Cells and Materials

Volume 7 | Number 1 Article 6

1997

Mechanism for Formation of Lamellar Constituents in Grain-Refined Pd-Cu-Ga Dental Alloys

William A. Brantley
The Ohio State University

Zhuo Cai
The Ohio State University

John C. Mitchell
The Ohio State University

Stanley G. Vermilyea
The Ohio State University

Cells and Materials Vol. 7, No. 1, 1997 (Pages 63-67) 1051-6794/97$5.00+.25
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

MECHANISM FOR FORMATION OF LAMELLAR CONSTITUENTS IN GRAIN-REFINED Pd-Cu-Ga DENTAL ALLOYS

William A. Brantley*, Zhuo Cai†, John C. Mitchell[1] and Stanley G. Vermilyea

College of Dentistry, Department of Geological Sciences[1], The Ohio State University, Columbus, Ohio 43210
†Present address: Dept. of Biomaterials Sci., Baylor Coll. Dentistry, Texas A&M Univ. System, Dallas, TX 75246

(Received for publication November 25, 1996 and in revised form August 8, 1997)

Abstract

Grain-refined Pd-Cu-Ga dental alloys solidify with a lamellar microstructural constituent that affects a variety of clinically relevant properties. While formation of this constituent has been attributed to eutectic solidification, an alternative mechanism of discontinuous precipitation has been proposed. Using a representative grain-refined Pd-Cu-Ga dental alloy, casting procedures involving two different rates of solidification were used: (a) A standard thin-walled coping configuration for a metal-ceramic restoration was cast into a room temperature mold, followed by rapid quenching into an ice-water mixture. (b) A thin plate specimen was cast into a standard elevated-temperature mold, with the same subsequent rapid quenching procedure. Neither casting was subjected to the standard air-abrasion procedure following devesting that is used in dental laboratories. An outer surface layer, approximately one grain thick, containing only the palladium solid solution, was observed in the microstructures of the two different castings, and the eutectic constituent was present at greater depths. This observation is consistent with physical metallurgy principles for the freezing of an alloy containing a eutectic constituent, and the alternate hypothesis that the lamellar constituents might represent discontinuous precipitates has been discarded.

Key Words: Palladium, dental alloy, microstructure, eutectic, solidification, scanning electron microscopy.

*Address for correspondence:
William A. Brantley
Section of Restorative Dentistry,
Prosthodontics and Endodontics
College of Dentistry
The Ohio State University
305 West 12th Avenue
Columbus, Ohio 43210-1241

Telephone: (614) 292-0773
FAX number: (614) 292-9422
E-mail: Brantley.1@osu.edu

Introduction

Under standard bench-cooling conditions recommended by the manufacturers, the fine-grained Pd-Cu-Ga dental casting alloys solidify with substantial amounts of a near-surface lamellar constituent that has been interpreted as a eutectic structure (Carr and Brantley, 1991; Brantley *et al.*, 1993, 1995a,b). However, in the written discussion for an article on the room temperature aging of these alloys (Brantley *et al.*, 1995b), Professor Raymond A. Fournelle noted that the surface regions of Pd-Cu-Ga alloy castings with equiaxed polycrystalline microstructures should not have any eutectic structure, since the first solid phase to form would be the primary palladium solid solution (Reed-Hill and Abbaschian, 1994). In response, the authors noted that after devesting, the castings were subjected to the standard air-abrasion procedure performed in dental laboratories, which might have caused the loss of a surface region containing only the palladium solid solution.

In the written discussion for an earlier article (Brantley *et al.*, 1993), Professor Fournelle had suggested that the lamellar constituents might form by discontinuous precipitation during cooling of the casting and not by eutectic solidification. This matter has potential clinical significance since elimination of the near-surface lamellar constituent, which has been proposed as relevant for *in vivo* corrosion and biocompatibility of the Pd-Cu-Ga alloys (Cai *et al.*, 1995), may be possible by control of the solidification conditions during casting or a post-casting heat treatment. In a recent study (Brantley *et al.*, 1996), rapid quenching after casting of an equiaxed polycrystalline Pd-Cu-Ga alloy used in these previous studies failed to eliminate the near-surface lamellar constituent. The presence of more rod-shaped morphology for this constituent was attributed to the rapid solidification conditions and the limited time available for diffusion. Moreover, since the castings used in this recent study were also air-abraded after devesting, a more complete explanation of the formation of these constituents was not possible because of the loss of the outermost near-surface region. The objective of this

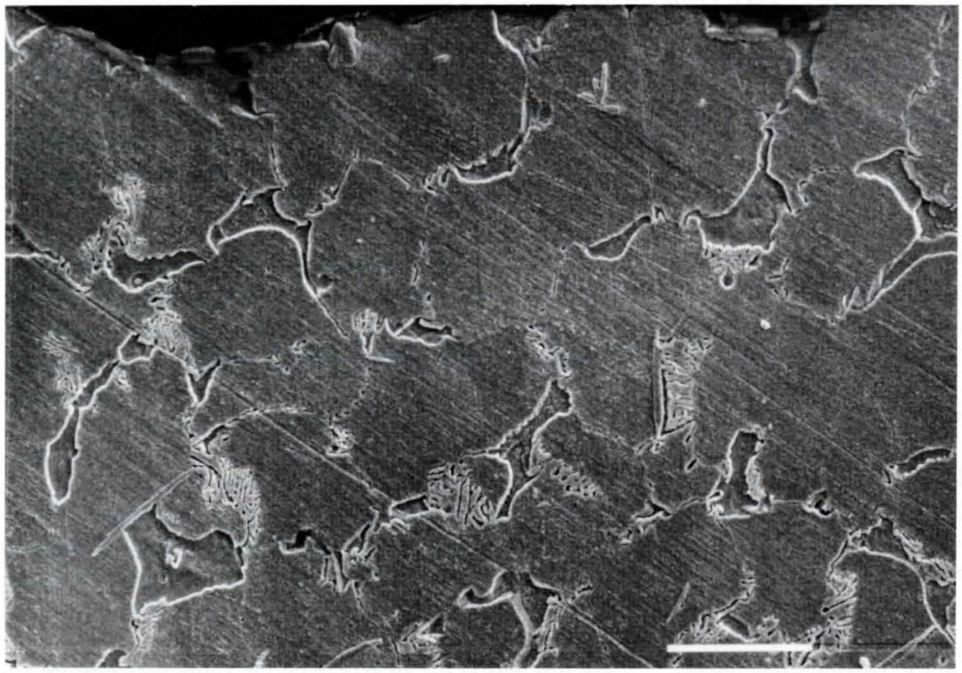

Figure 1. Secondary electron image of the near-surface microstructure of a cross-sectioned thin-walled coping specimen of the Liberty Pd-Cu-Ga alloy that had been cast into a room-temperature mold, followed by rapid quenching. The surface of the specimen is at the top of the micrograph. Bar = 10 μm. None of the specimens in Figures 1-4 were air-abraded after devesting.

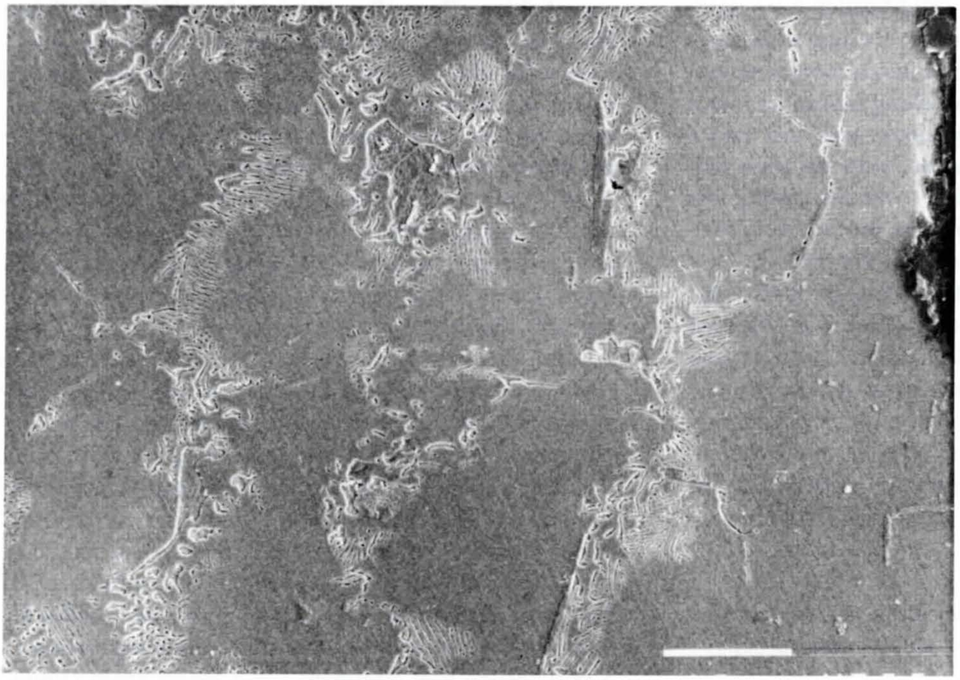

Figure 2. Secondary electron image of the near-surface microstructure of the thin plate-shaped specimen of the Liberty alloy that had been cast into a mold held at a peak burnout temperature of 1,400°F (760C) and then rapidly quenched into an ice-water mixture. The surface of the specimen is at the right side of the micrograph. Bar = 10 μm.

study was to establish the mechanism of formation for the lamellar constituent in the same representative grain-refined Pd-Cu-Ga alloy used in these previous investigations by employing new strategies for rapid solidification and surface preparation of the castings.

Materials and Methods

The high-palladium alloy selected for study was Liberty (J.F. Jelenko and Company, Armonk, NY), which has a nominal composition (weight percent) of 76Pd-10Cu-5.5Ga-6Sn-2Au (Carr and Brantley, 1991; Brantley *et al.*, 1993, 1995a,b). For the standard as-cast and bench-cooled condition, the Liberty alloy has a near-surface lamellar constituent, which has been interpreted in these articles as a eutectic structure. This alloy has a fine-grained equiaxed microstructure because of the use of ruthenium as a grain-refining element by the manufacturer (Carr and Brantley, 1991; Brantley *et al.*, 1993).

Two different casting procedures were employed: (a) A previous specimen design that simulated a coping

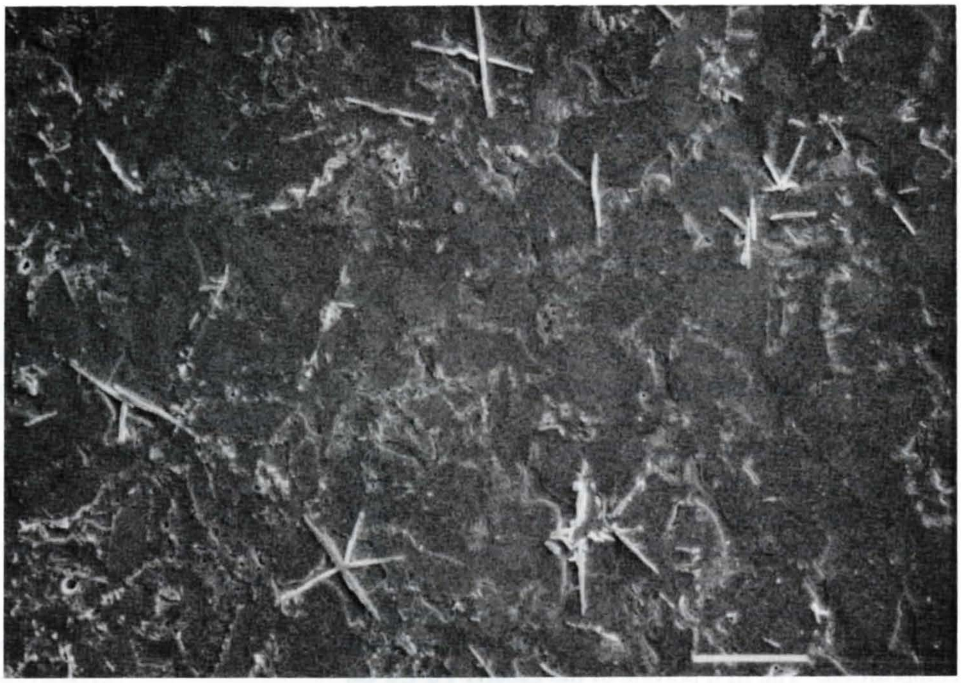

Figure 3. Secondary electron image of the microstructure of the thin plate-shaped specimen in Figure 2, after repolishing and intentionally under-etching to reveal the elongated ruthenium-rich precipitates which would be substantially removed with normal etching. Note that the grain boundaries evident in Figure 2 are no longer visible. Bar = 10 μm.

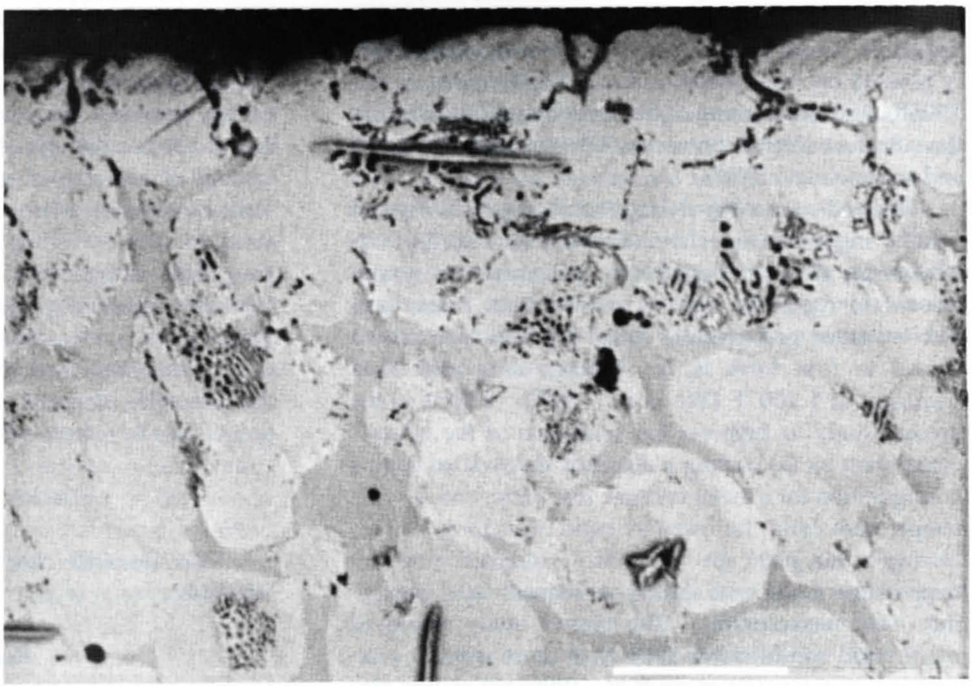

Figure 4. Backscattered electron image of the near-surface region of the coping specimen of the Liberty alloy in Figure 1. Darker regions with higher gallium content are located between grains of the palladium solid solution (lighter contrast). Regions of the eutectic constituent and the elongated ruthenium-rich precipitates can also be seen. The surface of the specimen is at the top of the micrograph. Bar = 10 μm.

(less than approximately 0.5 mm thickness) for a maxillary central incisor (Carr and Brantley, 1991) was first used. One specimen of the Pd-Cu-Ga alloy with this configuration was cast into a room-temperature investment mold (Cera-Fina, Whip Mix, Louisville, KY) and quenched as rapidly as possible into an ice-water mixture. (b) A second, approximately mm thick, plate-shaped specimen of the same alloy was cast with the use of a standard elevated burnout temperature (1,400°F) for the investment mold, followed by the same rapid quenching procedure. As noted above, in previous research, the castings had been air-abraded with 50 μm alumina particles after devesting, following standard dental laboratory procedures. Since it was possible that such air-abrasion might eliminate a surface layer that did not contain the lamellar constituent, the castings in this study were devesting by immersion in ultrasonically agitated distilled water and not subsequently air-abraded. The cast coping was embedded in metallographic resin and sectioned with a slow-speed water-cooled diamond saw (Carr and Brantley, 1991) to yield two specimens for observation. These specimens and the plate-shaped specimen (which was not sectioned after being embedded in resin) were polished through 0.05 μm alumina slurries and etched in aqua regia solutions (Mezger *et al.*, 1988).

The as-cast microstructures were investigated with a scanning electron microscope (JSM-820, JEOL Ltd., Tokyo, Japan), using the secondary electron and backscattered electron imaging modes. The resin-mounted specimens were vacuum sputter-coated with either a gold-palladium or carbon film, respectively, for examination in these two modes.

Results and Discussion

For both types of specimens, which represented different surface-to-volume ratios and solidification conditions, a thin surface layer of approximately one grain width that did not contain the lamellar microstructural constituent was observed (Figs. 1 and 2). This result is consistent with the principles of physical metallurgy for the freezing of alloys that do not have the exact eutectic composition. The first portion of the Liberty Pd-Cu-Ga alloy to freeze at the mold walls will have the composition of the primary palladium solid solution, as previously pointed out by Professor Fournelle (Brantley *et al.*, 1995b), and the freezing of the remaining liquid that has the eutectic composition occurs subsequently (Reed-Hill and Abbaschian, 1994).

While the scanning electron micrographs in Figures 1 and 2 suggest an association between the lamellar constituent and the grain boundaries, this constituent is considered to represent eutectic solidification rather than discontinuous precipitates, since the latter have been shown to first form in the Liberty alloy after heat treatment at 1,200°F (Wu *et al.*, 1997). Efforts in the present study to suppress the formation of the eutectic constituent by (a) casting a standard thin-walled coping configuration for a metal-ceramic restoration into a room temperature mold, followed by rapid quenching, and (b) casting a thin plate specimen into a standard elevated-temperature mold, with similar subsequent rapid quenching, were unsuccessful. The present study employed more rapid solidification rates than those used in a recent investigation (Brantley *et al.*, 1996) which was also unsuccessful in attempting to suppress formation of the near-surface eutectic constituent. In that previous study, specimens with the same coping configuration were cast into standard elevated-temperature molds, followed by rapid quenching.

When the Liberty alloy specimens in the present study were very lightly etched, narrow and elongated precipitates were observed (Fig. 3); these precipitates have been identified as ruthenium-rich in a concurrent study performed in our laboratory (Wu *et al.*, 1997). Our previous extensive microstructural observations of this alloy (Brantley *et al.*, 1993, 1995a,b, 1996) indicate that these precipitates would typically be removed with normal etching. In addition, backscattered electron image micrographs revealed areas of higher gallium concentration (darker contrast) between adjacent palladium solid solution grains (Fig. 4). Concurrent research has indicated that these areas represent a different phase of substantially higher hardness than that for the bulk Liberty alloy (Wu *et al.*, 1997).

Figure 4, which illustrates the microstructure for the coping specimen cast into the room-temperature mold, also shows some relatively short lamellae and rod-shaped morphology for the eutectic constituent. These changes in the lamellar morphology found with normal bench-cooling conditions (Brantley *et al.*, 1993) arise from the limited time available for solute diffusion and redistribution with the more rapid rates of solidification (Brantley *et al.*, 1996).

Conclusions

Rapid solidification strategies involving the use of a room-temperature mold and a thin plate-shaped specimen configuration failed to suppress formation of the near-surface lamellar constituent in castings of a Pd-Cu-Ga dental alloy, although shorter lamellae and a greater amount of rod-shaped morphology of this constituent were observed. When the standard procedure of air-abrasion after devesting was omitted, the outermost region of the castings consisted only of the palladium solid solution, followed by the lamellar constituent at depths greater than approximately one grain thickness. The present microstructural observations were consistent with the principles of physical metallurgy for the solidification of an alloy containing a eutectic constituent.

Acknowledgment

This research was supported by NIDR Grant DE10147.

References

Brantley WA, Cai Z, Carr AB, Mitchell JC (1993) Metallurgical structures of as-cast and heat-treated high-palladium dental alloys. Cells Mater **3**, 103-114.

Brantley WA, Cai Z, Foreman DW, Mitchell JC, Papazoglou E, Carr AB (1995a) X-ray diffraction studies of as-cast high-palladium alloys. Dent Mater **11**, 154-160.

Brantley WA, Cai Z, Wu Q, Carr AB, Mitchell JC (1995b) Room temperature aging of Pd-Cu-Ga dental alloys. Cells Mater **5**, 261-270.

Brantley WA, Cai Z, Vermilyea SG, Papazoglou E, Mitchell JC, Carr AB (1996) Effects of solidification conditions and heat treatment on the microstructures and Vickers hardness of Pd-Cu-Ga dental alloys. Cells Mater, in press.

Cai Z, Chu X, Papazoglou E, Bradway SD, Brantley WA (1995) On the biocompatibility of high-palladium dental alloys. Cells Mater **5**, 357-368.

Carr AB, Brantley WA (1991) New high-palladium alloys: Part I. Overview and initial studies. Int J Prosthodont **4**, 265-275.

Mezger PR, Stols ALH, Vrijhoef MMA, Greener EH (1988) Metallurgical aspects of high-palladium alloys. J Dent Res **67**, 1307-1311.

Reed-Hill RE, Abbaschian R (1994) Physical Metallurgy Principles. 3rd Edn. PWS Publishing, Boston. pp. 342-349.

Wu Q, Brantley WA, Vermilyea SG, Mitchell JC, Xiao J, Guo W (1997) Heat-treatment behavior of high-palladium dental alloys. Cells Mater, in press.

Discussion with Reviewers

H.J. Mueller: Since rapid solidification will likely not favor discontinuous precipitation, please explain the reasoning for casting the thin plate-shaped specimen into an investment mold at high temperature, instead of cooling the specimen as quickly as possible to prevent diffusion, especially diffusion along grain boundaries and other high-diffusivity paths.

Authors: Our experimental methodology was designed to examine separately two factors (mold temperature and surface-to-volume ratio of the casting) for formation of the near-surface lamellar constituent in the representative Liberty Pd-Cu-Ga dental alloy. The plate-shaped specimen, whose thickness was similar to that of the coping specimen, had much greater surface-to-volume ratio. This permitted examination of the effect of the second factor on the as-cast microstructure that initially formed in the elevated-temperature mold after solidification. Consequently, the same standard mold temperature was used for both specimens.

H.J. Mueller: If the lamellar eutectic structure does not form by discontinuous precipitation, what factors favor nucleation of this constituent near the grain boundaries with subsequent growth towards the grain interior, rather than formation in the grain interiors?

Authors: Major factors should be the lower surface energy required to form the eutectic structure near a grain boundary and the presence of a region that facilitates the vacancy formation and diffusion required for the extensive solute redistribution between this structure and the palladium solid solution matrix.

M.D. Bagby: Can you add more information about the composition of the ruthenium-rich precipitates in Figure 3?

Authors: Because of the very small width of these highly elongated precipitates, we have not performed quantitative energy-dispersive spectroscopic (EDS) analyses, due to concern about inaccuracy caused by interference from the palladium solid solution matrix. While qualitative EDS analyses indicate that these precipitates are highly ruthenium-rich, from the principles of physical metallurgy we assume that they also contain palladium. We have previously discussed the grain refinement of high-palladium alloys by the addition of very small amounts of ruthenium and shown the Pd-Ru phase diagram (Brantley *et al.*, 1993) that is relevant to the composition of the precipitates. However, the nonequilibrium conditions during solidification of these dental castings and the multicomponent nature of the alloy can result in predictions of phase compositions from binary equilibrium diagrams being highly approximate.

M.D. Bagby: Is the difference between the abraded and unabraded surfaces important to the adhesion of dental porcelain or an adhesive dental cement?

Authors: Numerous investigations on other dental casting alloys have shown that an air-abraded surface provides an important mechanical retention contribution to the metal-ceramic bonding, in addition to the chemical bonding associated with the oxide layer between the dental porcelain and alloy. In a similar manner, a properly air-abraded alloy surface should also provide much greater bond strength for an adhesive dental cement due to mechanical retention.