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Heat treatment effects on electrochemical corrosion parameters of high-Pd alloys

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Abstract This research determined the effect oxidation, as that occurs during porcelain firing, has upon the corrosion parameters of Pd-based ceramic alloys and how it may relate to Pd allergy. The 20 h open circuit potential (OCP), 20 h corrosion rate (Icorr), and anodic polarization (E–i) curves of 11 commercial Pd alloys were measured in a phosphate buffered saline solution. The alloys were divided into the following four groups based upon composition: PdGa(Ag), PdCu, PdAg, and AuPd and tested in both as-cast and oxidized conditions. In both the as-cast and oxidized conditions, the OCP of Ag-containing Pd alloys is significantly lower than non Ag-containing high-Pd alloys. The OCP of all alloys increased after oxidation. With regard to corrosion rate, the Ag-containing alloys showed a decrease in Icorr with oxidation. In contrast, three of the four non Ag-containing high-Pd (≥74 wt%) alloys exhibited a higher Icorr. A comparison of the anodic polarization curves showed only the alloys containing larger amounts (≥16 wt%) of Ag displayed a notable difference between as-cast and oxidized states. Oxidation as required during porcelain-fused-to-metal device preparation alters the electrochemical characteristics of the alloys studied. This alteration may be of importance with regard to their potential for Pd allergy.

Introduction

Corrosion characteristic of high-Pd alloys may provide an answer to the question why amongst all palladium-containing alloys, the PdCu-based alloys are associated with high risk of Pd allergy [1]. The corrosion of high-Pd alloys in their as-cast condition has been the subject of a number of studies [2–4]. These alloys, however, are used in the fabrication of porcelain-fused-to-metal restorations. Thus, they are subject to high temperatures before and during porcelain firing. For many of these alloys, such heat treatment alters their microstructure in a variety of ways [5–7], including homogenization and phase transformation. Heat treatment is also associated with oxidation [8]. With the exception of Au and possibly Ir, all constituents of these alloys are prone to internal and external oxidation. The nature of various oxides formed, their morphology, and growth both internally and externally are dependent on the composition of the respective alloys and their treatment conditions [9–11].

Several studies on the corrosion of oxidized high-Pd alloys have been reported in the past [12–16]. Syverud et al. [12] studied the effect of heat treatment on the corrosion of two high-Pd alloys. One of the alloys was a PdCu-based alloy, Option (79 wt% Pd, 10% Cu, 9% Ga, 2% Au) and the other was a PdGa-based alloy, IS85 (82% Pd, 6% Ga, 3.5% Sn, 3.5% In, 2.5% Ag, 2.5% Au). This study indicated that heat treatment enhances ion leaching (corrosion) from both alloys in a NaCl/lactic acid solution,

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and the total amount of ions leached, including Pd, was significantly higher in the oxidized PdCu alloy. These observations are in agreement with that reported earlier on 14 oxidized high-Pd alloys [13] in that ion leaching from those alloys was found to depend largely on alloy composition. Moreover, it was observed in this study that the PdCu-based alloys were associated with the highest Pd release, and the corrosion resistance of these alloys was markedly improved if they contained high amounts of Ag (20–38%) or Au (33–35%). The corrosion data obtained from potentiodynamic polarization testing of high-Pd alloys, however, are not as definitive and conclusive as the ion release results. For instance, Mezger et al. [14] studied three PdCuGa-based alloys in as-cast and oxidized condition in three different electrolytes. Their data showed polarization resistance increased or decreased depending upon alloy and electrolyte, with no general trend associated with oxidation. Cai et al. [15] examined three PdCuGa and two PdGa-based alloys in as-cast and heat-treated condition in two different electrolytes. They found no significant change in open circuit potential (OCP) at 10 h in comparing the same alloy under both conditions. Spartan Plus and Liberty (PdCuGa) were found to have significantly increased corrosion current densities with oxidation when tested in 0.09% NaCl, whereas Protocol (PdGaAg) had a decreased Icorr with oxidation in Fusayama solution; all other alloy and electrolyte testing combinations showed no significant difference in as-cast versus heat-treated conditions. Similarly, Sun et al. [16] found few significant differences in as-received versus heat-treated 24 h OCP when they examined two PdCuGa and 1 PdGa-based alloys in three electrolytes. They also found polarization resistance was not affected by heat-treatment.

The present study is a continuation of previous work examining the mechanism of corrosion of high-Pd alloys with a wide range of composition. The aim was to determine what effect heat treatment (oxidation) exerts on the electrochemical characteristics of high-Pd alloys. The results have been discussed in the context of studies mentioned above and in light of the mechanism of dealloying and electroformation associated with the corrosion of high-Pd alloys [3, 4].

Materials and methods

The compositions of the alloys used in this study are shown in Table 1. They consist of eleven commercial alloys based upon the following systems: PdGa (with and without Ag), PdCu, PdAg, and AuPd. All alloys were tested in both their as-cast and oxidized condition. Electrochemical data from these alloys in the as-cast condition have been presented previously [3] and is included in this study for comparison between as-cast and oxidized states. Oxidized specimens (n = 4 or 5 per alloy) were separate samples not previously tested electrochemically (as-cast). Oxidation of the alloys was achieved by first degassing and/or oxidizing using a computerized porcelain furnace (Model 120, Jeneric/Pentron, Inc., Wallingford, CT, USA) per manufacturer's instructions. Next, each alloy underwent a simulated

Table 1 Composition of commercial alloys studied

Materials	Composition (wt%)[a]								Manufacturer[b]
	Pd	Au	Ag	Cu	Ga	In	Sn	Zn	
	Group I. PdGa-based								
Argipal	79.9	–	–	–	4.1	–	16.0	–	Argen
Legacy	85.0	2.0	<1	–	11.0	1.0	–	–	Jelenko
LTA	80.0	–	5.0	–	6.0	6.0	2.0	1.0	Pentron
Zenon Plus	76.0	1.0	9.0	–	6.0	8.0	–	–	Pentron
Protocol	76.0	6.0	6.0	–	6.0	6.0	–	–	Williams
	Group II. PdCu-based								
Liberty	76.0	2.0	–	10.0	5.5	–	6.5	–	Jelenko
Correct Fit	79.0	–	–	10.0	5.0	6.0	–	–	Pentron
Athenium	74.0	–	–	14.5	1.5	5.0	5.0	–	Williams
	Group III. PdAg-based								
Rx 91	53.0	–	37.0	–	–	1.0	9.0	–	Pentron
	Group IV. AuPd-based								
Olympia	39.0	51.0	–	–	1.5	8.5	–	–	Jelenko
Cameo	27.0	52.5	16.0	–	–	2.5	2.0	–	Jelenko

[a] Composition source: literature or manufacturer

[b] Commercial alloys may also contain Re, Ru, or Ir in small quantities

porcelain firing schedule consisting of two steps. First, each specimen was fired from 600 °C to 925 °C at 55 °C/min under vacuum and held at the peak temperature for 4 min, after which it was allowed to cool to room temperature. For the second step, each specimen was again fired from 600 °C to 925 °C, but this time in air, and held for only 1 min before cooling to room temperature.

The specimen preparation consisted of mounting in epoxy and grinding the surface of the alloys with 600 grit SiC paper. As noted previously, oxidation of these alloys leads to the formation of an outer oxidation layer followed by an internally oxidized layer progressing to the non-oxidized bulk alloy core. While the outer layer consists solely of oxides, the subsequent internal oxidation products are dispersed in the alloy matrix. Grinding was limited to the removal of the outer layer, exposing the internally oxidized layer. This was accomplished by examining each specimen after every pass on the grinding paper under an optical microscope at 400×. Grinding was discontinued when the external oxidized scale was no longer visible. Such a surface is a fair representation of the final surface produced in dental laboratories during the fabrication of porcelain-fused-to-metal restorations. After grinding, the specimens were ultrasonically cleaned for 5 min in distilled water and placed in an aerated phosphate buffered saline (PBS) solution (pH = 7.4) at 20 °C for electrochemical testing. The PBS (#P-4417, Sigma Chemical Company, St. Louis, MO, USA) is of the following concentration: 137 mM NaCl, 2.7 mM KCl, and 10 mM $(PO_4)^{-3}$. It differs from the Fusayama and MTZ synthetic salivas commonly used in dental electrochemical studies by its higher Cl^- and $(PO_4)^{-3}$ contents (6× and 2× for Fusayama and 7× and ~3× for MTZ, respectively) and absence of urea (Fusayama) and lactic acid (MTZ).

Using a computer-driven potentiostat (PC3, Gamry Instruments, Inc., Warminster, PA, USA or a Model 263A, EG&G Instruments, Princeton, NJ, USA), electrochemical data was collected in the following order. For 20 h, the open circuit potential was monitored. Next, a polarization resistance (Rp) test, where the current was measured while the potential of the alloy was scanned at 0.01 mV/s from –15 mV to +25 mV (vs. OCP), was performed. Lastly, a second potentiodynamic test was conducted. It involved scanning the specimen at 0.5 mV/s from ±300 mV (vs. OCP) to obtain an E–i curve. The latter two tests are used in conjunction to determine the corrosion rate or Icorr of a particular specimen. The OCP and Icorr data was analyzed with the Kruskal–Wallis test followed by the Mann-Whitney test to determine if a significant ($p < 0.05$) difference existed between as-cast and oxidized conditions of each alloy and among oxidized specimens of all alloys.

Results

Tables 2 and 3 display the OCP and Icorr values for the as-cast and oxidized alloys, respectively. These tables also include the change, Δ, in each parameter due to oxidation and the statistical significance of the respective differences. These data are further displayed in graphical forms in Figs. 1 and 2. On the basis of the previous observation that high-Pd alloys that contain Ag exhibit electrochemical characteristics distinguishable from those that are Ag-free [3, 4], the 11 alloys are divided into two broad groups identified as Ag-containing and Ag-free in Figs. 1 and 2.

The results (Table 2 and Fig. 1) show that oxidation led to an increase in the OCP values of all alloys. The increase varied between 12 mV and 109 mV with no apparent link

Table 2 OCP values of as-cast and oxidized commercial high-Pd alloys

Alloy group	Material	OCP (mV) at 20 h			Statistical Significance[a] ($p < 0.05$)
		As-cast	Oxidized	Δ(Oxidized – as-cast)	
I. PdGa (Ag)	Argipal (Ag-free)	216.8 (16.8)	269.0 (7.1)	+52	✓
	Legacy	188.6 (21.2)	253.8 (5.1)	+65	✓
	LTA	130.7 (15.4)	230.2 (26.2)	+100	✓
	Zenon Plus	148.0 (17.8)	241.0 (7.9)	+93	✓
	Protocol	189.4 (19.5)	201.0 (21.2)	+12	
II. PdCu	Liberty	213.8 (11.9)	271.5 (7.9)	+58	✓
	Correct Fit	240.4 (17.8)	275.0 (6.7)	+35	✓
	Athenium	206.5 (27.2)	281.6 (41.4)	+75	✓
III. PdAg	Rx 91	70.8 (22.7)	126.4 (20.3)	+56	✓
IV. AuPd	Olympia	123.4 (41.5)	229.0 (22.9)	+106	✓
	Cameo	61.2 (5.6)	169.8 (66.1)	+109	✓

[a] (✓) indicates a statistically significant difference exists (Mann–Whitney test; $p < 0.05$) for the given alloy between the as-cast and thermally oxidized conditions

Table 3 Icorr values of as-cast and oxidized commercial high-Pd alloys

Alloy Group	Material	Icorr (nA/cm^2)			Statistical Significance[a] ($p < 0.05$)
		As-cast	Oxidized	Δ (Oxidized – as-cast)	
I. PdGa (Ag)	Argipal (Ag-free)	6.3 (1.5)	9.8 (3.3)	+3.4	
	Legacy	20.7 (24.4)	6.7 (0.5)	–14.1	
	LTA	29.3 (30.5)	6.4 (1.4)	–23.0	✓
	Zenon Plus	21.1 (15.5)	4.6 (0.6)	–16.6	✓
	Protocol	7.6 (2.4)	4.8 (1.2)	–2.8	✓
II. PdCu	Liberty	7.0 (1.6)	11.5 (6.7)	+4.4	
	Correct Fit	19.4 (13.0)	10.9 (2.6)	–8.5	
	Athenium	8.2 (3.7)	13.5 (3.2)	+5.3	
III. PdAg	Rx 91	5.5 (0.7)	2.5 (0.6)	–3.0	✓
IV. AuPd	Olympia	15.3 (11.8)	4.6 (1.0)	–10.7	✓
	Cameo	5.3 (1.9)	5.3 (4.1)	0.0	

[a] (✓) indicates a statistically significant difference exists (Mann–Whitney test; $p < 0.05$) for the given alloy between the as-cast and thermally oxidized conditions

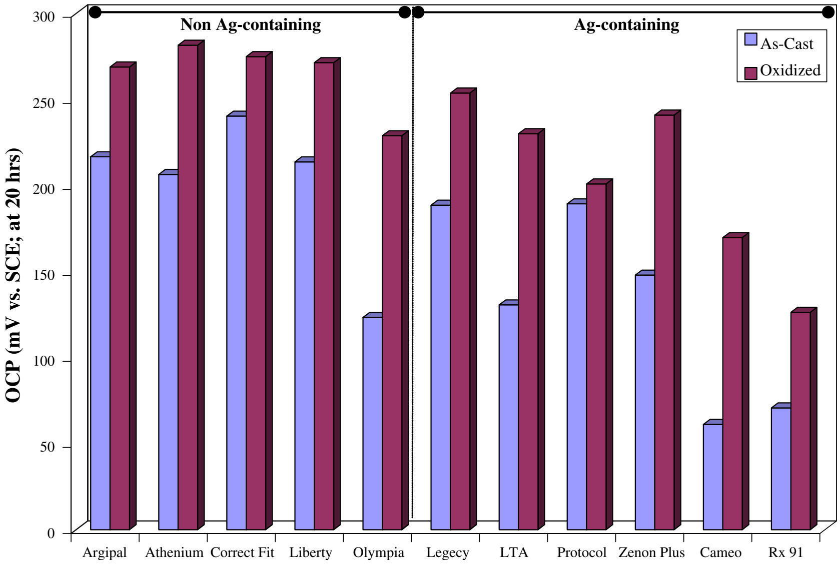


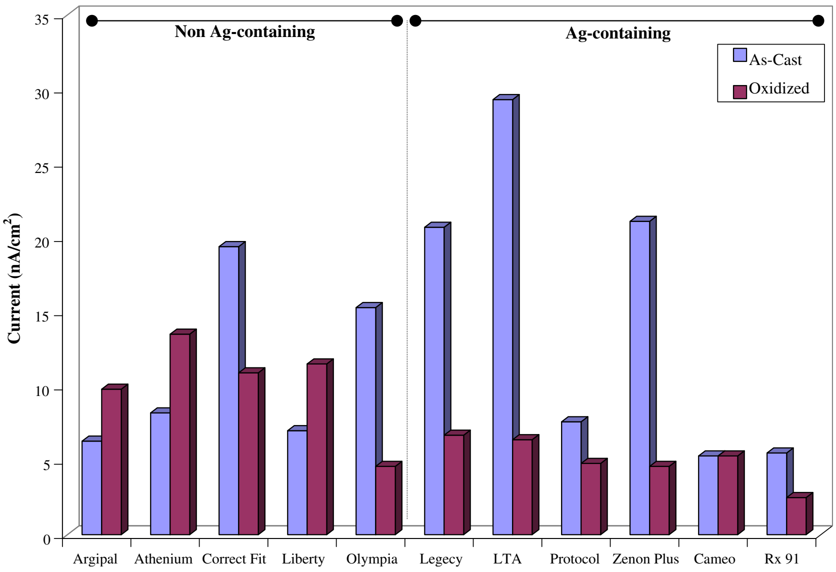
Fig. 1 Comparison of OCP of as-cast and oxidized Pd-alloys

between composition and the degree of excursion in OCP. The difference in OCP between as-cast and oxidized alloys was significant ($p < 0.05$) for all alloys but Protocol. A relatively stronger significance ($p < 0.01$) was noted for Cameo, Legacy, Liberty, LTA, and Olympia. These four alloys encompass both the Ag-free and Ag-containing alloys.

The data in Table 3 and Fig. 2 indicate that oxidation led to an increase in Icorr for three of the alloys, Argipal, Athenium, and Liberty, though this increase was not statistically significant ($p > 0.05$). For seven of the remaining eight alloys, Icorr decreased with oxidation with this being significant for five of the seven alloys. Cameo did not show a change in mean Icorr. In contrast to the absence of any link between oxidation induced change in OCP and the composition of various alloys noted above, a strong association between composition and the change in Icorr appeared to exist. For instance, a significant decrease in Icorr was found in all Ag-containing (≥5 wt% Ag) high-Pd alloys. On the other hand, with the five Ag-free alloys, Icorr was either increased or decreased with oxidation. However, this change was not statistically significant in any of these five alloys with the exception of Olympia.

Some significant ($p < 0.05$) differences between all oxidized alloys with respect to their OCP and Icorr were found (individual differences not presented). A similar analysis for the as-cast alloys has been reported before [3]. As observed in the as-cast alloys, there appears to be a distinction between oxidized Ag-containing alloys and Ag-free alloys with respect to their OCP values (Table 2). The

Fig. 2 Comparison of Icorr of as-cast and oxidized Pd-alloys



five Ag-containing alloys (≥5 wt% Ag) exhibited significantly ($p < 0.001$) lower OCP values (<245 mV) compared to Ag-free Argipal and the three PdCu-based alloys. These four alloys possessed OCP values above 268 mV. For the as-cast alloys [3], 200 mV was the value of demarcation in that the OCP values of the Ag-containing alloys were lower than 200 mV. With regard to the oxidized alloys, the Ag-containing alloys had a significantly lower ($p < 0.001$) Icorr compared to the Ag-containing alloys when grouped together (all alloys in Table 1) or just considering the high-Pd alloys (Pd > 74 wt%). This was not observed in the as-cast alloys [3].

The polarization, E–i, profiles of most of the oxidized alloys were similar to that of their as-cast counterparts reported previously [3, 4]. The exceptions were Cameo and Rx 91. The E–i curves of Rx 91 in the as-cast and oxidized condition are shown in Fig. 3 to illustrate their general behavior. In the as-cast state, the anodic current increases slowly up to an inflection at about 150 mV, and then increases at a relatively faster rate. In the oxidized state, the current increases rapidly, reaching a peak (~30 nA/cm^2) at about 80 mV, decreases immediately, and then increases again. The other Ag-containing alloys also exhibited a slight ripple or inflection in current density. The appearance of such peaks or inflections in current during anodic polarization has been observed in many Ag-containing alloys and is attributed to the chloridation of Ag [3, 17, 18].

Similar to the E–i curves of the as-cast specimens [3], the anodic polarization profile of the oxidized PdCu-based alloys and Argipal appeared slightly different from the rest of the oxidized alloys. To illustrate, Fig. 4 displays the E–i curves of Argipal and LTA. The current of the former alloy increases gradually in an upward sweep upon polarization above the corrosion potential. The Ag-containing (≥5 wt%) alloys and Olympia have an inflection in the upward sweep,

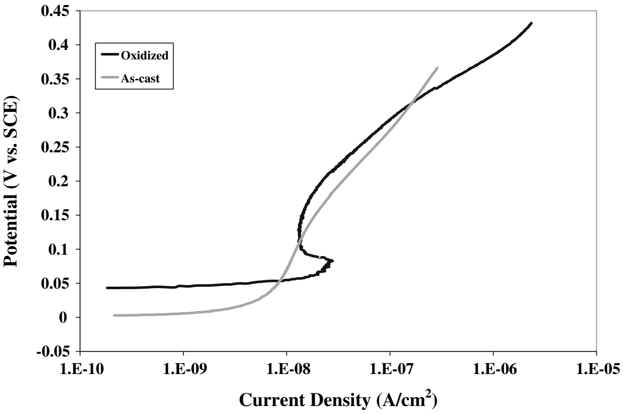


Fig. 3 Anodic potentiodynamic polarization curves of as-cast and oxidized Rx 91

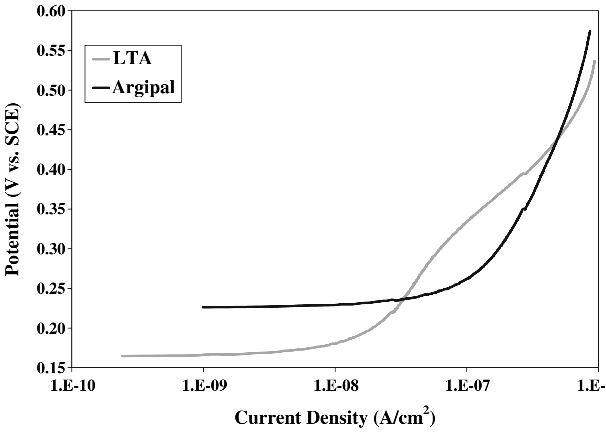


Fig. 4 Anodic potentiodynamic polarization curves of oxidized LTA and argipal

resulting in a larger slope within 150 mV above the corrosion potential. As pointed out above, Cameo and Rx 91, when oxidized, have more intense reactions in this area. The E–i curve of the oxidized Legacy, which contains 1 wt% Ag, appears to be a balance of the two types of curves (Argipal and LTA).

Discussion

It is known that heat treatment alters the microstructure of high-Pd alloys [5, 6, 10, 11]. The oxidation associated with heat treatment leads to a lowering of environmental reactivity of surface and sub-surface base metal alloy components [19]. Since corrosion is sensitive to structure and chemical potential of a material, it stands to reason that the corrosion behavior of the heat treated high-Pd alloys may be different from their as-cast counterparts. The results presented above are in accord with this rationale. Alteration in corrosion characteristics of the alloys studied is reflected in their respective electrochemical parameters (Tables 2 and 3 and Figs. 1 and 2). In most cases, the changes are significant, in a few cases they are not. Specifically, the following changes in high-Pd alloys are notable: (1) an increase in OCP in all alloys, (2) a decrease in Icorr in Ag-containing alloys, and (3) an increase in Icorr in three of the four Ag-free alloys.

Our results are in general agreement with the phenomenological observations reported previously in which corrosion induced ion release from high-Pd alloys was found to be dependent on their composition and heat treatment [12, 13]. The resistance to ion release from these alloys has been explained partly on the basis of their base metal content, in that, the larger the amount of base metal, greater was the corrosion. However, a direct comparison of the corrosion characteristics of different alloys containing elements that differ in species and concentration is complicated [12].

The mechanism of dealloying and electroformation proposed to explain the corrosion behavior of as-cast high-Pd alloys [4], we believe, resolves this complication and provide a better understanding of the effect of composition and heat treatment on the corrosion of the oxidized alloys. To elaborate, as noted previously, the base metal components of all of these alloys are highly oxidation prone. The oxides formed during heat treatment are soluble in varying degrees in the electrolyte studied. For the PdCu and PdGa groups, oxidation is massive extending internally into pores, interdendritic areas, and grain boundary networks [6, 10, 20]. According to the theory of dealloying, when the heat-treated alloys from these groups are exposed to the electrolyte for a certain time, these oxides dissolve, exposing a Pd-rich surface both externally and internally. The ennoblement of the OCPs of the PdCu and PdGa alloys attaining values in the range of 254 and 282 mV is an indication of Pd enrichment [4].

Severe corrosion associated with the PdCu alloys has been attributed to the dissolution of base metals. Whereas the release of base metal ions is a factor in the overall corrosion process, these ions have not been implicated in "Pd-allergy". Concomitant to the dissolution of base metal oxides, the development of a Pd-rich surface on these alloys is more important as this surface is the source of allergenic Pd ions. Heat treatment certainly increases the potential for increased Pd release by exposing a larger internal surface area to corrosion [12]. It is of interest to note that an increase in corrosion rate, Icorr, with heat treatment has also been noted in the present study.

The Ag-containing alloys will also oxidize during heat treatment leading to the oxidation of respective base metal components. However, for the Ag-containing alloys, on exposure to the electrolyte and dissolution of the oxides, these alloys develop a Ag-rich surface [3, 4, 17, 18]. This Ag-enrichment is supported by the OCP data and E–i curves discussed above. Enrichment with Ag and/or Au, we believe, has the ability to mask Pd from corrosion and thus suppress or eliminate Pd ion release.

With regard to the Icorr data, although the oxidized Ag-containing alloys exhibited a significantly lower Icorr compared to the Ag-free alloys, providing further supposition as to a difference in mechanism of corrosion, it should be noted that all alloys exhibited extremely low Icorr values. For example, the Icorr values of six of the eight alloys in both the as-cast and oxidized states were less than 10 nA/cm^2 which is the same order of magnitude as the scatter observed in electrochemical data measurements. Nonetheless, five of the eleven alloys showed some difference ($p < 0.05$) in Icorr between as-cast and oxidized alloys. Additionally, the degree of scatter in the electrochemical data associated with the two conditions suggests that the oxidation procedure contributed to some homogenization within the alloys. As listed in Table 3, the highest standard deviation among the oxidized alloys was 6.7 nA/cm^2, which is still lower than 5 of the 11 standard deviations of the as-cast alloys. With a less heterogeneous microstructure, one would expect a smaller deviation in measurements such as corrosion rate. Homogenization of Pd alloys during porcelain firing has been reported previously [6].

It should be noted that the microstructures of high-Pd alloys used for porcelain-fused-to-metal restorations are highly complex [21]. Equally complex is their oxidation behavior [6, 8]. The evaluation of the corrosion behavior of such alloys needs a multiphasic approach employing various complementary analytical techniques. The mechanism of corrosion as postulated in this study is based solely on the electrochemical data. Studies are in progress to overcome this limitation.

Conclusion

Oxidation of commercial Pd ceramic alloys led to a slight alteration in their corrosion properties. When compared to as-cast counterparts, oxidation led to the following effects: (1) an average increase of 69 mV in OCP; (2) a decrease in Icorr of all Ag-containing high-Pd alloys; (3) an increase in Icorr for three of the four Ag-free high-Pd alloys (>74 wt%); (4) an intensification of the current peak at 70–90 mV (SCE) in the higher Ag-containing alloys, Rx 91 and Cameo, but no significant alteration in the E–i curve of other alloys. It appears that oxidation results in an enhancement of the electrochemical activity of Ag on the surface of Ag-containing Pd alloys, possibly masking Pd from the oral environment. For PdCu-based alloys, oxidation results in the dissolution of base metal oxides into the electrolyte, resulting in a potentially sensitizing Pd-rich surface.

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