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EFFECTS OF SOLIDIFICATION CONDITIONS AND HEAT TREATMENT ON THE MICROSTRUCTURE AND VICKERS HARDNESS OF Pd-Cu-Ga DENTAL ALLOYS

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Abstract

Two representative Pd-Cu-Ga dental alloys, one with a dendritic as-cast microstructure containing a eutectic interdendritic constituent and the other with an equiaxed fine-grained as-cast microstructure containing a near-surface eutectic constituent, have been subjected to rapid quenching following casting, in addition to the conventional bench cooling recommended by the manufacturers. The quenched alloys were subsequently heat treated at temperatures of 1200°, 1500° and 1800°F that span the range of the firing cycles for dental porcelain. Scanning electron microscopic examination showed that the lamellar eutectic constituents normally present in the microstructures of the as-cast and bench-cooled alloys persisted when the alloys were rapidly quenched after casting, although microstructural changes were evident. A large decrease occurred in the Vickers hardness of the alloy with the dendritic as-cast microstructure after heat treatment at 1500°F, and in the hardness of both alloys after heat treatment at 1800°F.

Key Words: Palladium, dental alloy, solidification, heat treatment, microstructure, eutectic, hardness, strength, corrosion, biocompatibility, scanning electron microscopy.

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Introduction

High-palladium dental casting alloys containing greater than approximately 75 wt. % palladium and based upon the Pd-Cu-Ga and Pd-Ga systems have become popular over the past decade for metal-ceramic restorations (Carr and Brantley, 1991) and implant-supported prostheses (Stewart *et al.*, 1993), because of their lower cost than popular gold-based dental alloys and their good mechanical properties. The high-palladium alloys have also been proposed for removable partial denture frameworks (Asgar, 1988). The Pd-Cu-Ga alloys have substantially higher values of hardness than the Pd-Ga alloys, which has been attributed to a complex network of submicron face-centered tetragonal $Pd_3Ga_xCu_{1-x}$ precipitates observed by transmission electron microscopy (Odén and Herø, 1986). This relatively high hardness may cause greater difficulty with adjustments to cast restorations and prostheses by the dental laboratories and dentists, compared to that experienced with the traditional gold-based alloys (Carr and Brantley, 1991).

The Pd-Cu-Ga dental alloys containing small amounts of ruthenium as a grain-refining element solidify with an equiaxed fine-grained microstructure containing substantial quantities of a near-surface lamellar constituent, particularly in thin sections where the rate of solidification is more rapid (Carr and Brantley, 1991; Brantley *et al.*, 1993). Formation of this constituent, which was interpreted as a eutectic structure, has been attributed to two effects: (a) the role of copper in shifting the Pd-Ga eutectic composition to the higher Pd/Ga ratios found in the high-palladium dental alloys (Cascone, 1984) and (b) the change in the liquidus curve (Reed-Hill and Abbaschian, 1994) of the palladium-rich end of the Pd-Cu-Ga phase diagram due to the rapid solidification conditions encountered with the dental casting process, where the temperature of the investment mold is considerably lower than that of the molten alloy (Phillips, 1991). Other Pd-Cu-Ga dental alloys that do not contain a grain-refining element solidify with a dendritic as-cast microstructure where the eutectic constituent is located in the interdendritic regions (Brantley *et al.*, 1993; Brantley *et al.*, 1995a).

In the written discussions for recent articles on the metallurgical structures (Brantley *et al.*, 1993) and room temperature aging (Brantley *et al.*, 1995b) of these Pd-Cu-Ga dental alloys, Professor Raymond A. Fournelle (Marquette University, Milwaukee, WI) inquired if the lamellar microstructural constituents in Pd-Cu-Ga alloys might have arisen from a different mechanism other than eutectic solidification, namely, discontinuous precipitation involving boundary migration (Shewmon, 1969). This inquiry stimulated the present study, which had the first objective of determining whether the lamellar microstructural constituents in these as-cast alloys could be modified or eliminated under more rapid solidification conditions than exist for the bench-cooling recommended by the manufacturers and used in the previous investigations.

In the same written discussion (Brantley *et al.*, 1993), Dr. Herbert J. Mueller (American Dental Association, Chicago, IL) inquired if heat treatments are available to improve the mechanical properties of these alloys. This inquiry stimulated the second objective for the present study, which was to investigate the heat treatment response of Pd-Cu-Ga alloys over the range of temperatures corresponding to the porcelain firing cycles.

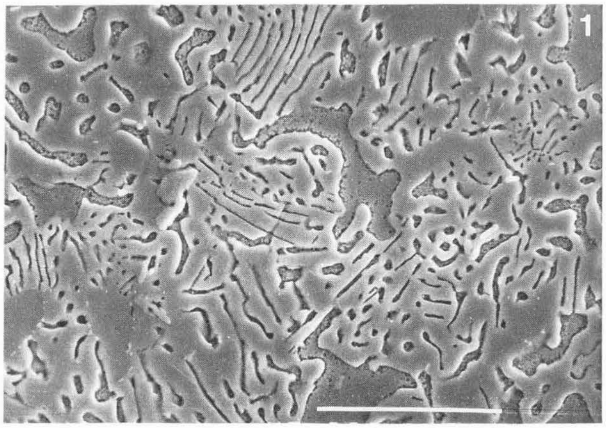
Materials and Methods

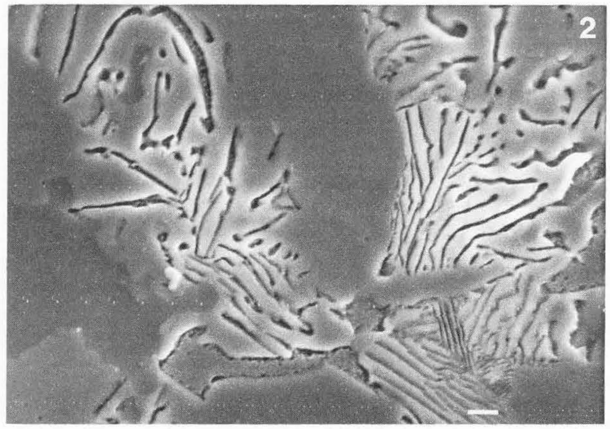
Two representative Pd-Cu-Ga alloys (Liberty, 76Pd-10Cu-5.5Ga-6Sn-2Au, J.F. Jelenko and Company, Armonk, NY; Spartan Plus, 79Pd-10Cu-9Ga-2Au, Ivoclar North America, Amherst, NY) were selected, where the nominal compositions provided by the manufacturers are in weight percent (Carr and Brantley, 1991; Brantley *et al.*, 1995b). As-cast Liberty has an equiaxed fine-grained microstructure and contains substantial near-surface eutectic constituent in the thin sections of castings (Carr and Brantley, 1991), while as-cast Spartan Plus has a dendritic microstructure with the eutectic constituent located in the interdendritic regions (Brantley *et al.*, 1995a).

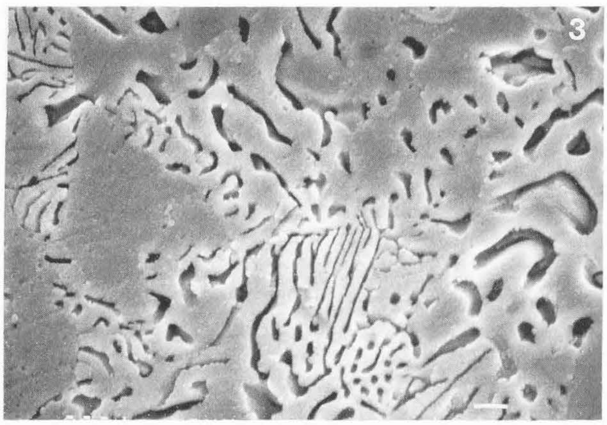
Following previously developed experimental procedures (Carr and Brantley, 1991), a practical casting design simulating the coping for a maxillary central incisor was employed, which has both relatively thin and thick areas that yield a range of solidification rates. Wax patterns were invested in a carbon-free, phosphate-bonded investment (Cera-Fina, Whip Mix, Louisville, KY), which was manipulated according to instructions from the manufacturer. Each alloy was fused in a dedicated ceramic crucible, using a multi-orifice gas-oxygen torch, and casting was performed in air with a standard broken-arm centrifugal casting machine. Three castings were prepared for each alloy, and two different solidification conditions were employed: (a) one casting of each alloy was subjected to the normal bench cooling recommended by both manufacturers; (b) two castings of each alloy were rapidly quenched, where the rotating arm of the centrifugal casting machine was stopped as soon as possible after casting the molten alloy into the investment mold and the casting ring was immediately quenched into an ice-water bath.

After devesting, the castings were abraded with 50 μm alumina, embedded in transparent metallographic resin (Epoxide, 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.) to yield two mirror-image specimens. After removal from the mounting resin with a slow-speed dental handpiece, individual rapidly quenched specimens of each alloy were heat treated for 10 minutes at one of three temperatures (1200°, 1500°, and 1800°F) which span the range of the firing cycles (Papazoglou *et al.*, 1993) for Vita VMK dental porcelain (Vident, Baldwin Park, CA), quenched into an ice-water bath and embedded again in the resin. As-cast (both bench-cooled and rapidly quenched) specimens for microstructural examination were metallographically polished through 0.05 μm alumina slurries, etched in aqua regia solutions (Mezger *et al.*, 1988) and sputter-coated with a thin gold-palladium film. The microstructures were examined in the secondary electron imaging mode with a scanning electron microscope (JSM-820, JEOL Ltd., Tokyo, Japan).

Vickers hardness measurements were made on the etched (not coated) specimen surfaces using a 1 kg load. To obtain an accurate baseline for assessing effects of heat treatment, ten hardness measurements were obtained on each of two as-cast and rapidly quenched specimens of both alloys, and on two as-cast and bench-cooled specimens of Spartan Plus where the dendritic microstructure frequently yields somewhat greater variability. Ten hardness measurements were made on a bench-cooled specimen of as-cast Liberty and on each heat-treated specimen of each alloy. Previous experience (Brantley *et al.*, 1993; Carr *et al.*, 1993) has shown that the hardness values for specimens of a given high-palladium alloy subjected to the same casting and heat treatment conditions have relatively little variability. The values for the five groups of as-cast and heat-treated specimens for each alloy were examined for overall significant differences using one-way analysis of variance. The Student-Newman-Keuls multiple range test was used to determine which specific specimen groups were significantly different from each other. A level of $\alpha = 0.01$ was used for statistical significance.







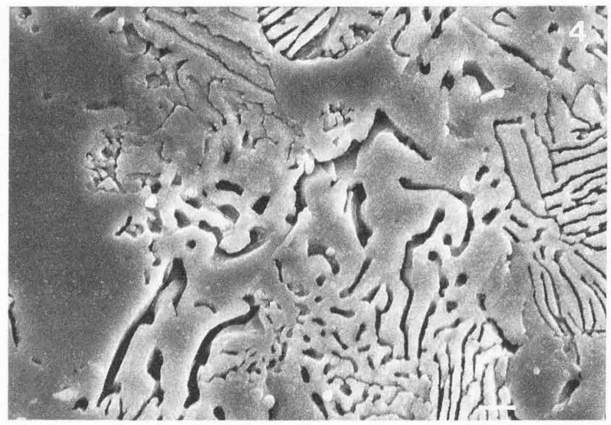


Figure 1. Near-surface microstructure of as-cast and bench-cooled (ACBC) Pd-Cu-Ga alloy Liberty, showing the lamellar eutectic microstructural constituent. Bar = 10 μm. The micrographs in Figs. 1-9 are secondary electron images.

Figure 2. Higher-magnification micrograph of the near-surface eutectic structure of ACBC Liberty. Bar = 1 μm.

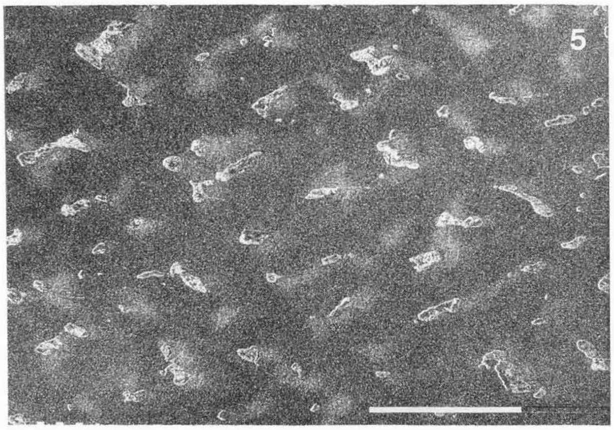
Figure 3. Near-surface microstructure of as-cast and rapidly quenched (ACRQ) Liberty, showing a substantial proportion of the rod-shaped eutectic morphology. Bar = 1 μm.

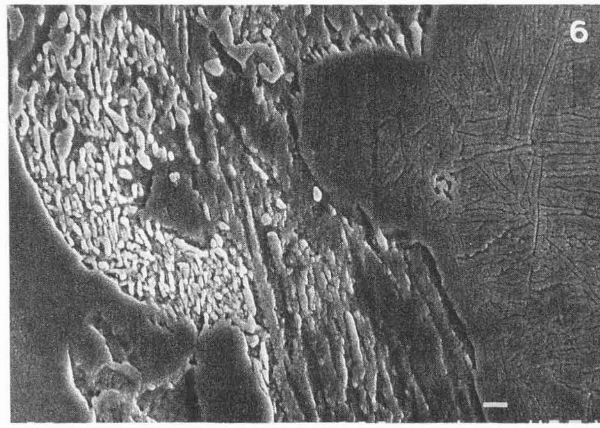
Figure 4. Another near-surface microstructure of ACRQ Liberty, where there is a greater proportion of the lamellar eutectic morphology compared to Fig. 3. Bar = 1 μm.

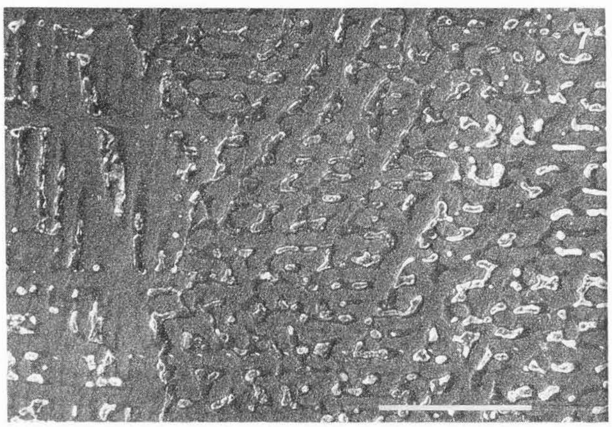
Results

Figs. 1 and 2 show the as-cast near-surface microstructure of Liberty after bench cooling (ACBC), and Figs. 3 and 4 show the as-cast near-surface microstructure of this alloy after rapid quenching (ACRQ). It was observed that the specimens generally exhibited a higher proportion of the rod-shaped eutectic morphology for the ACRQ condition compared to the ACBC condition where the lamellar (plate-shaped) morphology was generally observed.

Figs. 5 and 6 show the as-cast microstructure of Spartan Plus after bench cooling (ACBC), and Figs. 7 and 8 show the as-cast microstructure after rapid quenching (ACRQ). The scale of the dendritic microstructure was substantially smaller for the ACRQ condition compared to the ACBC condition. Comparison of Figs. 6 and 8 shows that the needle-shaped Widmanstätten precipitates (Brantley *et al.*, 1993) adjacent to the interdendritic regions for the ACBC condition were largely absent for the ACRQ condition. While Fig. 8 was somewhat overetched to facilitate the search for the Widmanstätten precipitates, it can also be seen that the interdendritic eutectic constituent for the ACRQ condition does not have the same lamellar appearance as for the ACBC condition in Fig. 6. The incidence of "hot tears" (Carr *et al.*, 1993) in Spartan Plus was much greater for the ACRQ condition, and Fig. 9 shows that the path of crack propagation for hot tears typically connected adjacent







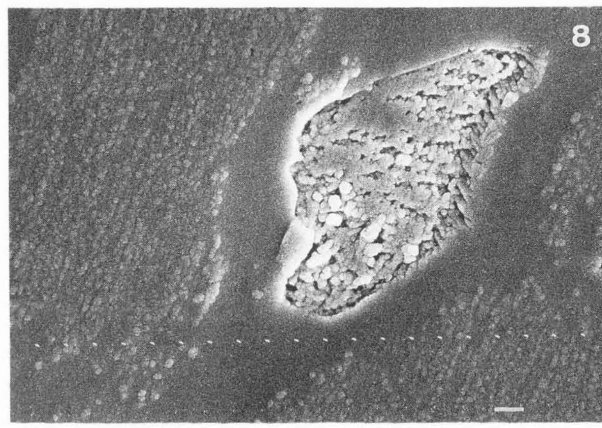


Figure 5. Low-magnification micrograph of the dendritic as-cast microstructure for the Pd-Cu-Ga alloy Spartan Plus in the ACBC condition. Bar = 100 μm.

Figure 6. High-magnification micrograph of ACBC Spartan Plus, showing the lamellar eutectic interdendritic constituent and the adjacent needle-shaped Widmanstätten precipitates. Bar = 1 μm.

Figure 7. Low-magnification micrograph of the dendritic microstructure for ACRQ Spartan Plus. Comparison with Fig. 5 indicates that the dendritic microstructure has a much finer scale for the ACRQ condition compared to the ACBC condition. Bar = 100 μm.

Figure 8. High-magnification micrograph of ACRQ Spartan Plus, showing changes in the interdendritic constituent and an absence of the Widmanstätten precipitates compared to the ACBC condition in Fig. 6. The pebbled appearance for the dendrites is due to microsegregation in this somewhat overetched specimen, and a denuded region of different composition can be seen surrounding the interdendritic region. Bar = 1 μm.

interdendritic regions.

Mean values and standard deviations of Vickers hardness are provided in Table 1 for the ACBC and ACRQ conditions of each alloy, and for heat treatments at 1200°, 1500° and 1800°F following rapid quenching. For both alloys the ACBC condition yielded the highest values of hardness. Alloy specimens in the ACRQ condition had significantly lower hardness than for the ACBC condition, although the differences probably would not have practical significance for the finishing and adjustment of cast restorations. The heat treatments at 1500° and 1800°F caused significant decreases in hardness compared to the ACBC condition for both alloys, although the effect of the heat treatment at 1500°F for Liberty would not be expected to have practical significance. Heat treatment at 1200°F resulted in significantly decreased hardness for Spartan Plus compared to the ACBC condition, although this difference may have little practical significance. There was no significant difference in the mean value of hardness for Liberty after heat treatment at 1200°F compared to the ACBC condition.

Table 1. Effect of solidification and heat-treatment conditions on Vickers hardness of Liberty and Spartan Plus Pd-Cu-Ga alloys.

Condition	Liberty		Spartan Plus	
As-cast and bench-cooled (ACBC)	333.8 ± 8.2	A	367.2 ± 15.7*	A
As-cast and rapidly quenched (ACRQ)	302.3 ± 12.7*	C	341.0 ± 19.4*	B
ACRQ followed by 1200°F heat treatment	327.7 ± 10.3	AB	334.4 ± 14.1	B
ACRQ followed by 1500°F heat treatment	315.5 ± 7.3	B	294.4 ± 6.5	C
ACRQ followed by 1800°F heat treatment	271.5 ± 9.6	D	275.4 ± 8.6	D

*N = 20 for the three specimen groups designated with an asterisk; for the other specimen groups, N = 10. Mean values for each alloy with the same letter are not significantly different from each other ($P > 0.01$).

Discussion

As discussed previously (Brantley *et al.*, 1993), the lamellar constituent in Liberty (Figs. 1-4) is interpreted as a eutectic structure, composed of the palladium solid solution (lighter-appearing phase) and a Pd_2Ga phase (darker-appearing and more heavily etched phase), that forms during solidification of the alloy. The present results demonstrate that the increase in solidification rate with the use of rapid quenching was insufficient to eliminate this constituent. It must be emphasized that this rapid quenching procedure, which was also used to retain the initial as-cast microstructure prior to heat treatment, would not be employed under normal dental laboratory conditions since the manufacturers recommend bench cooling of the Pd-Cu-Ga alloys after casting. Even with bench cooling, the high-palladium alloy castings are expected to solidify rapidly because the temperature of the investment mold is over 500°F lower than the melting ranges provided by the manufacturers for Liberty and Spartan Plus. The presence of a greater proportion of rod-shaped eutectic morphology (Chalmers, 1964; Winegard, 1964) for ACRQ Liberty (Figs. 3 and 4) compared to the ACBC condition (Figs. 1 and 2) is consistent with less time being available during solidification after rapid quenching for the growth of the lamellar eutectic morphology.

The appearances of some lamellar constituents adjacent to boundaries with the palladium solid solution matrix in Figs. 1-4 suggest that discontinuous precipitation may have occurred. Shewmon (1969) has discussed this type of phase transformation, where precipitation of a lamellar constituent occurs in cellular regions behind a moving grain boundary. The atomic diffusion and solute redistribution required for phase transformation occurs along this grain boundary, and all precipitates (Pd_2Ga lamellae or rods in the present case) in the two-phase cell would have same orientation relative to the matrix (palladium solid solution) grain in which they are embedded. Shewmon (1969) indicated that a requirement for discontinuous precipitation is the existence of a low-energy interface (*i.e.*, special orientation relationship) between the matrix phase and the precipitating phase, which results in movement of the grain boundary to minimize free energy.

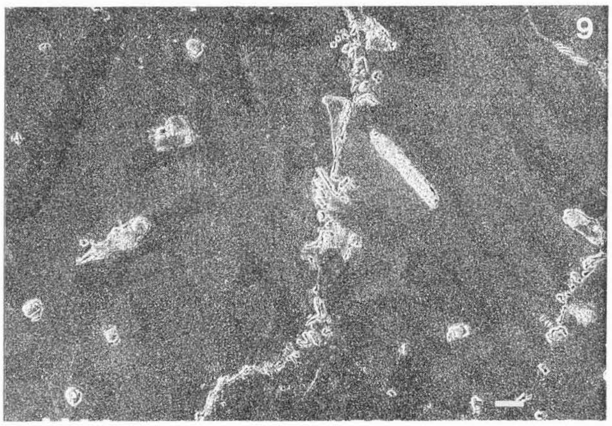


Figure 9. Micrograph of ACRQ Spartan Plus, showing two "hot tears" that connect adjacent interdendritic regions. Bar = 10 μm.

Cellular transformations have been observed in two dental gold casting alloys (Rajah, Midas; Jelenko) for all-metal restorations after heat treatment at 600 °F (Brantley *et al.*, 1986), whereas these alloys were single-phase for the standard as-cast and water-quenched condition. In contrast, the as-cast (bench-cooled or rapidly quenched) high-palladium dental alloy Liberty always contained the near-surface lamellar or rod-shaped constituent, along with a fine-grained microstructure of the palladium solid solution. As found in previous studies (Brantley *et al.*, 1993; Carr *et al.*, 1993), heat treatment simulating the dental porcelain firing cycles resulted in nearly complete elimination of the two-phase constituent. Moreover, the lamellar constituent in the near-surface region of as-cast Liberty was also no longer present after aging for five years at room temperature (Brantley *et al.*, 1995b).

The contrasting microstructures of the two dental gold alloys (Brantley *et al.*, 1986) and Liberty (Carr and Brantley, 1991; Brantley *et al.*, 1993; Carr *et al.*, 1993) for the as-cast and heat-treated conditions, as well as the loss of the near-surface lamellar constituent in the latter high-palladium alloy after room temperature aging (Brantley *et al.*, 1995b), suggest that this constituent does not form in Liberty by discontinuous precipitation. Under the present casting conditions, it was not possible to quench this Pd-Cu-Ga alloy rapidly enough to eliminate the two-phase constituent. Experiments are in progress to examine the effects of more rapid quenching procedures, including the use of room temperature molds rather than the normal (Carr *et al.*, 1993) investment temperatures (1400° - 1500°F) for high-palladium dental alloys.

Dramatic effects were evident when the solidification rate of Spartan Plus was changed, with the much finer scale of the dendritic structure for the ACRQ condition (Fig. 7) compared with the ACBC condition (Fig. 5), the longer lamellae of the interdendritic constituent for the ACBC condition (Fig. 6) and the near-absence of Widmanstätten precipitates adjacent to the interdendritic regions for the ACRQ condition (Fig. 8). As with Liberty, all of these phenomena can be explained by the reduced time available for atomic diffusion and phase transformation under the ACRQ conditions. Quantitative factors for the growth rate and interlamellar spacing during eutectic freezing are discussed elsewhere (Reed-Hill and Abbaschian, 1994).

As in our previous studies on the high-palladium dental alloys (Brantley *et al.*, 1993; Carr *et al.*, 1993; Brantley *et al.*, 1995b), measurements of Vickers hardness have been employed as a highly convenient method to assess relative changes in the mechanical properties of a given alloy as a result of various experimental conditions. Alternatively, a much more laborious procedure is necessary to determine specific values of modulus of elasticity, yield strength and percentage elongation, in which a cast alloy specimen with dimensions given in ANSI/ADA specification no. 5 is tested in uniaxial tension (Council on Dental Materials, Instruments and Equipment, 1988). If the rate of work hardening does not vary, there is an empirical proportionality between Vickers hardness and yield strength (Dieter, 1986). Research in our laboratory has shown that cast high-palladium (Stewart *et al.*, 1992) and gold-based (Reisbick and Brantley, 1995) dental alloys typically fracture along planes containing substantial porosity. Consequently, the ductility of a cast high-palladium alloy is strongly influenced by the presence of casting defects, in addition to the composition and microstructural phases. The modulus of elasticity is generally considered to be a structure-insensitive property (Dieter, 1986) and thus might not be expected to change greatly for the different experimental conditions of the two high-palladium alloys in the present study. Additional research is currently in progress in our laboratory to compare the mechanical properties of representative as-cast and heat-treated high-palladium alloys and test this hypothesis.

The submicron precipitate network found by Odén and Herø (1986) in an as-cast Pd-Cu-Ga alloy has also been recently observed in as-cast and bench-cooled Liberty and Spartan Plus in our laboratory (Cai, 1996), using transmission electron microscopy (TEM). TEM observations of both alloys after annealing at 1800°F and water-quenching indicated minimal changes in their ultrastructure, compared to the ACBC condition. Previous SEM observations (Brantley *et al.*, 1993; Carr *et al.*, 1993) have shown that heat treatment simulating porcelain firing cycles causes nearly complete elimination of the as-cast eutectic structure in Liberty and the dendritic structure in Spartan which has a nearly identical composition to that of Spartan Plus (Brantley *et al.*, 1995a). The substantial decreases found in the hardness of Liberty and Spartan after simulated porcelain firing (Carr *et al.*, 1993) were similar to those in Table 1 for the heat treatments at 1500° and 1800°F. Another recent study in our laboratory (Wu, 1996) has established a correlation between changes in Vickers hardness of representative high-palladium alloys due to heat treatment at temperatures from 200° to 1800°F and microstructural changes observed with the SEM. Moreover, discontinuous precipitates formed during elevated temperature heat treatment of high-palladium alloys were observed in this study. These extensive results will be described in separate publications.

In closing, it should be noted that attempts to modify the lamellar constituent normally found in the as-cast and bench-cooled Pd-Cu-Ga dental alloys can have important clinical consequences. In a recent review article (Cai *et al.*, 1995), the potential role of this microstructural constituent for the *in vivo* corrosion resistance and biocompatibility of these alloys has been emphasized, and it is recommended that the Pd-Cu-Ga dental alloys should be heat-treated before use in all-metal restorations. The heat treatment associated with the normal porcelain firing cycles is sufficient to largely eliminate this constituent in alloys used for metal-ceramic restorations (Carr *et al.*, 1993).

Conclusions

The increase in solidification rate achieved with rapid quenching following dental laboratory casting was insufficient to eliminate the as-cast eutectic and dendritic microstructures of the two representative Pd-Cu-Ga alloys found with conventional bench cooling. The observed effects from the rapid quenching procedure of more rod-shaped eutectic morphology in one alloy and a finer scale of the dendritic microstructure in the other alloy were consistent with the principles of solidification. The heat treatment responses of the two high-palladium dental alloys over the temperature range from 1200° to 1800°F spanning the porcelain firing cycles are attributed to the elimination of the as-cast eutectic constituent in one alloy and the as-cast dendritic microstructure in the other alloy. Additional experiments with even more rapid quenching after casting and other strategies may provide useful information on the relative contributions of eutectic solidification and discontinuous precipitation to formation of the as-cast constituents with lamellar and rod-shaped morphology.

Acknowledgements

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Discussion with Reviewers

M.D. Bagby: Are there any single-phase high-palladium alloys? Would such single-phase alloys, if they exist, have any clinical advantages or disadvantages compared to the alloys of this study?

Authors: After investigating many high-palladium alloys, we have not found any that have single-phase microstructures. This result would be anticipated from consideration of the Pd-Ga phase diagram and the practical goals of the manufacturers for melting and casting temperature ranges, as well as the compositions necessary to achieve other property requirements for these alloys. Some Pd-Ga alloys do contain relatively small amounts of secondary phases, as viewed in the scanning electron microscope. In general, while single-phase alloys would be expected to have superior corrosion resistance (as well as higher ductility and decreased yield strength and hardness) compared to multi-phase alloys, the *in vitro* corrosion resistance of the high-palladium alloys compares favorably to gold-based alloys (Cai, 1996), and the mechanical properties of recently marketed alloys are excellent.

R.A. Fournelle: Table 1 shows that the hardness of both alloys decreases as the annealing temperature increases. Do the authors feel that the precipitate structure is being redissolved or is the precipitate structure being overaged?

Authors: Extensive recent scanning microscopic observations (Wu, 1996) suggest that a substantial portion of the hardness of the Liberty alloy is associated with a newly discovered grain boundary phase. The decrease in hardness at higher annealing temperatures appears to be principally due to the dissolution of the as-cast eutectic structure, although transformation of discontinuous precipitates that form during heat treatment may also have a role. For the Spartan Plus alloy, research in our laboratory has indicated that the substantial decrease in hardness due to heat treatment is associated with transformation of the hard interdendritic region into a variety of secondary phases (Carr *et al.*, 1993).

R.A. Fournelle: While the authors have pointed out that the needle-shaped Widmanstätten precipitates present in ACBC Spartan Plus (Fig. 6) are largely absent in the ACRQ alloy (Fig. 8), they have not commented on the apparent spheroidal precipitates in the ACRQ alloy which may replace the Widmanstätten precipitates in the ACBC alloy. This might be an important consequence of increasing the cooling rate. Can the authors comment on this point?

Authors: We concur that the change in precipitate morphology appears to be a kinetic effect associated with the greater cooling rate for the rapidly quenched condition, compared to the standard bench-cooling after casting.

R.A. Fournelle: The authors might comment on the precipitate-free zones around the interdendritic regions for both the ACBC (Fig. 6) and ACRQ (Fig. 8) conditions of Spartan Plus. Are these zones due to microsegregation, solute depletion or vacancy depletion?

Authors: At present we have no experimental evidence to suggest which of these hypotheses for formation of the precipitate-free zones is correct. We are currently completing a study comparing the heat treatment response of three dendritic Pd-Cu-Ga alloys and plan to perform x-ray energy-dispersive spectroscopic analyses on these denuded zones.

R.A. Fournelle: A low-energy interface between precipitate and matrix is not necessary for discontinuous precipitation. In some systems (Pb-Sn, Fe-Ni-Ti), there are low-energy interfaces; in other systems (Cu-In), there are not. Whether or not there is a low-energy interface depends only on the crystal structures of the precipitate and matrix and how well the atoms in each match up on certain crystallographic planes. Judging from the irregularity and curvature of many of the Pd_2Ga lamellae, I suspect that there is no well-defined orientation relationship or habit plane between solid solution matrix and the precipitate in the ACBC alloy.

Authors: We appreciate receiving these important points from Professor Fournelle. Extensive research on the detailed heat treatment response of the Liberty alloy (Wu, 1996) has shown that discontinuous precipitates with regular fine-scale lamellae form when this alloy is annealed at approximately 1200° to 1400°F. While we have obtained microhardness data and x-ray diffraction information for these precipitates, further research is necessary to establish their orientation relationship with the parent palladium solid solution matrix.

H.J. Mueller: The authors have the philosophy that, for a liquid within a composition range controlled by a eutectic reaction and cooled at a super-fast rate, the two-phase solid structure predicted from thermodynamics can be replaced with a homogeneous structure. Barring amorphous alloys and mechanical alloying, this does not appear to be consistent with phase rule principles. It appears that greater emphasis should be placed on post-casting heat treatments, although again the as-cast structures can only be modified to the extent of eliminating the heterogeneity created by the nonequilibrium cooling. Can the authors comment on these points?

Authors: Our hypothesis was that, since formation of the eutectic structure in these as-cast Pd-Cu-Ga alloys requires diffusion and solute redistribution, very rapid cooling might yield a metastable single-phase structure. This eutectic constituent is a nonequilibrium structure and tends to disappear after long aging times at room temperature (Brantley *et al.*, 1995b), as well as after annealing at elevated temperatures (Wu, 1996).

H.J. Mueller: Although this reviewer is not questioning the hardness results, there would appear to be some difficulty in explaining that the ACRQ group for both alloys was statistically softer than the ACBC group and that post-(ACRQ) casting heat treatment also softened the alloys. The latter data indicate that the heat treatment processing eliminated the heterogeneities and residual stresses retained from the nonequilibrium cooling. One would think that a more severe rapid quenching (ACRQ), instead of bench-cooling (ACBC), would generate more heterogeneities and residual stress. Can the authors comment on these points?

Authors: The main effect of the rapid quenching on the hardness (and presumably yield strength) may be to alter the morphology of the eutectic constituent in the two as-cast Pd-Cu-Ga alloys studied. We concur that the residual stresses retained in the castings due to the nonequilibrium solidification conditions should be greater for the ACRQ condition, compared to the standard ACBC condition. As previously noted, our SEM observations suggest that microstructural changes in the annealed alloys account for the decreased hardness.

G.W. Marshall, Jr.: The authors have used a one-way analysis of variance (ANOVA) to compare the hardness results obtained with each alloy for the different solidification and heat treatment conditions. The five sample groups are not strictly independent, since these groups came from only three parent castings and repeated measurements of hardness were made after the various treatments. Thus, a repeated-measures multi-factorial ANOVA seems to be needed. Can the authors comment on their choice of statistical analysis?

Authors: For each alloy, a single bench-cooled casting (yielding two sectioned half-coping specimens) was used for the ACBC hardness measurements, whereas two rapidly quenched castings (yielding four sectioned half-coping specimens) were used for hardness measurements of the ACRQ condition and after the heat treatments. SEM examination showed that the metallurgical structures for the ACBC and ACRQ castings of each alloy were different. We considered the half-coping specimens from the same parent ACRQ casting to be potentially independent, because of possible orientation variations for the eutectic constituent (Liberty) or the dendritic microstructure (Spartan Plus). A single half-coping ACRQ specimen of each alloy was heat treated at each of the three temperatures, and specimens from two different (independent) parent castings were necessarily used. Each heat-treated specimen for a given alloy must have a different metallurgical structure to some extent and would also be independent. Since the two Pd-Cu-Ga alloys are microstructurally very distinct from each other, one-way ANOVA thus appeared to be appropriate for this study. A multiple range test was used to determine which experimental groups were significantly different from each other.

G.W. Marshall, Jr. and Reviewer IV: The authors have failed to note that hardness measurements may not reflect the bulk properties of the castings, especially for alloys that form near-surface precipitates.

Authors: The Vickers hardness measurements were made on the bulk portion of each heat-treated specimen, after careful removal of the near-surface region by metallographic polishing and etching, and should directly reflect the yield strength for the bulk heat-treated alloy, provided that the work hardening characteristics do not vary for the different solidification or heat treatment conditions. We plan to test this hypothesis for the as-cast (ACBC) and simulated porcelain-firing heat treatment conditions of representative Pd-Cu-Ga alloys in forthcoming experiments. As the reviewers point out, the surface hardness of an alloy that forms near-surface precipitates should be substantially different from that of the bulk alloy.