Journal of Dental Sciences (2016) 11, 156–163

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.e-jds.com

ORIGINAL ARTICLE

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

Hao-Sheng Chang [a,b], Chao-Sen Yang [c], Yao-Dung Hsieh [d], Ming Chen [c*]

[a] Department of Stomatology, Kaohsiung Veteran General Hospital, Kaohsiung, Taiwan
[b] Department of Dental Technology, Shu-Zen Junior College of Medicine and Management, Kaohsiung, Taiwan
[c] Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Kaohsiung, Taiwan
[d] Kaohsiung Veteran General Hospital, Pingtung Branch, Pingtung, Taiwan

Received 15 June 2015; Final revision received 3 October 2015
Available online 5 January 2016

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 $10 \times 9 \times 4$ mm^3 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: In_2O_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

* Corresponding author. Department of Materials and Optoelectronic Science, National Sun Yat-sen University, 70 Lien-Hai Road, Kaohsiung 80424, Taiwan.
E-mail address: mingchen@faculty.nsysu.edu.tw (M. Chen).

http://dx.doi.org/10.1016/j.jds.2015.10.001

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.

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 metal[11—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 ceramometal crowns of a Pd—Ag alloy, with equivalent morphologies to the maxillary second premolar, were duplicated on a Straumann straight screw-retained abutment (Lot No.: 048.605; Straumann, Basel, Switzerland) connected to a Straumann regular neck tissue-leveled implant analog (Lot No.: 048.124) under a 35N preload. Additionally, Pd—Ag alloy sheets with a dimension of $10 \times 9 \times 4$ mm^3 were prepared. Ten ceramometal crowns and six sheets of Pd—Ag alloy were fabricated following the manufacturer's instructions, involving five standard dental preparation stages (Figure 1):

(1) To make the castings, wax patterns were prepared, sprued, and invested with gypsum-bonded cristobalite investment material (Shofu Inc., Kyoto, Japan). The alloy was melted using a multiorifice gas-oxygen torch, cast into the mold using a centrifugal dental casting machine, and then bench cooled.
(2) After devesting, the alloy was blasted with 50 μm Al_2O_3 particles (Bego, Bremen, Germany).
(3) Specimens were grounded smoothly and were blasted again with 50 μm Al_2O_3 particles, and then the blasted surface was cleaned with steam.
(4) After surface treatment, the specimens were oxidized by heating them in a mild vacuum (10 mmHg) in a dental ceramic furnace (Programat P300; Ivoclar Vivadent Inc., Amherst, NY, USA) from 450°C to 1000°C at a rate of 45°C/min with a 1-minute hold at the peak temperature. The specimens were bench cooled to room temperature (RT). Three of these sheet specimens were left in this oxidized state. Their surfaces were first examined with XPS. SEM/EDX

Table 1 Bulk composition of Pd—Ag alloy as supplied by the manufacturer, surface composition obtained from EDX and XPS analyses after surface oxidation of the alloy, and surface composition of fractured crown on alloy side (in wt %).

	M[a]	EDX	XPS[b]	XPS	Upper[c]	Middle[c]	Lower[c]
Pd	49.6	21.6	0.9	1.0	47.3	46.0	39.5
Ag	40.0	28.0	1.2	1.3	41.1	45.4	41.7
In	5.0	27.7	49.8	57.0	0.0	0.0	0.0
Sn	4.0	12.6	17.4	20.6	0.0	0.0	0.0
Zn	1.0	10.1	30.8	20.1	11.7	8.6	18.8

EDX = energy dispersive X-ray analysis; XPS = X-ray photoelectron spectroscopy.
[a] Manufacture.
[b] Atom%.
[c] Obtained from EDX analysis on three different areas along the fracture path. Compositional data are expressed in wt% by adopting sum of Pd, Ag, In, Sn, and Zn as 100 wt%.