------------|-------|-------|-------|--------|-------|
| Pd          | 49.6  | 21.6  | 0.9   | 47.3   | 46.0  |
| Ag          | 40.0  | 28.0  | 1.2   | 41.1   | 45.4  |
| In          | 5.0   | 27.7  | 49.8  | 57.0   | 0.0   |
| Sn          | 4.0   | 12.6  | 17.4  | 20.6   | 0.0   |
| Zn          | 1.0   | 10.1  | 30.8  | 20.1   | 11.7  |

EDX = energy dispersive X-ray analysis; XPS = X-ray photoelectron spectroscopy.

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was then used to analyze the surface morphology and composition of these three specimens.

Fabrication of the crowns used eight-PFM firing cycles under a low vacuum of 10 mmHg in a dental ceramic furnace (Programat P300). Two layers of opaque dental porcelain (VITA VMK 68; Sirona Germany, Bensheim, Germany), with a combined thickness of 0.4 mm, were fired onto the crown surfaces by increasing the temperature from 600°C to 930°C over 3 minutes and holding at the peak temperature for 3 minutes for each firing cycle. Three layers of dentin porcelain (VITA VMK 95), with a combined thickness of approximately 1.0 mm, were fired onto the crowns by increasing the temperature from 600°C to 930°C over 6 minutes and holding at the peak temperature for 6 minutes. The crowns were bench set at RT after each firing cycle. The total porcelain thickness was approximately 1.4 mm. Two layers of glaze were fired onto the crowns by increasing the temperature from 600°C to 930°C over 3 minutes and holding at the peak temperature for 1 minute, and the completed crowns were allowed to cool to RT.

A layer of approximately 0.5 mm opaque dental porcelain (VITA VMK 68) and then a layer of approximately 1.0 mm dentin porcelain (VITA VMK 95) were PFM fired onto the other three sheet specimens. These three specimens were bench set at RT in each firing cycle. Each specimen with a cross-section of 9 × 5.5 mm² was embedded in a resin that was cured from a mixture of 1/3 conducting mounting compound (psi# 212-1; Precision Surfaces International, Houston, TX, USA) and 2/3 epoxy mounting powder (psi# 211-5). The mounted specimens were mechanically polished by sequentially using a series of SiC papers (400–2000 grit), and additionally polished by diamond pastes of 6 μm, 3 μm, and 1 μm, leaving a mirror finish. The surfaces were then carefully wiped with a detergent solution, ultrasonically cleaned in acetone and deionized water, and air dried. Distribution of elements around the interface of ceramic and alloy after two PFM firing cycles was examined using EPMA.

**Compressive fracture testing**

Compressive fracture tests of ceramometal crowns were performed by using a universal testing machine. A custom-built loading apparatus (Figure S1) was made following the design of Torrado et al. The upper member of the apparatus consisted of a 15-mm-diameter hardened stainless-steel shaft connected to the end of the loading part of a universal testing machine (Model 5582; Instron, Norwood, MA, USA). The opposite end of the shaft was machined to house a 3-mm-diameter loading pin with rounded edges. The pin was secured in place using a lateral setscrew. Only the loading pin contacted the porcelain during testing, and a new pin was used to load each crown. The crown was set on the abutment—analog model mounted on the lower part of the testing machine. An axial load was applied to the inner inclination of buccal and lingual cusps of the occlusal table at the same distance (1.5 mm) from the central groove. Specimens were subjected to a vertical compressive load at a crosshead speed of 0.5 mm/minute until failure to obtain the ultimate fractural strength.

**X-ray photoelectron spectroscopy**

The outermost part of the oxidized sheet specimens was subjected to XPS analysis using a JAMP-9500F photoelectron spectroscopy system.
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Spectrometer (JEOL, Tokyo, Japan), which typically analyzes a depth of 5 nm. An Al Kz X-ray source (1486.6 eV) was obtained using a 10 kV accelerating voltage and a 10 mA filament current. The vacuum level of the analyzing chamber during measurement was of the order of $10^{-10}$ Torr. The measured binding energies (BEs) were calibrated by referencing the BE of the C 1s line of hydrocarbon contamination ($285.0 \pm 0.2$ eV). The atomic percentages of Pd, Ag, In, Sn, and Zn on the surface area of the oxidized specimens were calculated according to the relative peak areas, and corrected using Wagner’s atomic sensitivity factors.

Scanning electron microscopy/energy dispersive X-ray analysis

The fracture surfaces on both sides of the failed crowns were sputter coated with carbon to produce a thin conductive layer (Cressington 108carbon; Ted Pella Inc., Redding, CA, USA). The oxidized sheet specimens were also coated with carbon after XPS analysis. Morphological features of these specimens were examined using a field emission SEM JSM-6330TF (JEOL) at 10 kV accelerating voltage and 56 \mu A beam current. An EDX spectrometer (Oxford model 7557; Buck, England) incorporated into the SEM was used to characterize the local elemental composition associated with observed features on the fracture surfaces. EDX spectra were collected from the upper, middle, and lower regions on both sides of the failed crowns, or from different regions of each sheet specimen using an area scan mode. Finally, quantitative EDX area analysis was performed to determine the weight percentage values of Pd, Ag, Zn, Si, Zr, Al, K, and Na, and to calculate the mean values of Pd, Ag, In, Sn, and Zn.

Electron probe microanalysis

A cross-sectioned crown was embedded in resin cured from a mixture of a 1/3 conducting mounting compound (psi# 212-1) and 2/3 epoxy mounting powder (psi# 211-5). The mounted crown was mechanically polished using the same procedures as described for the sheet specimens. These metallographically polished specimens were coated with carbon by sputtering using a carbon coater (Cressington 108carbon). The backscattered electron image (BEI) and secondary electron image were taken over an area of $66 \times 66$ \mu m$^2$ (1500 \times) by a JEOL JXA-8900R EPMA at 15 kV and 10 $\cdot 8$ \(\AA\). For elemental mapping, the electron beam was scanned over an area of $66 \times 39$ \mu m$^2$, and simultaneously characteristic X-ray intensities of the corresponding elements were acquired. Elemental concentration profiles in the cross-sectional layer of the ceramic and metal interface were measured using a 1-\mu m-diameter beam.

Results

Load—displacement plots were acquired during the fracture testing (Figure 2). The maximum load corresponds to the onset of a catastrophic fracture of the crown. Nine load and displacement paired values are listed with plot symbols. The average fractural force was $1425 \pm 392$N. A photograph of the fracture surfaces of a representative ceramometal crowns is presented in Figure 3. Arrows show the localized areas in filled circles that were analyzed by EDX. The majority of fractures occur in the opaque porcelain layers, with some porcelain remnants being present on the alloy surface.

The three representative BEI micrographs (upper, middle, and lower) and the elemental EDX area scans of the fracture surface on the alloy side show Pd, Ag, Zr, Si, Zn, K, and Al peaks in order of decreasing wt% (Figure S2). For brevity, results on the porcelain side are also not presented here (Figure S3). The elemental composition of the crown’s fractural surfaces obtained by EDX analysis is listed in Table 2. Pd, Ag, or Zn was not detected on the porcelain side of the fracture, and no Na was found on the alloy side. The observed composition may not represent a surface phenomenon because the overall depth sampled by EDX is approximately 1 \mu m. The crown suffered from cohesive failure, with the fracture occurring within the ceramic. The schematic diagram shown in Figure 4 uses solid lines to represent the crack path. The initial crack started at the 3-mm-diameter loading pin/crown interface, propagated...
through the dentin porcelain layers, spread into the opaque porcelain layers, and then traced a meandering path between the two interfaces (alloy/opaque porcelain) layer, and then traced a meandering path through the dentin porcelain layers, spread into the opaque porcelain layer. Finally, the crown fractured as the crack approached the dentin porcelain interface.

EPMA was employed to scan the elemental distribution mappings in the metallographically polished specimens after eight PFM firing cycles. A compositional contrast between the alloy and porcelain phases was observed using backscattered and secondary electron detectors, as presented on the left side of Figure S9. The compositional contrast between the metal and porcelain phases was observed using backscattered and secondary electron detectors, as presented on the left side of Figure S9. The results of EDX analysis on the elemental composition of the alloy surfaces are presented in the third column of Table 1. The BEI micrograph and elemental EDX scans for the oxidized alloy indicate that all these elements are evenly distributed over the surface of the specimens (Figure S8). The observed homogeneous distribution is not necessarily a surface phenomenon because the overall depth sampled by EDX is of the order of 1 μm.

The EPMA method was employed to scan the elemental distribution mappings in the metallographically polished sheet specimens after two PFM firing cycles. The compositional contrast between the metal and porcelain phases was observed using backscattered and secondary electron detectors, as presented on the left side of Figure S9. The results of Pd, Ag, In, Sn, and Zn peaks (Figures 8 and S7). The results of EDX analysis on the elemental composition of the alloy surfaces indicate that all these elements are evenly distributed over the surface of the specimens (Figure S8). The observed homogeneous distribution is not necessarily a surface phenomenon because the overall depth sampled by EDX is of the order of 1 μm.

A representative BEI micrograph and its elemental EDX area scan of the oxidized sheet specimen show the Pd, Ag, In, Sn, and Zn peaks (Figures 8 and S7). The results of EDX analysis on the elemental composition of the alloy surfaces are presented in the third column of Table 1. The BEI micrograph and elemental EDX scans for the oxidized alloy indicate that all these elements are evenly distributed over the surface of the specimens (Figure S8). The observed homogeneous distribution is not necessarily a surface phenomenon because the overall depth sampled by EDX is of the order of 1 μm.

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A typical survey scan over a BE range of 0–1100 eV for the Pd–Ag alloy sheet after surface oxidation is displayed in Figure 6. This spectrum reveals the presence of Pd, Ag, In, Sn, and Zn. Their atomic concentrations (atom%) based on curve fitting analysis are listed in column 4 of Table 1. For comparison, atom% was converted to wt%, which is listed in column 5 of Table 1. A narrow scan of the Zn 2p line after deconvolution shows two peaks (at 1021.2 eV and 1022.2 eV) originating from the metallic state (Zn0) and the oxide state (Zn2+) respectively (Figure 7)22,23. This result indicates the presence of ZnO on the specimen surface. For brevity, the narrow scans of In 3d and Sn 3d are not shown; they reveal the presence of In2O3, In, SnO2, and Sn (Figures S5 and S6).22–25

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oxide layer, particularly during the oxidation procedure. While firing the ceramic, the alloy was twice heated to 930°C, re-entering a single-phase zone each time. Owing to the high energy at high temperatures, the atoms are enabled to diffuse in the crystal lattice and forced to distribute randomly at the atomic sites (Figure S8). It has been proposed that the mechanism of the resulting enhanced oxide adherence arises from a reduction in the vacancy concentration at the metal–oxide interface.27 The formation of metal-oxide top layers is essential in bringing elements to the surface that are directly involved in the metal–ceramic bond ($\text{In}_2\text{O}_3$, $\text{SnO}_2$, and $\text{ZnO}$). Considering the XPS results, SEM observation, and EPMA analysis, it appears that $\text{ZnO}$ was integrated into the ceramic phase as a result of atomic diffusion.

In addition to the chemical bonding between porcelain fused to the alloy interface, micromechanical interlocking was also reported in previous research.28–31 The advantages of blasting of the alloy surface with $\text{Al}_2\text{O}_3$ particles, prior to porcelain application, are increases in surface roughness and surface area. This process has been demonstrated to increase the metal–ceramic adherence.12,32,33 The micrographs of SEM (Figure S10) and EPMA (Figure S9) provide evidence of mechanical interlocking in this study.

The average and minimum fracture forces ($1425 \pm 392\text{N}$ and $1000\text{N}$, respectively) for Pd–Ag ceramometal crowns

![Figure 5](image5.png)

**Figure 5** EPMA color photomicrograph showing element distributions of Zn around interface within the crown. EPMA = electron probe microanalysis.

![Figure 6](image6.png)

**Figure 6** XPS wide scan of alloy after surface oxidation. XPS = X-ray photoelectron spectroscopy.

![Figure 7](image7.png)

**Figure 7** XPS narrow scan of alloy after surface oxidation showing $\text{Zn} 2p_{3/2}$ peak spread over 1015–1029 eV and covering $\text{Zn}^0$ and $\text{ZnO}_2$. XPS = X-ray photoelectron spectroscopy.
were substantially greater than the maximal molar region biting force of 847N for men and 597N for women. In the present study, the interface conditions between the crown to abutment and implant analog were assumed to be fully intimate contact for the tested models. However, a completely passive interfacial fit does not usually occur in real clinical situations, and screw designs and rough surfaces of dental implants are dissimilar to each other. These variables for a real dental implant may affect the efficiency of an occlusal load transfer to the surrounding bone, and may cause stress concentration in the occlusal table or at the connection of the abutment and dental implant. Testing casts have their limitations because the biomechanical properties and nonlinear behavior of biological tissues in a real oral cavity cannot be predicted precisely. In the laboratory, the use of a single-cycle load-to-failure and mouth-motion fatigue tests with simplified geometries provide limited data for guiding the development of PFM systems. However, the fracture surface and interface analyses conducted in this study are still vital for successful ceramometal restoration. It is suggested that mechanical interlocking contributes to the interface strength based on the rough morphologies seen at the alloy–porcelain boundaries (Figures S4, S9, and S10). Based on the observation that the fractural pathway remained within the opaque porcelain layer and the results from EDX analysis, it is suggested that an adhesive bonding force between the alloy and ceramic is greater than the ceramic cohesive forces. The results from this study are consistent with the findings of other studies.

Accumulation of easily oxidized elements at ceramic–metal interfaces has been reported in several studies to improve the adherence of porcelain to alloys of noble metals. Such data are generally found to support the chemical bonding mechanisms. In$_2$O$_3$ and SnO$_2$ were found only on the alloy side of the interface, suggesting that they contribute to the interface bond strength. Trace ZnO present at and across the interface is also responsible for improving bonding, and it is suggested that this is a main factor in the observed high fracture resistance of the ceramic–metal interface.

In conclusion, In$_2$O$_3$, SnO$_2$, and ZnO were found along the interface; the presence of these oxides at the boundary promotes ceramic–metal adhesion, and this resulted in cohesive failure of the ceramic layer. ZnO was found to

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**Figure 8** Representative SEM micrograph for oxidized alloy. SEM = scanning electron microscopy.

**Figure 9** EPMA color photomicrograph showing element distributions of Zn between interface of ceramic and metal after two porcelain-fused-to-metal firing cycles. EPMA = electron probe microanalysis.
diffuse into the ceramic phase, and it is suggested to be beneficial for high fracture resistance in the present study.

Conflicts of interest
The authors have no conflicts of interest relevant to this article.

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Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jds.2015.10.001.

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