1 | INTRODUCTION

While the current trend is for dental crown restorations to be fabricated from esthetic ceramic materials such as lithium disilicate and zirconia, there is still widespread usage of metallic materials for porcelain-fused-to-metal restorations. The high-palladium casting alloys, which contain over 75% (wt%) Pd with Ga as the secondary element, are often selected for PFM restorations because of their favourable cost compared to alternative gold alloys, excellent mechanical properties and good bond strength to porcelain (Brantley & Laub, 2016). These alloys are classified into the two groups of Pd–Cu–Ga and Pd–Ga, and they contain secondary elements such as tin and indium which modify mechanical properties and enhance porcelain bond strength (Brantley, Cai, Carr, & Mitchell, 1993; Carr & Brantley, 1991).

High-Pd alloys contain multiple microstructural phases and generally contain ruthenium as a grain-refining element, which yields fine grain cast microstructures (Brantley et al., 1993; Carr & Brantley, 1991; Vermilyea, Cai, Brantley, & Mitchell, 1996). The matrix is a Pd-rich solid solution, and secondary precipitates appear along the grain boundaries and/or inside the grains. In the absence of a grain-refining element, the high-Pd alloy has a less desirable dendritic cast microstructure (Carr & Brantley, 1991), which can lead to the formation of "hot tears" in thin sections.
Corrosion resistance is a highly important property of dental alloys because of its relationship to biocompatibility. Due to the variation in chemical composition, microstructural phases in the high-Pd alloys would be expected to exhibit a range of corrosion tendencies. However, linear polarization (Sun, Monaghan, Brantley, & Johnston, 2002a) and electrochemical impedance spectroscopy (Sun, Monaghan, Brantley, & Johnston, 2002b, 2002c) laboratory studies have shown that the corrosion resistance of the high-Pd alloys is comparable in simulated body fluids and an artificial saliva to a popular gold–palladium alloy with excellent clinical performance.

The excellent corrosion resistance of high-Pd alloys has been attributed to the predominant content of the noble element palladium. Nonetheless, differences in corrosion potentials of the microstructural phases might be anticipated to cause some level of galvanic corrosion, and dealloying causing microstructural phase composition changes (Sarkar, Berzins, & Prasad, 2000) can occur. Because the slow ion release of Pd from high-Pd alloys in vivo can potentially lead to concerns about biocompatibility, detailed information about corrosion mechanisms for these alloys is highly important.

Scanning Kelvin Probe Force Microscopy (SKPFM) is a powerful tool (Guillaumin, Schmutz, & Frankel, 2001; Schmutz & Frankel, 1998a, 1998b, 1999) to study localized corrosion by directly measuring the surface Volta potential (electrostatic potential differences between phases or regions). It has been proven for engineering alloys that the surface Volta potential map is directly correlated with the corrosion potential of the surface in an electrolyte (Yee, Oriani, & Stratmann, 1991). This has also been demonstrated by exploring the linear correlation between the surface Volta potential and the corresponding open circuit potential in water and saline solution for pure metals with different nobility (Guillaumin et al., 2001; Schmutz & Frankel, 1998a). Thus, the Volta potential map can be regarded as representing the practical in situ nobility of the surface. Combining SKPFM with Atomic Force Microscopy (AFM) can simultaneously provide the topographic image and the corresponding Volta potential map of the surface with potential resolution approaching the nanometre range. SKPFM/AFM has been successfully developed to study the role of different phases in the localized corrosion of aluminium alloys (Schmutz & Frankel, 1998a, 1998b, 1999), but these two complementary techniques have not previously been employed for dental alloys.

In this initial study, SKPFM/AFM was used to explore the relative corrosion tendencies of different microstructural phases in representative high-palladium dental alloys. We show that this electrochemical biomedical sensor provides novel information about localized corrosion in these alloys, which can potentially have important health consequences for dental patients.

2 | EXPERIMENTAL

2.1 | Alloy selection and specimen preparation

High-palladium alloys for metal-ceramic restorations were selected for study. For the figures to follow, the Pd–Cu–Ga alloy Freedom Plus has the composition 78Pd–8Cu–5Ga–6In–2Au–Ru; the Pd–Ga alloy Legacy has the composition 85Pd–10Ga–1ln–2Au–1Ag–Ru (all wt%; Heraeus Kulzer Jelenko, now available from Argen). Dish-shaped castings of 12 mm diameter and 1.3 mm thickness were prepared by following previously described standard dental laboratory procedures and manufacturer recommendations for high-Pd alloys (Carr & Brantley, 1991). Heat treatment of the specimens was performed to simulate the initial oxidation step (Heraeus Kulzer Jelenko) and the firing cycles for Vita VMK dental porcelain (Vident), which is known to be compatible with the high-Pd alloys. The heat-treated alloy specimens were ground and polished with diamond paste using an alcohol solution (DP-Lubricant Blue; Struers) to 1 µm surface roughness.

2.2 | Protocol for SKPFM/AFM experiments

The polished specimens were immediately observed by SKPFM/AFM (Nano III; Veeco Instruments). During operation, the surface area of interest was scanned line-by-line using a cantilever silicon tip. The topographic profile was first determined by scanning along a line, using the tapping mode of AFM operation. The tip was then lifted off the surface by 100 nm, and the line was rescanned by switching to the SKPFM lift mode, with the tip maintained at exactly the same distance at every point along the line as that for the AFM mode. During the SKPFM scanning mode, an ac voltage (±1 V) was applied to the tip to create an oscillating dipole. In the presence of an external electric field (such as from the Volta potential), this dipole will also induce an oscillation of the cantilever; a dc voltage ramp was superimposed on the ac signal to null the cantilever oscillations. At this point, the potential on the tip and on the sample was the same; therefore, the Volta potential was the same as the dc voltage.

2.3 | Microstructural phase observations

After completion of the SKPFM/AFM analyses, the same areas of interest were observed with a scanning electron microscope (SEM, XL30 ESEM FEG; Philips). The chemical compositions of the phases of interest were analysed by an X-ray energy-dispersive spectrometer (EDS) coupled to the SEM. After etching in aqua regia, the microstructures of the bulk alloy specimens were again examined by...
SEM. Some polishing scratches were intentionally left on the surface of each specimen to aid in locating the same area during subsequent examination with the SEM after the SKPFM/AFM analyses.

3 | RESULTS AND DISCUSSION

3.1 | SKPFM/AFM and SEM observations

Figure 1 shows the topographic image (a) and Volta potential image (b) acquired by SKPFM/AFM for a typical microstructural area of the Freedom Plus Pd–Cu–Ga alloy. The corresponding secondary electron image (c) and backscattered electron image (d) were obtained with the SEM. The scratches in the topographic image provide markers for the SEM observations. Five rod-shaped particles are evident in both the topographic image of Figure 1a and the Volta potential map (b), where they have bright appearances. At the top of the SEM images in Figure 1c,d, a pore arising from the casting process is evident. Their bright appearance indicates that these rod-shaped particles protrude above the nominal plane of the sample in the topographic map (a) and have higher hardness than the matrix. In the Volta potential map (b), their bright appearance indicates that these particles have higher nobility relative to the adjacent Pd solid solution matrix. EDS analyses with the SEM showed that the rod-shaped particles (in both Figures 1 and 2) are enriched in Ru, with an approximate composition of 75 Ru and 25 Pd (wt%).

Similar findings occurred with SKPFM/AFM examination of another Pd–Cu–Ga alloy Liberty (76Pd–10Cu–5.5Ga–6Sn–2Au–Ru; Heraeus Kulzer Jelenko/Argen), where the ruthenium-rich particles also had bright appearances in the topographic and Volta potential maps, the latter again indicating higher nobility for these particles than the Pd solid solution matrix. The analogous images for this alloy to those in Figure 1 have been omitted for the sake of brevity.

Consideration of Figure 1c,d indicates that these SEM images show a portion of only a single grain of the Pd solid solution matrix in the Freedom alloy. From the magnification scale bar, the grain size is in excess of 30 μm. No other phase, besides the ruthenium-rich particles, is evident. The appearance of these two phases and the grain size are similar in the microstructure for the heat-treated Freedom alloy (Vermilyea et al., 1996), which has a similar composition (76Pd–10Cu–6.5Ga–7In–Ru) to Freedom Plus (78Pd–8Cu–5Ga–6In–2Au–Ru). Consideration of the microstructure for as-cast Freedom (Vermilyea et al., 1996) suggests that the ruthenium-rich particles in Figure 1c,d for Freedom Plus were originally associated with subgrain regions that coalesced to form a single grain as a result of the simulated porcelain-firing heat treatment.

The Ru-rich particles were also found in the Pd–Ga alloy, Legacy, where the AFM image for a typical microstructural area in Figure 2a shows these rod-shaped particles again with a bright appearance in the topographic image. In the Volta potential map (b), the Ru-rich particles now have almost the same potential as the Pd solid solution matrix, compared to the much more evident potential difference in Figure 1b. Three white marker lines were inserted in Figure 2b to show the position of the now much less prominent scratch and facilitate locating the two nearby ruthenium-rich particles that were evident in the upper portion of Figure 2a. The elongated ruthenium-rich particle in Figure 2a is located adjacent to the right marker bar in Figure 2b. The other group of less bright Ru-rich particles located at the right of centre in Figure 2a are also difficult to distinguish from the Pd solid solution matrix in Figure 2b. This group of particles can be located in Figure 2b from measurement of their position in Figure 2a.

Note in the legend information that the Volta potential sensitivity of 50 mV is twice as great in Figure 2b, compared to Figure 1b where the Volta potential sensitivity is 100 mV. This different result for the Legacy Pd–Ga alloy is attributed to its higher palladium content, yielding a more noble Pd solid solution matrix, compared to the Pd solid solution matrix for the Pd–Cu–Ga Freedom Plus alloy. The greater uniformity of the Volta potential in the microstructure of Legacy contributes to lower resolution of the image in Figure 2b, compared to Figure 1b for Freedom Plus.

Surrounding these Ru-rich particles in the Volta potential maps of Figures 1b and 2b are dark-appearing areas with much lower Volta potential relative to other areas of the Pd solid solution matrix. However, no difference in composition between these dark areas surrounding the Ru-rich particles and the Pd solid solution matrix could be discriminated at the level of accuracy available with EDS analyses. Other precipitates and a fine grain size of about 10–15 μm, which are evident for Legacy from the secondary electron (c) and backscattered electron (d) SEM images, were reported in previous studies (Brantley et al., 1993; Carr & Brantley, 1991). The precipitates other than the Ru-rich particles do not show a noticeable difference in Volta potential compared with the Pd solid solution matrix in this alloy.

It can also be seen in Figures 1 and 2 that some surface scratches, which are not evident in the SEM secondary electron images, have been resolved in the corresponding AFM topographic images. The much higher resolution of the AFM topographic images, compared to the SEM images, is an advantage of the SKPFM/AFM analytical technique, along with the simultaneous acquisition of the localized Volta potential map. The surface scratches on the microstructures do not necessarily have lower Volta potential than the matrix. In Figure 1a, the largest scratch exhibits higher Volta potential in the middle than at the side edges. This specimen had been carefully polished and cleaned before observation, and the reason for the Volta potential difference is unknown. At the top of Figure 1a–d, the pore may be a site for localized corrosion, based on the large difference in Volta potential (b) inside and around this flaw.

3.2 | Insights from SKPFM/AFM analyses

While the in vitro corrosion behaviour of high-Pd alloys has been previously investigated by the combination of linear polarization (Sun et al., 2002a) and electrochemical impedance spectroscopy (Sun et al., 2002b, 2002c), information about the contributions
of specific microstructural phases to the corrosion processes could not be provided by these two analytical techniques. The use of SKPFM/AFM has provided new insights into the roles of microstructural phases. The Ru-rich phase found in the high-Pd alloys, which arises from the use of Ru by dental alloy manufacturers as a grain-refining element (Brantley et al., 1993; Carr & Brantley,
particles in Figures 1 and 2 and the surrounding Pd solid solution represents an average of the compositions of these small precipitate interaction volume for the incident electron beam (Goldstein et al., 1991), has been shown for the first time in this investigation to be more noble than the Pd solid solution matrix for the Pd–Cu–Ga alloys Freedom Plus (78Pd–8Cu–5Ga–6In–2Au–Ru) and Liberty (76Pd–10Cu–5.5Ga–6Sn–2Au–Ru). However, the difference in nobility for the Ru-rich particles and the Pd solid solution matrix was much less evident for the Pd–Ga alloy Legacy, (85Pd–10Ga–1n–2Au–1Ag–Ru), whose composition has higher nobility than Freedom Plus from the increased Pd content.

When the half-cell potentials for equilibria between Pd$^{2+}$ ions and solid Pd and between Ru$^{2+}$ ions and solid Ru, with respect to the standard hydrogen electrode, are compared, Pd is more noble than Ru (CRC Handbook of Chemistry and Physics). However, the incorporation of alloying elements lowers the nobility of Pd in the Pd solid solution matrix to less than that of Ru for these high-Pd alloys.

Transmission electron microscopic EDS examination of high-Pd alloys (Guo et al., 2003), which uses a much smaller analysis area than SEM/EDS, suggests that this Ru-rich phase may be nearly pure ruthenium, but further research is necessary to establish the composition of these particles unambiguously. Considering the material interaction volume for the incident electron beam (Goldstein et al., 1981), the SEM/EDS result of approximately 75% Ru composition represents an average of the compositions of these small precipitate particles in Figures 1 and 2 and the surrounding Pd solid solution matrix.

The SKPFM/AFM observations suggest that the Ru-rich particles in the microstructure can potentially cause localized galvanic corrosion in Pd–Cu–Ga alloys, leading to selective attack of less noble phases, notably the Pd solid solution matrix. This localized attack of the Pd solid solution matrix would occur to a lower extent in Pd–Ga alloys where there appears to be much less nobility difference with the Ru-rich particles. If the resulting slow Pd ion release in vivo is sufficient, biocompatibility problems may occur for some patients with metal-ceramic prostheses fabricated from high-Pd alloys. It should be noted that reports of palladium allergy in dental patients have been associated with high-Pd alloys, although compositional details were absent (Cai, Chu, Bradway, Papazoglou, & Brantley, 1995), and this phenomenon has been attributed to the electrochemical character of these alloys (Berzins, Kawashima, Graves, & Sarkar, 2000).

Since the corrosion potentials of the Pd solid solution and other secondary precipitates are less than that of the Ru-rich particles in the Freedom Plus Pd–Cu–Ga alloy, all elements except Ru (including Pd) can in principle be galvanically corroded from this alloy. The Pd–Cu–Ga alloy, Liberty, having a similar composition to Freedom Plus, was found using inductively coupled plasma-mass spectroscopic (ICP/MS) analyses (Tufakci et al., 2002) to release considerably more Pd into an aqueous lactic acid/NaCl corrosion testing medium over an approximately one-month period than the Cu-free Legacy alloy that has a higher Pd content, which would be expected from the present results. Both cast alloys in this ICP/MS study had received the simulated porcelain-firing heat treatment before immersion into the corrosion testing medium, in the same manner as for the high-Pd alloys in the present SKPFM/AFM study. This much lower release of Pd ions from the Legacy alloy into the corrosion testing medium than the Liberty alloy is consistent with the hypothesized role of the Ru-rich particles causing much more localized galvanic corrosion of the Pd solid solution matrix in Pd–Cu–Ga alloys compared to Pd–Ga alloys.

Palladium ions released from the high-Pd alloys would presumably be the cause of palladium allergy for patients, since uncorroded Pd (in the solid solution matrix) on the alloy surface seems unlikely to cause an allergic reaction. Pure Pd has been previously reported to be nontoxic from local and systemic toxicity evaluations (Bessing & Kallus, 1987; Murdoch & Pepys, 1986). The reported contact hypersensitivity to palladium (Camarasa, Burrows, Mengé, Wilkinson, & Shaw, 1991; Todd & Burrows, 1992) may be caused by corroded Pd ions, but it should be noted that such case reports of Pd allergy lack information about the specific dental alloys found to be problematic; other corroded ions from the dental alloy could potentially be the source of allergic reaction. Nevertheless, concerns have been expressed in the dental literature about the clinical use of dental alloys containing Pd (Wataha & Hanks, 1996). From the present study, it is evident that manufacturers should not incorporate more Ru in high-Pd alloys than needed for grain refinement. However, because information about alloy formulation is proprietary with the manufacturers, details about optimum Ru content and Ru–Pd particle sizes used in empirical alloy development are not available.

While much information is available on the microstructural phases in the high-Pd alloys (Brantley et al., 1993, 1995, 1996; Vermilyea et al., 1996), precise compositions of the individual phases are unknown. At the level of resolution in Figure 2b, the other microstructural phases than the Ru-rich particles in the Legacy Pd–Cu high-Pd alloy show minimal observable differences in Volta potential compared with the Pd solid solution matrix. The present SKPFM results in Figure 2b indicate that the difference in corrosion potential among the other microstructural phases than the Ru-rich particles in the Legacy high-Pd alloy should not be more than 30 mV, the approximate resolution limit of the SKPFM technique (Schmutz & Frankel, 1998a, 1998b).

In closing, it should be noted that this initial use of the SKPFM analytical technique as a sensor has provided only descriptive information and not quantitative details about the relative corrosion tendencies of different microstructural phases in representative Pd–Cu–Ga and Pd–Ga high-Pd alloys. Greater resolution of the Volta potential differences with quantitative data is needed to assess better the relative corrosion tendencies of the other microstructural phases compared to the Pd solid solution matrix. Nonetheless, the greater nobility of the Ru-rich phase compared to the other microstructural constituents in the Pd–Cu–Ga alloys is evident from this investigation. The potential for this phase being a locus for galvanic corrosion of the Pd solid solution matrix indicates that manufacturers of Pd–Cu–Ga alloys should use the minimal amount of Ru that will provide the desired grain refinement of the cast alloy. A similar approach would also be prudent
for the manufacture of Pd–Ga alloys and further reduce the level of Pd ion release.

4 | CONCLUSIONS

High resolution, good accuracy and experimental convenience enable SKPFM/AFM to be an excellent sensor method for evaluating the relative corrosion tendencies of different phases in alloys. For the high-Pd dental alloys, manufacturer incorporation of ruthenium for grain refinement results in a Ru-rich microstructural phase that shows higher nobility than the Pd solid solution matrix in the representative Pd–Cu–Ga alloys examined. These Ru-rich particles may be the locus of localized galvanic corrosion in Pd–Cu–Ga alloys, leading to the release of palladium ions and potential biocompatibility concerns for some patients. A similar substantial difference in Volta potential was not observed for the Ru-rich particles and the Pd solid solution matrix in the representative Pd–Ga alloy, indicating that these particles would cause much less localized galvanic corrosion and release of Pd ions, which is supported by a previous ICP/MS study investigating ion release from high-Pd alloys into a corrosion testing medium. Future research should focus on obtaining higher resolution images and quantitative data with the SKPFM/AFM technique to assess the localized potential differences among microstructural phases in high-Pd alloys. Manufacturer use of the minimal Ru content needed for grain refinement is recommended.

ACKNOWLEDGEMENTS

The authors are grateful to Professor Gerald S. Frankel, Department of Materials Science and Engineering and Director of the Fontana Corrosion Center, for providing laboratory facilities to perform the SKPFM/AFM analyses and for critical comments on the manuscript. We thank the NIDCR for financial support of this study through Grant DE10147.

ORCID

William A. Brantley https://orcid.org/0000-0002-0932-5683
Reza H. Heshmati https://orcid.org/0000-0003-2380-686X
William M. Johnston https://orcid.org/0000-0002-4977-6569

REFERENCES

Berrizgs, D. W., Kawashima, I., Graves, R., & Sarkar, N. K. (2000). Electrochemical characteristics of high-Pd alloys in relation to Pd allergy. Dental Materials, 16, 266–273. https://doi.org/10.1016/S0109-5641(00)00016-6
Bessing, C., & Kallus, T. (1987). Evaluation of tissue response to dental alloys by subcutaneous implantation. Acta Odontologica Scandinavica, 45, 247–255. https://doi.org/10.3109/00016358709097537
Brantley, W. A., Cai, Z., Carr, A. B., & Mitchell, J. C. (1993). Metallurgical structures of as-cast and heat-treated high-palladium dental alloys. Cells and Materials, 3, 103–114.
Brantley, W. A., Cai, Z., Foreman, D. W., Mitchell, J. C., Papazoglou, E., & Carr, A. B. (1995). X-ray diffraction studies of as-cast high-palladium alloys. Dental Materials, 11, 154–160. https://doi.org/10.1016/0109-5641(95)80011-5
Brantley, W. A., Cai, Z., Papazoglou, E., Mitchell, J. C., Kerber, S. J., Mann, G. P., & Barr, T. L. (1996). X-ray diffraction studies of oxidized high-palladium alloys. Dental Materials, 12, 333–341. https://doi.org/10.1016/S0109-5641(96)80043-1
Brantley, W. A., & Laub, L. W. (2016). Metal selection. In S. F. Rosenstiel, M. F. Land & J. Fujimoto (Eds.), Contemporary fixed prosthodontics (5th ed., pp. 529–541). St. Louis: Mosby/Elsevier.
Brantley, W. A., Wu, Q., Cai, Z., Vermilyea, S. G., Mitchell, J. C., & Comerford, M. C. (1999). Effects of casting conditions and annealing on microstructures and Vickers hardness of dendritic Pd-Cu-Ga dental alloys. Cells and Materials, 9, 83–92.
Cai, Z., Chu, X., Bradway, S. D., Papazoglou, E., & Brantley, W. A. (1995). On the biocompatibility of high-palladium dental alloys. Cells and Materials, 5, 357–368.
Camarasa, J. G., Burrows, D., Menné, T., Wilkinson, J. D., & Shaw, S. (1991). Palladium contact sensitivity. Contact Dermatitis, 24, 370–371. https://doi.org/10.1111/j.1600-0536.1991.tb01755.x
Carr, A. B., & Brantley, W. A. (1991). New high-palladium casting alloys: Part 1. Overview and initial studies. International Journal of Prosthodontics, 4, 265–275.
Goldstein, J. I., Newbury, D. E., Echnik, P., Joy, D. C., Fiori, C., & Lifshin, E. (1981). Scanning electron microscopy and X-ray microanalysis. New York, NY: Plenum Press.
Guillaumin, V., Schmutz, P., & Frankel, G. S. (2001). Characterization of corrosion interfaces by the scanning Kelvin probe force microscopy technique. Journal of the Electrochemical Society, 148, B163–B173. https://doi.org/10.1149/1.1359199
Guo, W. H., Brantley, W. A., Clark, W. A. T., Xiao, J. Z., & Papazoglou, E. (2003). Transmission electron microscopic studies of deformed high-palladium dental alloys. Dental Materials, 19, 334–340. https://doi.org/10.1016/S0109-5641(02)00635-3
Morch, R. D., & Pepys, J. (1986). Enhancement of antibody production by mercury and platinum metal halide salts. International Archives of Allergy and Applied Immunology, 80, 405–411. https://doi.org/10.1159/000234089
Sarkar, N. K., Berzins, D. W., & Prasad, A. (2000). Deallloying and electroformation in high-Pd dental alloys. Dental Materials, 16, 374–379. https://doi.org/10.1016/S0109-5641(00)00454-2
Schmutz, P., & Frankel, G. S. (1998a). Characterization of AA2024-T3 by scanning Kelvin probe force microscopy. Journal of the Electrochemical Society, 145, 2285–2295. https://doi.org/10.1149/1.1838633
Schmutz, P., & Frankel, G. S. (1998b). Corrosion study of AA2024-T3 by scanning Kelvin probe force microscopy and in situ atomic force microscopy scratching. Journal of the Electrochemical Society, 145, 2295–2306. https://doi.org/10.1149/1.1838634
Schmutz, P., & Frankel, G. S. (1999). Influence of dichromate ions of pure aluminum and AA2024-T3 in NaCl solution studied by AFM scratching. Journal of the Electrochemical Society, 146, 4461–4472. https://doi.org/10.1149/1.1392659
Sun, D., Monaghan, P., Brantley, W. A., & Johnston, W. M. (2002a). Potentiodynamic polarization study of the in vitro corrosion behavior of high-palladium alloys in five media. Journal of Prosthetic Dentistry, 87, 86–93. https://doi.org/10.1067/mpr.2002.121239
Sun, D., Monaghan, P., Brantley, W. A., & Johnston, W. M. (2002b). Electrochemical impedance spectroscopy study of high-palladium dental alloys. Part I. Behavior at open-circuit potential. Journal of Materials Science: Materials in Medicine, 13, 435–442.
Sun, D., Monaghan, P., Brantley, W. A., & Johnston, W. M. (2002c). Electrochemical impedance spectroscopy study of high-palladium dental alloys. Part II. Behavior at elevated potentials. Journal of Materials Science: Materials in Medicine, 13, 443–448. https://doi.org/10.1023/A:1014719513624
Todd, D. J., & Burrows, D. (1992). Patch testing with pure palladium metal in patients with sensitivity to palladium chloride. Contact Dermatitis, 26, 327–331. https://doi.org/10.1111/j.1600-0536.1992.tb00128.x
Tufekçi, E., Mitchell, J. C., Olesik, J. W., Brantley, W. A., Papazoglou, E., & Monaghan, P. (2002). Inductively coupled plasma-mass spectroscopy measurements of elemental release from 2 high-palladium dental casting alloys into a corrosion testing medium. *Journal of Prosthetic Dentistry, 87*, 80–85. https://doi.org/10.1067/mpd.2002.121238

Vermilyea, S. G., Cai, Z., Brantley, W. A., & Mitchell, J. C. (1996). Metallurgical structure and microhardness of four new palladium-based alloys. *Journal of Prosthodontics, 5*, 288–294. https://doi.org/10.1111/j.1532-849X.1996.tb00513.x

Wataha, J. C., & Hanks, C. T. (1996). Biological effects of palladium and risk of using palladium in dental casting alloys. *Journal of Oral Rehabilitation, 23*, 309–320. https://doi.org/10.1111/j.1365-2842.1996.tb00858.x

Yee, S., Oriani, R. A., & Stratmann, M. (1991). Application of a Kelvin microprobe to the corrosion of metals in humid atmospheres. *Journal of the Electrochemical Society, 138*, 55–61. https://doi.org/10.1149/1.2085578

---

**How to cite this article:** Sun D, Brantley WA, Heshmati RH, Johnston WM. Novel sensor to investigate microstructural contributions to corrosion of high-palladium dental alloys. *Med Devices Sens*. 2020;3:e10060. [https://doi.org/10.1002/mds3.10060](https://doi.org/10.1002/mds3.10060)