1995

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William A. Brantley
The Ohio State University

Zhuo Cai
The Ohio State University

Qiang Wu
The Ohio State University

Alan B. Carr
The Ohio State University

John C. Mitchell
The Ohio State University

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ROOM TEMPERATURE AGING OF Pd-Cu-Ga DENTAL ALLOYS

William A. Brantley*, Zhuo Cai, Qiang Wu, Alan B. Carr and John C. Mitchell1

College of Dentistry and 1Department of Geological Sciences,
The Ohio State University, 305 West 12th Avenue, Columbus, Ohio 43210

(Received for publication September 27, 1995 and in revised form November 30, 1995)

Abstract

Specimens of three Pd-Cu-Ga dental alloys cast five years ago and subsequently stored at room temperature were reexamined and observed to have lower amounts of the eutectic constituents in the near-surface region than originally present, along with other microstructural changes. This previously unreported room temperature aging behavior of these alloys is attributed to the presence of high-diffusivity paths in the non-equilibrium as-cast eutectic structures and to the essential role of the surface for the vacancy diffusion mechanism. These results may have important clinical significance for the in vivo corrosion resistance and long-term biocompatibility of the Pd-Cu-Ga alloys.

Key Words: Palladium, dental alloy, aging, microstructure, eutectic, scanning electron microscopy, X-ray energy-dispersive spectroscopy, diffusion, electrochemical corrosion, biocompatibility.

Introduction

There has been increasing clinical usage of dental high-palladium alloys containing greater than approximately 75 wt.% palladium since their introduction in the early 1980s (Carr and Brantley, 1991). Because of their excellent mechanical properties and much lower unit metal cost compared to traditional gold-based alloys, the high-palladium alloys have become popular for metal-ceramic restorations, as well as for implant-supported prostheses (Stewart et al., 1992). Recently, castings of three high-palladium alloys based upon the Pd-Cu-Ga system, that had been stored five years at room temperature, were reexamined and found to have undergone substantial near-surface microstructural changes compared to the original as-cast condition (Carr and Brantley, 1991). These unanticipated results are described in this article, and are attributed to the fine-scale and non-equilibrium nature of the eutectic constituents in the as-cast microstructures, along with the essential role of the surface in the associated diffusion processes. This aging behavior may be clinically important for the in vivo corrosion resistance and biocompatibility of the Pd-Cu-Ga alloys.

Materials and Methods

Castings, simulating a coping for a maxillary central incisor, were fabricated from three high-palladium alloys marketed for use with porcelain: Athenium (74Pd-14.5Cu-1.5Ga-5In-5Sn), Spartan (79Pd-10Cu-9Ga-2Au) and Liberty (76Pd-10Cu-5.5Ga-6Sn-2Au), where the amounts of the component elements in the nominal compositions are in weight percent (Carr and Brantley, 1991). Athenium and Spartan are manufactured by Ivoclar North America, Amherst, NY, and Liberty is manufactured by J.F. Jelenko and Co., Armonk, NY. The composition given for Liberty differs from that in our previous publication (Carr and Brantley, 1991) because the indicated amount of tin assumes that ~ 0.5 wt.% ruthenium is present as a grain-refining element (Brantley et al., 1993). Although not listed in the
Table 1. Comparison of compositions for bulk and near-surface regions of aged Athenium determined by EDS analyses. *

<table>
<thead>
<tr>
<th>Region</th>
<th>Pd</th>
<th>Cu</th>
<th>Ga</th>
<th>In</th>
<th>Sn</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>76.7 (0.6)</td>
<td>10.4 (0.7)</td>
<td>1.4 (0.2)</td>
<td>5.5 (0.2)</td>
<td>4.8 (0.8)</td>
<td>1.0 (0.1)</td>
</tr>
<tr>
<td>Near-surface</td>
<td>70.0 (2.4)</td>
<td>11.4 (0.6)</td>
<td>2.3 (0.6)</td>
<td>5.8 (0.9)</td>
<td>6.3 (0.9)</td>
<td>3.7 (2.0)</td>
</tr>
</tbody>
</table>

*Entries are mean value (standard deviation) for a total of six analyses in the bulk region and five analyses in the near-surface region for two different specimens.

Table 2. Summary of Vickers hardness measurements for aged Pd-Cu-Ga alloys. *

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athenium</td>
<td>252 ± 6</td>
</tr>
<tr>
<td>Liberty</td>
<td>326 ± 9</td>
</tr>
<tr>
<td>Spartan</td>
<td>403 ± 20</td>
</tr>
</tbody>
</table>

*Each entry is mean ± standard deviation for measurements on two specimens (N = 20). For the original as-cast specimens, the mean values of pooled Vickers hardness were: Athenium (260), Liberty (330) and Spartan (409) (Carr et al., 1993).

The original high-palladium alloy castings were bench-cooled as recommended by the manufacturers, de-vested, air-abraded, mounted in transparent metallographic resin (Epoxyde, Leco Corp., St. Joseph, MI) and sectioned perpendicular to the sprue base with a low-speed, water-cooled, diamond-coated saw (Vari/Cut VC-50, Leco Corp.). This procedure yielded two mirror-image specimens that were used for study of both the as-cast microstructures (Carr and Brantley, 1991) and the effects of porcelain firing heat treatment (Carr et al., 1993).

After five years (air) storage in a desiccator at room temperature, as-cast specimens were polished through 0.05 μm alumina slurries, etched in aqua regia solutions (Mezger et al., 1988) and examined in the secondary electron imaging mode with a JSM-820 (JEOL Ltd., Tokyo, Japan) scanning electron microscope. X-ray energy-dispersive spectroscopic (EDS) spot analyses were performed with a Link eXL microanalysis system having a PentaFET detector and an ultra-thin window (Oxford Instruments Group, High Wycombe, U.K.). Vickers hardness measurements (1 kg load, 30 seconds dwell time) were obtained for comparison with the original as-cast condition (Carr and Brantley, 1991).

Results

The near-surface microstructure for as-cast Athenium after aging at room temperature for five years is shown in Figure 1. A layer of particles, approximately 5 μm in width, was located adjacent to the surface, followed by a zone substantially denuded of the original near-surface eutectic structure which remained at greater depths. Extension of these particles along grain boundaries at several places is evident in Figure 1. The particles, which were not present in the original as-cast alloy (Carr and Brantley, 1991), have typical dimensions of ~ 0.25 μm (Fig. 2). From the results of EDS spot analyses, summarized in Table 1, the near-surface region is enriched in copper, gallium and tin, compared to the bulk alloy, and the particles are assumed to be oxides, as will be discussed later. Because the ~ 1 μm dimensions of the interaction volume (Goldstein et al., 1988) were much larger than the individual particles, the spot analysis mode was deemed acceptable for near-surface elemental analyses. An increased concentration of ruthenium was also detected in the near-surface region. The residual bulk eutectic structure in this aged Athenium specimen is shown in Figure 3.

The near-surface microstructure of as-cast Liberty, after five years aging at room temperature, also showed dramatic evidence of structural transformation. While considerable bulk eutectic remained (Fig. 4), a near-surface region depleted of this constituent was observed (Fig. 5) in some specimens. The near-surface grain boundaries in Figure 5 are very similar to grain boundaries in Liberty after the porcelain firing cycles (Carr et al., 1993) where the eutectic constituent has largely disappeared. The morphology of the ruthenium-rich phase
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**Figure 1.** Near-surface microstructure for as-cast Athenium after aging at room temperature for five years. The metallographic mounting resin is at the right edge, and the gap is due to polymerization shrinkage. Bar = 10 μm.

**Figure 2.** High-magnification photomicrograph of oxide particles in the subsurface layer for the aged Athenium specimen in Figure 1. Bar = 1 μm.

in the bulk microstructure of this alloy (Brantley et al., 1993) appeared to be disk-shaped (Fig. 6). No subsurface layer of oxide particles similar to that found in Athenium (Fig. 1) was observed for aged Liberty.

After five years aging at room temperature, the dendritic structure of as-cast Spartan specimens (Carr and Brantley, 1991) persisted, as illustrated in Figure 7. However, a photomicrograph of the central interdendritic region of this figure at higher magnification (Fig. 8) suggests that there has been substantial transformation of the eutectic constituent originally located within the bounded areas, which are generally surrounded by needle-shaped Widmanstätten precipitates (Brantley et al., 1993). Two different morphologic forms of the residual eutectic constituent are evident for the more lightly etched specimen shown in Figure 9: regions with white-appearing (topographic contrast) lamellae reminiscent of areas in Figure 7, and lamellar structures in the upper
center and upper left of Figure 9 which are similar in appearance to the eutectic constituents in Athenium (Fig. 3) and Liberty (Fig. 4). Relatively long Widmanstätten precipitates can also be seen to the left of the interdendritic region in the center of Figure 9. The near-surface region (Fig. 10) of aged Spartan contained microstructural constituents very similar to those in Figures 7, 8 and 9. However, Figure 10 shows that there was no well-defined near-surface zone in aged Spartan which was devoid of the eutectic interdendritic constituent, analogous to that for aged Athenium (Fig. 1) and Liberty (Fig. 5), and no subsurface layer of oxide particles was observed.

Table 2 presents the Vickers hardness values for aged Athenium, Liberty and Spartan. The minimal differences between these mean values and the mean values for the original as-cast alloys (Carr and Brantley, 1991; Carr et al., 1993) are not clinically significant.
Figure 5. Microstructure of aged Liberty, showing the region adjacent to the specimen surface (left edge) that is denuded of the eutectic constituent. Bar = 10 μm.

Figure 6. Microstructure of aged Liberty, illustrating the disk-shaped morphology of the ruthenium-rich phase (Brantley et al., 1993). The specimen has been somewhat over-etched. Bar = 1 μm.

Discussion

The room temperature aging behavior of these three Pd-Cu-Ga dental alloys is attributed to the non-equilibrium nature of the as-cast microstructures, which contain many high-diffusivity paths in the fine-scale eutectic constituents, and to the essential role of the surface for the diffusion processes. As previously discussed (Brantley et al., 1993), the effect of copper and indium in shifting the Pd-Ga binary eutectic to the higher Pd/Ga ratios found in dental alloys (Cascone, 1984), along with a similar effect on the liquidus curve from rapid solidification conditions (Reed-Hill and Abbaschian, 1994) such as those encountered in dental casting (Phillips, 1991), cause the formation of substantial amounts of near-surface eutectic in Athenium and Liberty, particularly in thin sections. In as-cast high-palladium alloys that do not contain a grain-refining element, such as Spartan,
the eutectic constituent is found in the interdendritic regions, whereas as-cast alloys, such as Athenium and Liberty that contain ruthenium as a grain-refining element, have areas of eutectic structure along with equiaxed grains of the palladium solid solution matrix (Brantley et al., 1993). The two-phase eutectic structure in these alloys consists of the palladium solid solution and a Pd$_2$Ga phase which has been detected by X-ray diffraction (Brantley et al., 1995). The non-equilibrium nature of this eutectic constituent is consistent with its near-disappearance in Athenium, Liberty and Spartan after heat treatment which simulates the porcelain firing cycles (Brantley et al., 1993; Carr et al., 1993).

The Vickers hardness of the aged Pd-Cu-Ga alloys (Table 2) was nearly the same as that for the original as-cast alloys (Carr and Brantley, 1991; Carr et al., 1993), despite substantial loss of the near-surface eutectic constituent in Athenium and Liberty and the microstructural
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Figure 9. Photomicrograph of another aged Spartan specimen, illustrating different morphologic forms of the lamellar eutectic interdendritic constituent and relatively long Widmanstätten precipitates. Bar = 10 μm.

Figure 10. Photomicrograph of the near-surface region for an aged Spartan specimen. Bar = 10 μm.

Transformations observed in Spartan. This result implies that the aging has little effect upon the yield strength of these alloys (Dieter, 1986). While transmission electron microscopic experiments are required for unambiguous proof, it is assumed that the network of submicron face-centered tetragonal Pd₃Ga-Cu₁₋ₓ precipitates, considered to be principally responsible for the relatively high strength and hardness of Pd-Cu-Ga dental alloys (Odén and Herø, 1986), were essentially unaltered during room temperature aging.

It is apparent from Figure 1 for Athenium and Figure 5 for Liberty that the surface has a pivotal role in the room temperature aging process, since substantial eutectic constituent remained at depths greater than ~20 μm. Both figures suggest that the aging initially involves grain boundary diffusion, analogous to the previous observation for these two alloys after simulated porcelain firing heat treatment which results in loss of
the eutectic constituent (Carr et al., 1993; Brantley et al., 1993). Subsequently, there would be additional rapid diffusion along the interlamellar boundaries which are in contact with the grain boundaries, as well as diffusion thereafter in a direction perpendicular to the lamellae, to eliminate the eutectic constituent. If only diffusion over the very small interlamellar distances (typically ~ 0.25 μm) were involved for the room temperature aging, loss of the eutectic constituent would occur throughout the microstructure, rather than solely in the near-surface region. The widths of the denuded zones in Figures 1 and 5 are assumed to correspond to the distances of the grain boundary diffusion from the surface to the eutectic lamellae that enables the aging phase transformations to occur. Since the overall diffusion process has multiple components, it is not possible to estimate a single diffusion coefficient for the room temperature aging of Athenium and Liberty.

The less dramatic microstructural changes in as-cast Spartan during room temperature aging are attributed to the absence of an equiaxed fine-grained microstructure where eutectic lamellae are in contact with grain boundaries, as occurs in as-cast Athenium and Liberty. For simplicity, the room temperature aging of Spartan, where some transformation of the bulk interdendritic eutectic constituent appears to occur, can be considered as a single thermally activated diffusion process described by an Arrhenius equation of the form (Shewmon, 1963): 

\[ A = k \exp(-\Delta G/RT) \]

where \( A \) is the rate of aging (inversely proportional to time), \( k \) is a constant, \( \Delta G \) is the free energy change for the associated diffusion process, \( R \) is the gas constant (1.987 cal/mol·°K), and \( T \) is the absolute temperature (°K). For example, a simple process involving the diffusion of gallium atoms by a vacancy mechanism might be conjectured.

Previously, it was found that heat treatment simulating the firing cycles for Vita VMK dental porcelain (Papazoglou et al., 1993) largely eliminated the as-cast dendritic structure in this alloy (Brantley et al., 1993; Carr et al., 1993). If an equivalent time of 15 minutes at the single intermediate temperature of 800°C in the porcelain firing range is selected, and it is assumed that a comparable amount of microstructural homogenization occurs after 5 years at room temperature (20°C), then an approximate value of \( \Delta G = 10 \) kcal/mol would be required for complete loss of the interdendritic constituent in Spartan. While this approach is an oversimplification, it nevertheless provides insight into the approximate values of the parameters that would be associated with room temperature aging by diffusion between the fine-scale eutectic lamellae. An approximate diffusion coefficient (D) for bulk aging to eliminate the eutectic constituent in Spartan over five years can be estimated from the relationship (Shewmon, 1963) that \( x^2 = 4Dt \), where \( x \) is the diffusion length and \( t \) is the time. For a diffusion length of 0.25 μm, the required room temperature diffusion coefficient is \( D = 10^{-18} \) cm²/sec, which provides an upper limit since there is residual eutectic constituent in Spartan after five years aging. Published information about high-diffusivity processes (Shewmon, 1963) indicates that these estimates of \( \Delta G \) and \( D \) are plausible. For the room temperature aging of Athenium and Liberty, much greater overall diffusion coefficients are appropriate, since there is complete elimination of the near-surface eutectic constituent by the multiple processes previously noted.

The conclusion that the subsurface layer in aged Athenium consists of oxide particles is based upon previous observations of high-palladium alloys after oxidation at elevated temperatures (Hautaniemi et al., 1990; Brantley et al., 1993; Carr et al., 1993), the presence of an air environment during specimen storage, and the absence of such particles in the bulk microstructure. Recent X-ray diffraction studies in our laboratory of oxidized Liberty and Spartan Plus (whose composition is nearly identical to that of Spartan) suggest that the near-surface region of Athenium after oxidation at elevated temperatures might contain four phases: \( \text{CuGa}_2\text{O}_3 \), \( \beta\text{-Ga}_2\text{O}_3 \), \( \text{SnO}_2 \) and \( \text{In}_2\text{O}_3 \). While the EDS results in Table 1 are consistent with the presence of \( \text{CuGa}_2\text{O}_3 \), \( \beta\text{-Ga}_2\text{O}_3 \) and \( \text{SnO}_2 \), X-ray diffraction analysis of Athenium after low temperature aging would be required to identify the near-surface phases. The reason for the increased mean concentration of ruthenium in the near-surface region of aged Athenium (Table 1) is unknown, although the EDS results were highly variable, as indicated by the large coefficient of variation (quotient of standard deviation and mean). The absence of a subsurface layer for aged Liberty and Spartan could be due to the loss of this fragile feature during metallographic preparation, or to differences in the amounts and proportions of oxidizable elements (Cu, Ga, Sn and In) compared to Athenium.

The persistence of the dendritic structure in Spartan after prolonged room temperature aging is consistent with recent experiments in our laboratory which have shown that heat treatment at temperatures above approximately 800°C is required to completely eliminate this as-cast structure. The interdendritic regions are replaced by precipitates of several different morphologic forms (Brantley et al., 1993). Elimination of the eutectic constituent in any of the three Pd-Cu-Ga alloys studied can be accomplished by diffusion over considerably shorter distances than would be required for homogenization of the bulk dendritic microstructure in Spartan, whose scale has been shown elsewhere (Carr and Brantley, 1991; Brantley et al., 1993). This is supported by the present photomicrographs of aged Spartan that show some trans-
formation of the interdendritic eutectic constituent.

The eutectic microstructural constituent in as-cast Pd-Cu-Ga dental alloys is hypothesized to have an important role for decreasing the in vivo corrosion resistance and biocompatibility of these alloys. The Pd$_2$Ga phase in the eutectic structure is expected to be anodic to the more noble palladium solid solution in the oral environment, and therefore subject to electrochemical corrosion and slow release of palladium and gallium ions. Consequently, low-temperature aging of the Pd-Cu-Ga alloys is a phenomenon that may have important beneficial clinical significance. Our research is continuing on the aging behavior of these alloys to define the nature, kinetics and consequences of the resulting phase transformations. In closing, it is interesting to note that dimensional changes related to ordering at intraoral temperature ($37^\circ$C) have been recently reported for an AuCu-3 wt% Ga dental alloy (Watanabe et al., 1994).

Conclusions

The room temperature aging behavior of the three Pd-Cu-Ga dental alloys investigated in the as-cast condition appears to be a natural consequence of their microstructures which contain fine-scale eutectic constituents and the role of the surface in facilitating the diffusion processes involved. For the alloy with a dendritic as-cast microstructure, a simple model of uniform diffusion by gallium atoms is hypothesized for the aging transformation of the eutectic constituent. Approximate calculations, based upon diffusion theory and the estimated distance for atomic movement from the interlamellar spacing, yield plausible values of 10 kcal/mole for the free energy change and $10^{-18}$ cm$^2$/sec for the diffusion coefficient at room temperature. The persistence of the as-cast dendritic structure after aging is consistent with the extensive phase transformations at elevated temperatures required for its elimination. For the other two alloys with as-cast eutectic microstructures, the surface has a pivotal role for the room temperature aging process, along with rapid grain boundary diffusion to the eutectic lamellae. Calculation of an overall diffusion coefficient describing the aging for these two alloys is not possible because of the multiple high-diffusivity paths. It is conjectured that long-term aging of these alloys in the oral environment may have important beneficial consequences for their in vivo corrosion resistance and biocompatibility.

Acknowledgement

This study was supported by NIDR Grant DE10147.

References


Discussion with Reviewers

H.J. Mueller: In Figure 1, there are some remnants of grain boundaries attached to the inner-side of the oxidized surface layer and extending more into the interior
than the thickness of the oxidized layer. Could not this mean that the grain boundaries, besides acting as diffusion pipeways in an outward direction for Cu, Ga, Sn and perhaps In, also provided diffusion pipeways in an inward direction for oxygen from the exterior or outer surface layer? Could not this also suggest that internal oxidation may somehow be involved?

**Authors:** We concur that internal oxidation processes involving grain boundary diffusion of oxygen are likely to be responsible for formation of the subsurface oxide in aged Athenium.

**H.J. Mueller:** In Figure 5, it appears that the microstructure of the aged Liberty alloy has a somewhat different texture or contrast in a surface layer about 4 μm thick, about the same depth to which the eutectic is depleted from the grain boundaries. Do the authors have any opinions or data supporting that this is a distinct layer different from the bulk?

**Authors:** Careful examination of this feature suggests that it may be defined by the start of grain boundary widening, presumably from the products of internal oxidation. We have no data about the differences in composition for this region, but suggest that there may be little variation from the bulk matrix composition except at the grain boundaries.

**H.J. Mueller:** In order to minimize any deleterious effects from non-homogenized microstructures, do the authors recommend that cast prostheses made from these alloys be subjected to a homogenization heat treatment?

**Authors:** We concur that cast prostheses should be subjected to a homogenization heat treatment.

**M.D. Bagby:** If such microstructural changes occur in these as-cast Pd-Cu-Ga alloys after five years at room temperature, how long would it take for the same changes to occur at mouth temperature?

**Authors:** Since the diffusion processes are thermally activated and the difference between room temperature and mouth temperature is not great when expressed in absolute temperature (°K), one would expect very little increase in the rate of aging at 37°C. There may be additional effects on the aging kinetics because of differences between the oral environment and the storage ambient for the alloys in this study.

**M.D. Bagby:** What clinical events might be observed after room temperature aging of these alloys?

**Authors:** Besides potentially improved in vivo tarnish and corrosion resistance, as well as enhanced biocompatibility, other clinical events might be small changes in the dimensions and surface roughness of the casting. It should be noted that the normal porcelain firing cycles for metal-ceramic restorations largely eliminate the eutectic constituent in these alloys. The results of this study are relevant for use of Pd-Cu-Ga alloys for all-metal restorations, implant-supported prostheses and removable partial denture frameworks.

**R.A. Fournelle:** It is not clear to this reviewer why one should get a lot of eutectic near the surface in Athenium and Liberty. Normally, metal near the surface solidifies first during casting and is rich in the high melting point component (in this case Pd). This solidification of Pd-rich solid solution would then be followed by eutectic solidification of the remaining liquid which has now been enriched in the alloying elements. Could the authors comment on this?

**Authors:** Our extensive observations, described in three of the references, have shown that the near-surface eutectic constituent in as-cast Athenium and Liberty always extended to the specimen surface. However, the as-cast specimens were initially subjected to air-abrasion with 50 μm alumina before mounting in resin, followed by sectioning and metallographic preparation. It is possible that the outermost portion of the original casting had a somewhat different microstructure than was subsequently observed for the polished and etched specimens.

**R.A. Fournelle:** The fine lamellar morphologies in Figures 1, 5, 9 and 10 look like they were formed by a solid state reaction such as discontinuous precipitation and not by eutectic solidification. Could these structures have formed during aging at room temperature, rather than during solidification?

**Authors:** The lamellar morphologies for the three Pd-Cu-Ga alloys were always characteristic for the initial as-cast condition and did not form during the room temperature aging. We have tried rapidly quenching Pd-Cu-Ga alloys as soon as possible after solidification, rather than the standard bench-cooling procedure recommended by the manufacturers, but still always observed the lamellar constituents.