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ABSTRACT

A transmission electron microscopic (TEM) investigation was performed on four representative commercial high-palladium dental alloys in both as-cast and simulated porcelain-firing heat-treated conditions. The results indicated that a tweed ultrastructure (space between striations ~ 20 nm) associated with shear strain on the \{110\} planes in the \langle110\rangle directions of the fcc lattice is the common feature for both the Pd-Cu-Ga and Pd-Ga alloys. An overall band structure (band width ~ 60-100 nm) was associated with the tweed structure for both the Pd-Cu-Ga and Pd-Ga alloys. The persistence of the tweed ultrastructure in the specimens of the two Pd-Cu-Ga alloys annealed at 1,800°F and subsequently quenched in ice water indicated that the formation of this structure occurs by a rapid martensitic transformation. The transformation from the palladium solid solution into the fct phase of the tweed structure may only involve small atomic movements, based on a previously proposed the fcc-fct transformation. The formation of the tweed ultrastructure in these alloys may be associated with the minimization of strain energy arising from the peritectoid transformation, and \{100\} and \{110\} forbidden reflections observed for the \langle001\rangle zone of all the high-palladium alloys studied suggest
that the fct phase are ordered. The band structures observed were considered to be antiphase boundaries between different domains of the ordered structure.

*In vitro* corrosion resistance of five representative commercial high-palladium dental alloys in the as-cast and simulated porcelain-firing heat-treated conditions was evaluated by potentiostatic/potentiodynamic polarization, using two deaerated stagnant electrolytes: 0.09% NaCl and the Fusayama solutions. The deaerated Fusayama solution was considered to be a more corrosive environment, compared to the 0.09% NaCl solution, based on the results of this study. The Pd-Cu-Ga and Pd-Ga alloys showed similar electrochemical properties. The somewhat active electrochemical behavior for the two heat-treated Pd-Cu-Ga alloys, Liberty and Spartan Plus, was attributed to casting defects and microstructural phases on the test specimen surface. The results from this *in vitro* study indicated that the high-palladium alloys in both the as-cast and heat-treated conditions show either an active-passive transition or retain passivity under electrochemical conditions similar to the oral environment. Heat-treated Freedom Plus had an unstable oxide film form on the surface during anodic polarization and appeared to have a tendency for crevice corrosion in the Fusayama solution.

With the widespread use of high-palladium alloys for metal-ceramic and all-metal restorations in many countries, many adverse effects related to these alloys have been publicized lately. This study provided a systematic summary of published information about the biocompatibility of palladium and some palladium compounds. The current literature on the biocompatibility of high-palladium dental alloys is discussed with particular attention to certain metallurgical and microstructural factors which may have
important roles *in vivo*. Based on the currently available information, high-palladium dental alloys appear to be biocompatible materials, except for the hypersensitivity problem associated with these alloys in certain populations. Until a reliable method to test the hypersensitivity of a subject to high-palladium alloys is developed, it is still the responsibility of a dentist to choose the appropriate dental alloy for his or her patient.
To My Family
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First and foremost, I would like to express my sincere gratitude to Dr. William A. Brantley, my mentor and academic adviser, for his guidance, encouragement, inspiration and friendship during my last six years study at the Ohio State University. I would like to thank Dr. William A. T. Clark for his guidance and constant support during the transmission electron microscopic portion of this study and to thank Dr. Stanley G. Vermilyea for his guidance and support during the electrochemical corrosion portion of this study. My appreciation goes to Dr. William M. Johnston for taking time from his busy schedule to serve as my committee member. My special gratitude is extended to Hendrick O. Colijn for his patience and assistance in my TEM study. Lastly, I would like to acknowledge Professor Gerald Frankel of the Department of Materials Science and Engineering, the Graduate School Representative on my Dissertation Committee, for numerous constructive comments on the possible electrochemical corrosion behavior of the high-palladium alloys.

Finally, I would like to thank my wife, Dr. Xiaohong Chu, for her understanding, encouragement and love through these years.
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CHAPTER 1

INTRODUCTION

High-palladium dental casting alloys (containing 75-80 wt.% Pd) have been used extensively for metal-ceramic restorations (Goodacre, 1989; Carr and Brantley, 1991), as well as for implant-supported prostheses (Stewart et al., 1992), since their introduction in the early 1980’s (Schaffer, 1983). These multiple uses are possible because of the excellent mechanical properties and much lower cost of the high-palladium alloys, compared to traditional gold-based alloys.

High-palladium dental alloys are based on either the Pd-Cu-Ga or Pd-Ga system, and contain additional elements such as In, Sn, Ag, Au, Co, Ru, Re and B. On the Pd-rich side of the Pd-Ga phase diagram (Fig. 2.1), there is a peritectoid reaction at 850°C and about 82 wt.% Pd - 18 wt.% Ga, where the orthorhombic Pd\textsubscript{2}Ga and the face-centered cubic (fcc) Pd-rich terminal solid solution transform upon cooling into Pd\textsubscript{2}Ga with the face-centered tetragonal (fct) structure. It has been observed that Pd-Cu-Ga alloys usually have much higher hardness and yield strength compared to the Pd-Ga alloys (Odén and
Here, 1986; Carr and Brantley, 1991; Brantley et al., 1993). Due to the complex compositions and multiple phases, the strengthening mechanisms for the high-palladium alloys are complicated. The presence of multiple solute elements in the palladium solid solution matrix (Mezger et al., 1988) results in substantial solid solution strengthening. In a transmission electron microscopic (TEM) investigation of an as-cast Pd-Cu-Ga alloy (Odén and Here, 1986), a complex, thin (5-25 nm) lamellar structure was observed. The existence of two alternating fct Pd$_5$Ga$_x$Cu$_{1-x}$ phases with different lattice parameters was proposed. It was considered that these fct phases would provide considerable resistance to dislocation movement and hardening of the alloy. An earlier x-ray diffraction (XRD) study (Khabliyev et al., 1980) on a non-dental Pd-Cu-Ga alloy of similar composition also showed the presence of two fct phases after annealing of the wrought alloy. The alloy strengthening after annealing was attributed to the formation of these two phases. In a subsequent study by Mezger et al. (1988) on commercial high-palladium dental alloys using XRD and microprobe analysis, the fcc phase of the palladium solid solution matrix dominated the spectra for all alloys. Body-centered cubic and simple cubic secondary phases were reported, and Cu$_5$Ga and PdGa phases were tentatively identified. However no fct structures were detected. Though many studies have been published on the metallurgical structures of these alloys (Asgar et al., 1986; Mezger et al., 1988; Böning and Walter, 1990; Carr and Brantley, 1991; Brantley et al., 1993; Brantley et al., 1995a), there is still considerable uncertainty about the metallurgical structures of these alloys. It was considered imperative to further elucidate the ultrastructures of the high-palladium alloys with TEM in order to develop new alloys with improved properties.
Corrosion resistance is a very important property for dental alloys, in addition to other properties such as strength, ductility and casting accuracy. Corrosion of dental alloys in the oral environment not only results in the deterioration of a restoration, but also involves a release of ions which is directly related to the biocompatibility of the alloys. The potentiostatic/potentiodynamic polarization test is the major method commonly used to study the corrosion of dental alloys (Holland et al., 1986; Holland, 1990). Since the introduction of high-palladium dental alloys more than a decade ago, several studies have reported their corrosion resistance (Sumitra et al., 1983; Paradiso 1984; Lane et al., 1985; Mezger et al., 1985; Mezger et al., 1989; Goehlich and Marek, 1990; Meyer and Reclaru, 1995). In general, high-palladium alloys exhibited superior in vitro corrosion resistance, compared to other types of dental alloys. Although substantial research has been performed over the last decade to evaluate the corrosion resistance of the high-palladium alloys, the detailed relationships among the corrosion properties, microstructures and compositions for these alloys are still not available.

In this study, potentiostatic/potentiodynamic polarization tests were performed for five representative commercial high-palladium alloys in the as-cast and simulated porcelain-firing heat-treated conditions, using two deaerated stagnant electrolytes: 0.09% NaCl and the Fusayama solutions. These electrolytes had previously been selected by numerous investigators to study the in vitro corrosion resistance of dental alloys.

With the widespread use of high-palladium alloys for metal-ceramic and all-metal restorations in many countries, especially in Europe, many adverse effects related to these alloys have been publicized lately. A recent article in the German press (Der Spiegel, 1993)
indicated that large numbers of dental patients with palladium alloy crowns had experienced a variety of health problems, such as headaches, joint pains and feelings of exhaustion. In March 1993, a special commission under the auspices of the German Ministry of Health recommended that Pd-Cu-based alloys no longer be used in dentistry (The Dentist's Weekly, 1993). This adverse experience has stimulated considerable recent interest in the biocompatibility of the high-palladium alloys. This study provided a systematic summary of published information about the biocompatibility of palladium and some palladium compounds. The current literature on the biocompatibility of high-palladium dental alloys is discussed with particular attention to certain metallurgical and microstructural factors which may have important roles in vivo. Recent research on the immune system responses to foreign substances has also been reviewed to provide fundamental information about the complex cellular mechanisms for the hypersensitivity to these alloys.
CHAPTER 2

TRANSMISSION ELECTRON MICROSCOPIC INVESTIGATION OF HIGH-PALLADIUM DENTAL CASTING ALLOYS

2.1 Introduction

High-palladium dental casting alloys (containing 70-85 wt.% Pd) have been one of the alternatives to traditional gold alloys for metal-ceramic restorations since their introduction more than ten years ago (Schaffer, 1983). These alloys are based on either the Pd-Cu-Ga or Pd-Ga system, and contain additional elements such as In, Sn, Ag, Au, Co, Ru, Re and B. Because of their excellent mechanical properties and much lower price compared to alternative gold alloys, high-palladium alloys have gained substantial popularity during the last decade (Goodacre, 1989; Carr and Brantley, 1991).

Both equiaxed polycrystalline microstructures and dendritic microstructures with multiple phases have been observed for the high-palladium alloys in the as-cast condition (Asgar et al., 1986; Mezger et al., 1988; Böning and Walter, 1990; Carr and Brantley, 1991; Brantley et al., 1993). Lamellar eutectic microstructures observed in Pd-Cu-Ga alloys have been interpreted as consisting of Pd₂Ga and Pd solid solution phases, based on the Pd-Ga
phase diagram (Brantley et al., 1993). The existence of Cu and In in the alloy reduces the solubility of Ga in Pd (Cascone, 1984) and, along with rapid solidification of the alloy under dental casting conditions (Phillips, 1991), results in increased percentages of eutectic constituent in the microstructure, particularly near the surfaces and in thin sections of castings where the rate of solidification is most rapid (Carr and Brantley, 1991; Brantley et al., 1993). For Pd-Cu-Ga alloys with dendritic microstructures, lamellar eutectic structures have been observed in the interdendritic regions, while needle-shaped Widmanstätten precipitates occurred in the dendrites (Brantley et al., 1993; Brantley et al., 1995a).

Significant microstructural changes were observed for Pd-Cu-Ga alloys after simulated porcelain firing heat treatment (Brantley et al., 1993; Carr et al., 1993). For one Pd-Cu-Ga alloy (Liberty, Jelenko), the large amount of lamellar constituent at the near-surface region of the as-cast alloy almost disappeared after heat treatment, and there was largely homogenization of the overall elemental composition within grains of the bulk specimens. The as-cast dendritic microstructure of another Pd-Cu-Ga alloy (Spartan, Williams/Ivoclar) was nearly eliminated after heat treatment, and a new rectangular-shaped phase was observed. In contrast to the Pd-Cu-Ga alloys, simulated porcelain firing heat treatment caused much smaller changes in the bulk microstructures of two Pd-Ga alloys (Legacy, Jelenko; Protocol, Williams/Ivoclar).

On the Pd-rich side of the Pd-Ga phase diagram (Fig. 2.1), there is a peritectoid reaction at 850°C and about 82 wt.% Pd - 18 wt.% Ga, where Pd\textsubscript{2}Ga and the Pd-rich terminal solid solution transform upon cooling into Pd\textsubscript{5}Ga. This peritectoid reaction was
reported to occur very slowly (Schubert et al., 1959), which is consistent with the nature of this solid-state transformation (Rhines, 1956). At the relatively rapid solidification conditions in dental casting (Phillips, 1991), it would be expected that substantial bulk transformation of the Pd solid solution and Pd$_2$Ga to Pd$_3$Ga cannot occur.

Due to the complex compositions and multiple phases, the strengthening mechanisms for the high-palladium alloys are complicated. The presence of multiple solute elements in the palladium solid solution matrix (Mezger et al., 1988) results in substantial solid solution strengthening (Odén and Herrera, 1986). The strengthening effects of In and Sn in some palladium-based alloys of lower Pd content have also been related to an ordering process involving the formation of Pd-rich regions by spinodal decomposition (German, 1982). In a transmission electron microscopic (TEM) investigation of an as-cast Pd-Cu-Ga alloy (Odén and Herrera, 1986), a complex, thin (5-25 nm) lamellar structure was observed. The existence of two alternating face-centered tetragonal (fct) Pd$_3$Ga$_x$Cu$_{1-x}$ phases with different lattice parameters was proposed. It was considered that these fct phases would provide considerable resistance to dislocation movement and hardening of the alloy.

An earlier x-ray diffraction (XRD) study (Khabliyev et al., 1980) on a nondental Pd-Cu-Ga alloy of similar composition also showed the presence of two fct phases after annealing of the wrought alloy. The alloy strengthening after annealing was attributed to the formation of these two phases. In a subsequent study by Mezger et al. (1988) on commercial high-palladium dental alloys using XRD and microprobe analysis, the face-centered cubic (fcc) phase of the palladium solid solution matrix dominated the spectra for
all alloys. Body-centered cubic and simple cubic secondary phases were reported, and $\text{Cu}_2\text{Ga}$ and $\text{PdGa}$ phases were tentatively identified. However no fct structures were detected.

Despite the extensive use of high-palladium alloys in metal-ceramic restorations and implant-supported prostheses (Stewart et al., 1992), and the foregoing publications, there is still considerable uncertainty about the metallurgical structures of these alloys. The objective of this study was to investigate the metallurgical structure of several representative commercial Pd-Cu-Ga and Pd-Ga dental alloys with transmission electron microscopy and energy-dispersive x-ray spectroscopic (EDS) analysis, and to elucidate the possible strengthening mechanisms in these alloys.

2.2 Materials and Methods

Two Pd-Cu-Ga alloys and two Pd-Ga alloys used for dental restorations were selected for this study. These alloys had previously been studied extensively by optical microscopy, electron microprobe analysis, scanning electron microscopy and x-ray diffraction (Carr and Brantley, 1991; Carr et al., 1993; Brantley et al., 1993; Brantley et al., 1995a). The compositions and manufacturers of these alloys are listed in Table 2.1.

Alloy castings were prepared in the shape of a maxillary central incisor coping (Carr and Brantley, 1991). Each wax pattern was sprued and invested individually with a carbon-free, phosphate-bonded investment (Cera-Fina, Whip-Mix Corp., Louisville, KY). A peak burnout temperature of 1,400°F (760°C) was chosen, based on recommendations
from the alloy manufacturers, and burnout was accomplished using a dental furnace (Accu-
Therm II 1000, J.F. Jelenko & Co., Armonk, NY). Each alloy was melted in an individual
ceramic crucible with a conventional multiorifice gas-oxygen torch. Casting was performed
in air with a broken-arm centrifugal casting machine (Kerr/Sybron, Romulus, MI).
Following standard dental laboratory procedures, each casting was bench-cooled in air. The
sprue of each casting was sectioned parallel to the base into several disks with thickness of
about 1 mm, using a low-speed, water-cooled saw (Vari/Cut VC-50, Leco Corp., St. Joseph,
MI) with a diamond-coated blade. For each alloy, TEM specimens were prepared in both
the as-cast and heat-treated conditions. Heat treatment included both the oxidation and
porcelain firing procedures recommended by the manufacturer. For the Spartan Plus and
Protocol alloys, oxidation was performed in a dental porcelain furnace (Ultra-Mat CDF,
Unitek/3M, Monrovia, CA) at reduced atmospheric pressure (720 mm Hg) with a 5 minute
hold at the 1,850°F (1,010°C) peak temperature. The Liberty and Legacy alloys were
oxidized in air at the same peak temperature but without any hold. Subsequent heat
treatment in this porcelain furnace followed the full firing cycles for Vita VMK dental
porcelain (Vident, Baldwin Park, CA), simulating the application of one opaque porcelain
layer, two body porcelain layers and a glaze (Carr et al., 1993). The specimens were
subsequently bench cooled in air, following recommended dental laboratory practice. For
the Liberty and Spartan Plus alloys, additional specimens were prepared from castings
annealed at 1,800°F (982°C) for 10 minutes and quenched in ice water.
The 1 mm thick disks were further thinned by hand grinding on wet SiC metallographic abrasive paper strips through 320, 400 and 600 grit, and polished with 5 μm SiC abrasive paper until a thickness of about 50 to 60 μm was attained. Then 3 mm diameter foil specimens were produced, using a special punch (LADD Research Industry, Burlington, VT).

The desired foil specimens of the high-palladium alloys for TEM examination were thinned using both twin-jet electrochemical polishing and ion milling. The specimens that had been metallographically polished were initially thinned on a twin-jet polisher (Tenupol 2, Struers, Copenhagen, Denmark), with the aid of an electrolyte having the following composition (vol. %): 70% acetic acid, 18% glycerol, 8% butyl cellosolve and 4% perchloric acid (Witcomb, 1989). The jet polishing was performed at 20 V and 6°C, using a slow flow rate. Each specimen was jet polished for approximately 2 minutes without any perforations being produced. Then the jet-polished specimens were finally thinned using an argon ion mill (Dual Ion Mill, Model 600, Gatan, Warrendale, PA). The ion mill was operated at a constant voltage of 6 kV, using dual ion guns at 1 mA total current. Surface artifacts on the thin foil specimens, which were observed after the ion milling on both the Pd-Cu-Ga alloys and the Pd-Ga alloys, were completely removed by 20 minutes of plasma cleaning (Plasma Cleaner, EA Fischione, Pittsburgh, PA).

Microstructures of the specimens were examined using two transmission electron microscopes (EM400T and CM200, Philips, Eindhoven, The Netherlands). The TEM photomicrographs (bright-field images) of the ultrastructures of the alloys were obtained at
a variety of magnifications from 22 kX to over 100 kX. Use of selected-area electron
diffraction (SAED) and dark-field images aided in the analyses of the photomicrographs.
Conventional standardless energy-dispersive x-ray spectroscopic (EDS) spot analyses were
performed on the foil specimens, using the EDAX system and EDAX MX TM Version
1.002 computer software (EDAX International, Mahwah, NJ).

2.3 Results

As previously noted, surface artifacts were observed on the thin foil specimens after
ion milling for both the Pd-Cu-Ga alloys and the Pd-Ga alloys. Twenty minutes of plasma
cleaning effectively removed these artifacts. Figure 2.2 is a bright-field image of as-cast
Spartan Plus, obtained without the use of plasma cleaning. Lamellar structures in the near-
horizontal direction are superimposed on a fine tweed structure (Tanner, 1966; Robertson
and Wayman, 1983a). Broad contours due to the uneven foil thickness are also visible.
After the plasma cleaning these artificial lamellar structures were removed, and only the
true tweed structure of the alloy remained (Fig. 2.3).

2.3.1 Pd-Cu-Ga Alloys

A pronounced band structure, with individual bands lying approximately along
<100> directions and having widths of 60 - 100 nm, was observed on the dark-field images
of as-cast Liberty (Fig. 2.4). Very fine striations with spacing ~ 20 nm, frequently oriented
90° to each other in <011> directions and forming a tweed structure (Robertson and
Wayman, 1983a), can be seen within these bands. Some bands with striations in a $<010>$
average direction can be seen in the micrograph. Figures 2.5, 2.7 and 2.9 are the bright-
field images taken from the same area with the incident beam direction close to the $[011]$ direction. Figures 2.6, 2.8 and 2.10 are the SAED patterns corresponding to each of the three images. Indexing of the SAED patterns is discussed in texts on transmission electron microscopy (Edington, 1976). In Fig. 2.5, where the $(200)$ reflection (reciprocal lattice vector $\mathbf{g}$) was excited, the tweed structure consisted of striations along the $<11\bar{1}>$ and $<1\bar{1}1>$ directions, which are the traces of the $(0\bar{1}1)$ and $(10\bar{1})$ planes, respectively. The average spacing of the striations was $\sim 20$ nm. Diffuse streaks extending in the direction of
$<01\bar{1}>$ and $<10\bar{1}>$ perpendicular to the striations were observed on the $(200)$ reflections in the corresponding SAED pattern (Fig. 2.6); diffuse streaks along the $<200>$ direction were also observed. When the excited condition (g vector) was changed to the $11\bar{1}$ reflection (Fig. 2.7), the striations along the $(10\bar{1})$ plane disappeared, and only striations lying along the $(0\bar{1}1)$ plane remained. On the corresponding SAED pattern (Fig. 2.8), diffuse streaks again extended in the direction perpendicular to the striations. When the $1\bar{1}1$ reflection was excited (Fig. 2.9), the striation along the $(0\bar{1}1)$ plane disappeared, and a striation lying along the $(10\bar{1})$ plane reappeared. On the corresponding SAED pattern (Fig. 2.10), diffuse streaks again extended in the direction perpendicular to the striations. It is obvious that there is a one-to-one correspondence between the streaks and the sets of striations, and the striations show the same extinctions as the diffraction streaks.
The SAED pattern of Liberty for the <011> zone (Fig. 2.11) corresponds to a face-centered cubic (fcc) lattice with no additional spots. Diffuse streaks were observed on the {200} and {111} reflections. For the {111} reflections, the diffuse streaks lie in two directions, which are normal to the {110} striations seen in the tweed contrast, while for the {200} reflections additional diffuse streaks lie along the <200> direction. Although no figure has been shown, diffuse streaks were also observed on the SAED pattern for the <111> zone. The SAED pattern for the <001> zone (Fig. 2.12) also shows a lattice similar to the fcc, but with diffuse streaks on the {220} and {200} reflections along the <110> directions and one <100> direction. The streaks in the <100> direction on the {220} and {200} reflections are on the lower-angle side of these reflections which gives rise to only two-fold symmetry to this pattern. Forbidden spots for the {110} and {100} reflections in the fcc lattice are also revealed on this diffraction pattern.

The EDS spot analyses of the band structures of as-cast Liberty indicated that compositional differences between the neighboring bands are not significant. The individual striation regions were too small for conventional EDS analysis with the TEM. The result of the EDS spot analyses are listed in Table 2.2.

A similar tweed microstructure (Fig. 2.13) and corresponding SAED patterns were observed for Liberty specimens subjected to simulated porcelain firing heat treatment and to annealing at 1800°F.

The other Pd-Cu-Ga alloy Spartan Plus also exhibited a tweed microstructure (Fig. 2.14). Figures 2.15-2.19 are bright-field images of as-cast Spartan Plus from the same area.
with the incident beam direction close to the [011] zone axis. Figure 2.14 shows a tweed microstructure with an average distance between striations of ~20 nm. Figure 2.15 exhibits a band structure with individual band widths of 60 - 100 nm, and the tweed structure can be seen inside some bands. These two types of ultrastructures were observed for different regions on the same specimen. The electron diffraction pattern indicated that these two areas have the same crystallographic orientation. In Figs. 2.14 and 2.15, where the same 200 reflection was excited, the two striations of the tweed microstructure lay along the (01\bar{1}) and (10\bar{1}) planes. In Figs. 2.16 and 2.17 and in Figs. 2.18 and 2.19, where the (11\bar{1}) and (1\bar{1}1) reflections, respectively, were excited, only striations along one of the \{011\} planes appear for each set of images. Diffuse streaks extending along the directions perpendicular to the striations, in the same manner found for Liberty, were observed on the corresponding SAED patterns for each of the bright-field image conditions. The only difference in these ultrastructures compared to those of Liberty is that the diffuse streaks on \{200\} reflections were only in the directions perpendicular to the striations; no streaks in the \(<200>\) directions were visible.

An fcc lattice with diffuse streaks on the \{200\} and \{111\} reflections in the direction perpendicular to the striations is shown in the SAED pattern of the \:<011>\ zone for as-cast Spartan Plus (Fig.2.20). However, no \:<200>\ direction streaks are visible on the \{200\} reflections. The SAED pattern for the \:<001>\ zone in this alloy (Fig. 2.21) shows a lattice similar to the fcc, with forbidden \{001\} and \{011\} reflections. The \{001\} reflections also show diffuse streaks in \:<001>\ directions. Two diagonal \{220\} reflections
in this figure show diffuse streaks in the <200> and <220> directions, as well as splitting of the major spots, while each of the other two {220} reflections are split into four smaller spots. Splitting of spots is also observed for the {200} reflections. Figure 2.22 is the dark-field image obtained from one of the {011} forbidden reflections in the SAED pattern for the <011> zone. Particles near the thinnest area and having dimensions less than ~10 nm are shown.

After the simulated porcelain-firing heat treatment and the 1,800°F annealing heat treatment, the as-cast structure of Spartan Plus was maintained as previously noted for the Liberty Pd-Cu-Ga alloy. Figure 2.23 is a bright-field image of Spartan Plus after annealing at 1,800°F. The beam direction is close to the <011> zone axis, and one of the {200} reflections is excited.

Results of the EDS spot analyses on as-cast Spartan Plus are listed in Table 2.2.

2.3.2 Pd-Ga Alloys

The bright-field image of as-cast Legacy (Fig. 2.24) exhibited a structure very similar to that seen for the other two Pd-Cu-Ga alloys. A pronounced band structure with an internal tweed ultrastructure composed of striations in <111> directions can be seen in this figure, where the beam direction is near the <110> zone axis and the 200 reflection is excited. Figures 2.25 and 2.26 are bright-field images from the same area as Fig. 2.24 and also near the <011> zone axis, but with two different <111> reflections excited. No tweed contrast can be seen in these two figures; only striations parallel to the excited {111} vector
are visible. Again, as previously described for Liberty and Spartan Plus, a one-to-one correspondence between streaks in the SAED patterns and sets of striations in the bright-field image is observed for this alloy. On another as-cast Legacy specimen, a tweed microstructure with no association of an overall band structure was observed (Fig. 2.27). Correspondence between the streaks on the SAED pattern and the set of striations in this figure was also found. In addition, a twin grain boundary with \{111\} twin plane was found on this specimen and verified by electron diffraction pattern near the \(<011>\) zone (Hirsch et al., 1965).

The SAED patterns from the two as-cast Legacy TEM specimens exhibited the same features. The electron diffraction pattern for the \(<011>\) zone corresponded to an fcc lattice, but with diffuse streaks in two directions similar to that previously described for the Spartan Plus alloy. The SAED pattern for the \(<001>\) zone in this alloy (Fig. 2.28) shows a lattice similar to the fcc with diffuse streaks in \(<110>\) directions on both the \{220\} and \{200\} reflections. Careful examination of these reflection spots revealed that each spot was composed of four individual spots. In addition, \{110\}, but not \{100\}, forbidden reflections can be seen on this diffraction pattern. Each \{110\} forbidden reflection is composed of four individual spots streaking in \(<110>\) directions and forming a square.

EDS spot analyses were performed on both as-cast Legacy TEM specimens, and no significant differences were observed. On the specimen with the band structure, no significant composition differences were detected for the band structures and the areas between the bands. The results of the EDS analyses are listed in Table 2.3.
After simulated porcelain-firing heat treatment, the tweed microstructure was maintained in Legacy, as previously found for the Liberty and Spartan Plus alloys. No changes were observed in the SAED patterns for the <011> and <001> zones.

The as-cast alloy Protocol also exhibited a tweed microstructure with an overall band structure. Figure 2.29 is a bright-field image near the <011> zone axis where the {200} reflection was excited. This figure shows a tweed structure with striations parallel to the <111> directions. The same tweed microstructure remained for Protocol after the porcelain-firing heat treatment. Figures 2.30 to 2.32 are bright-field images of heat-treated Protocol near the <011> zone axis where different reflections were excited. A one-to-one correlation between streaks on the SAED patterns and striations on the bright-field images was also observed for this alloy.

The SAED pattern for the <011> zone was similar to that for the Legacy alloy. The SAED pattern for the <001> zone in as-cast Protocol (Fig. 2.33) shows a fcc lattice with diffuse streaks along the <011> directions on both the {220} and {200} reflections. Splitted {110} forbidden reflections are also visible in this figure. The same features were observed on the SAED patterns for heat-treated Protocol.

The results of EDS spot analyses on as-cast Protocol are listed in Table 2.3. The analyses yielded only < 1 wt. % of indium, which is far below the nominal 6 wt.% for the alloy composition (Carr and Brantley, 1991).
2.4 Discussion

Tweed microstructures have been observed in a wide range of metallic systems and in ceramic systems, and have been associated with a wide variety of phase transformations, such as the martensitic transformation, order-disorder transformation and Guinier-Preston (G.P.) zone precipitation. The tweed microstructure was first characterized by Tanner (1966) in a Cu-2 % Be alloy having disc-shaped G.P. zone precipitates. The bright-field image showed a uniform diffuse "basket-weave" of light and dark striation contrast, parallel to the traces of \{110\} planes, and the electron diffraction patterns contained <110> relrods (rod-shaped reciprocal lattice spots) normal to these planes. Based on the kinematic electron diffraction theory, it was concluded that these striations were a strain contrast effect, arising from elastic shear strains induced by tetragonal coherency in the initial stage of precipitation and ordering. In a later paper (Laughlin et al., 1980), a more restricted definition of tweed microstructure was given to avoid confusion with other similar microstructures. Robertson and Wayman (1983a, 1983b, and 1983c) investigated the tweed contrast associated with the phase transformation in a 63 at.% Ni-Al alloy system, which involves martensitic transformation and incoherent precipitation of \(\gamma\) and Ni\(_5\)Al\(_3\) phases. The average striation direction in this system corresponded to the traces of the \{110\} planes. There was a one-to-one correspondence between the streaks on the electron diffraction patterns and the sets of striations in the bright-field image. The striations showed the same extinctions as the streaks in the SAED patterns, which was consistent with
the shear displacement on \{110\} planes in \langle 1\bar{1}0 \rangle \) directions. The tweed contrast was explained by \((110)[1\bar{1}0]\) displacement waves of long wavelength and was considered to be a premartensitic effect. In a later review, Christian (1990) considered nucleation at defects and growth by interface migration, rather than the tweed microstructure, to be an essential mechanistic feature of all martensitic transformations. Modulated, tweed-like microstructures were also observed in a Ti-Al-Nb alloy system (Strychor et al., 1988), whose decomposition involved formation of hexagonal close-packed (hcp) martensite, an order-disorder transformation and the formation of an \(\omega\)-type phase following the ordering.

In a TEM study on Fe - ~30 at.% Pd alloys (Oshima et al., 1988), tweed structures were observed to be associated with an fcc-fct martensitic transformation. The tweed structure was found to be induced by the displacement of atoms occurring during the formation of disc-shaped martensite nuclei on the \{110\} planes of the parent austenite phase. A tweed microstructure is also found in the superconducting compound V\(_3\)Si which undergoes a cubic-tetragonal martensitic transformation (Onozuka et al., 1988). Formation of the tweed structure was attributed to the presence of lattice distortion arising from the softening of the shear modulus. In a review on the microstructures of quenched \(\beta\)-brass type alloys (Delaey et al., 1972), however, a similar type of mottled contrast observed with the TEM was attributed to a combination of surface rippling and Moiré fringe effects.

Though the general origin of tweed contrast has been elucidated, it is still difficult to distinguish between the contrast effects arising from various phase transformations. In this study, the distinct tweed ultrastructures observed in the Pd-Cu-Ga and Pd-Ga alloys clearly
indicated a dispersion of very small regions of elastic strain. The observed striations of the tweed contrast, which always lay along the traces of \{110\} planes and shows dramatic changes when the excited reflections are varied, suggest that the atomic displacements causing the contrast are induced by shear on the \{110\} planes in the directions parallel to the \(\langle 1\bar{1}0\rangle\) directions of the fcc structure.

Diffuse streaks on spots in the electron diffraction patterns are normal to the direction of the striations and exhibit the same extinction rule as the striation contrast when the excited reflection is changed (Tanner, 1966). The one-to-one correspondence between the striation contrast and the diffuse streaks indicates that these streaks in the \(\langle 111\rangle\) direction are due to the static (shear) displacements of atoms and not to thermal scattering.

The persistence of the tweed ultrastructure in the specimens of Liberty (Fig. 2.13) and Spartan Plus (Fig. 2.23) annealed at 1,800°F and subsequently quenched in ice water indicates that the formation of this structure occurs by a rapid displacive transformation process. The transformation from the palladium solid solution into the fct structure may only involve small atomic movements, based on the fcc-fct transformation proposed by Odén and Herø (1986). The simulated porcelain firing heat treatment and the 1,800°F annealing procedure used in this study may cause the fct structure to revert to the high-temperature single-phase fcc palladium solid solution. However, this solely fcc structure evidently could not be preserved at room temperature with the quenching method used. The formation of a tweed structure in these alloys may be associated with the minimization of strain energy arising from the transformation of the fcc palladium solid solution into the
fct phase (Warlimont, 1971). Since Legacy and Protocol do not contain copper, the tweed structures observed in these Pd-Ga alloys may consist of two Pd₃Ga phases containing small amounts of the other component elements (Table 2.3).

Comparison of the bright-field images of Liberty from the same area (Figs. 2.5, 2.7 and 2.9) reveals that, although the striation contrast in bands with tweed structure varies with different exciting reflections, the striations in the bands without tweed contrast are barely changed. This suggests that these latter bands may not contain small regions of elastic strain associated with the tweed structure. Diffuse streaks in the <200> directions for the <011> and <001> zones of Liberty (Figs. 2.11 and 2.12) indicate the presence of thin precipitate plates parallel to {200} plane faces (Thomas and Goringe, 1979). The average direction of these striations (Figs. 2.4 and 2.13) is parallel to a <200> direction.

Forbidden reflections for the fcc lattice in the SAED pattern for the <001> zone (Fig. 2.12) suggest a possible superlattice which may arise from an ordering transformation in fct martensite. This ordered structure is probably associated with the two alternating Pd₃CuₓGa₁₋ₓ fct phases with slightly different a/c ratios, which were proposed by Odén and Hervo (1986). Two fct phases have been previously identified by x-ray diffraction between 30⁰ and 600⁰C in an industrial palladium alloy of similar composition (Khabliyev et al., 1980). Recent thermomechanical (dilatometric) analyses on both Pd-Cu-Ga and Pd-Ga alloys (Wu, 1996) suggest that there is a second-order transformation at ~ 600⁰C. All these observations indicate that there is an ordering transformation around that temperature.
following the fcc-fct martensitic transformation. This ordering process may greatly reduce the shear strain associated with the martensite and results in a constant striation structure.

The \{011\} and \{001\} forbidden reflections in the SAED pattern for the \langle001\rangle zone of Spartan Plus (Fig. 2.21) also suggest an fct superlattice. The dark-field image using one of these \{011\} reflections shows some bright spots in the thin area of the foil specimen (Fig. 2.22) that may arise from the ordered fct martensite. A band structure similar to that found in Liberty was also observed in Spartan Plus, and all of the bands had internal tweed structures. It is concluded that the region within each band is a single domain of the ordered structure (Reed-Hill, 1973), and the boundaries between the bands are antiphase boundaries formed during the cooling of the alloy (Hirsch et al., 1965). The slightly different morphologies of these boundaries observed in Liberty, Spartan Plus and Legacy may arise from the differences on the surface energies of these boundaries due to different secondary elements in these alloys.

The SAED patterns for the \langle001\rangle zones in the Legacy and Protocol Pd-Ga alloys (Figs. 2.28 and 2.33) show similar features to those observed in the Liberty and Spartan Plus Pd-Cu-Ga alloys. The split square-shaped \{011\} forbidden reflections may arise from double diffraction at the antiphase boundaries of the ordered fct structure, due to the phase shift of the lattice (Hirsch et al., 1965).

Results of the standardless EDS spot analyses on as-cast Liberty, Spartan Plus and Legacy are relatively close to the compositions provided by the manufacturers, while the results for as-cast Protocol alloy revealed a much lower indium content (< 1%) compared
suggests possible depletion of this element by formation of In-Au, In-Ag or In-Ru intermetallic compounds (Massalski, 1986).

It was demonstrated in a previous study (Carr et al., 1993) that the Spartan (composition nearly identical to that of Spartan Plus) and Liberty Pd-Cu-Ga alloys have higher Vickers hardness (and presumably yield strength) than the Protocol and Legacy Pd-Ga alloys. Odén and Hero (1986) suggested that the two fct $\text{Pd}_3\text{Cu}_x\text{Ga}_{1-x}$ phases with slightly different $(a/c)$ ratios are responsible for the high strength of a Pd-Cu-Ga alloy that has a composition very similar to Spartan Plus. However, the results of our current study indicate that the tweed structure is a common ultrastructural feature in both Pd-Cu-Ga and Pd-Ga alloys and thus these structures are not closely related to the high strength reported by the manufacturers for the Pd-Cu-Ga alloys. However, it is reasonable that such tweed structures would provide effective obstacles to dislocation movement and some strengthening for both Pd-Cu-Ga and Pd-Ga alloys, although this structure does not account for the higher strength of the Pd-Cu-Ga alloys compared to the Pd-Ga alloys. Current research in our group (Wu, 1996) has revealed a new grain boundary phase with a very high Vickers hardness (approximately 500 VHN) in Liberty which appears to account for the high hardness of this alloy; the interdendritic region in Spartan Plus has a similar very high Vickers hardness.

The TEM results from this study also explain our previous observation (Carr et al., 1993) that simulated porcelain firing heat treatment does not significantly change the hardness of these alloys. Although the fct tweed structure may be transformed back to the
The shear strain associated with the fct Pd$_3$Ga$_4$Cu$_{1-x}$ phases (Odén and Herø, 1986) indicated by the tweed ultrastructures observed in this study suggests that these alloys may undergo further ordering transformation at lower temperature to reduce the strain. The near surface microstructure changes on high-palladium alloys after five year room-temperature aging have been observed (Brantley et al., 1995). It is reasonable to expect that long-term body temperature aging would result in changes on the tweed ultrastructure on these alloys although further verification is needed. Such structural changes may also affect the corrosion resistance and biocompatibility of these alloys.

2.5 Conclusions

Pd-Cu-Ga alloys and Pd-Ga alloys have very similar ultrastructures, consisting of ordered Pd$_3$Ga fct phases in a tweed structure morphology formed from the fcc palladium solid solution via martensitic transformation. It is reasonable to expect that an alloy with such structure would have high hardness and strength because the large number of phase boundaries provide substantial resistance to dislocation movement. The higher hardness observed for Pd-Cu-Ga alloys compared to Pd-Ga alloys cannot be explained by their ultrastructures, which were similar for both alloy types.
The results of this TEM investigation, using four representative commercial high-palladium dental alloy compositions, suggest that the tweed ultrastructure is inevitable in these alloys. As suggested by the Pd-Ga phase diagram in Fig. 2.1, cast commercial high-palladium alloys with the present range of Pd/Ga ratios will undergo the peritectoid transformation on cooling to yield the tweed ultrastructure. Even though the solvus line at the Pd-rich end is uncertain, dental alloys containing much higher percentages of palladium that would avoid this transformation could not be readily cast with standard laboratory equipment. The melting temperature for such alloy much be in excess of 1,450°C, requiring a casting temperature of nearly 1,550°C.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Pd</th>
<th>Cu</th>
<th>Ga</th>
<th>In</th>
<th>Sn</th>
<th>Au</th>
<th>Ag</th>
<th>Other</th>
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<tbody>
<tr>
<td>Liberty†</td>
<td>76 (70.6)</td>
<td>10 (15.6)</td>
<td>5.5 (7.8)</td>
<td>-</td>
<td>6 (5.0)</td>
<td>2 (1.0)</td>
<td>-</td>
<td>Ru</td>
</tr>
<tr>
<td>Spartan Plus†</td>
<td>79 (71.5)</td>
<td>10 (15.1)</td>
<td>9 (12.4)</td>
<td>-</td>
<td>-</td>
<td>2 (1.0)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Protocol†</td>
<td>75 (75.5)</td>
<td>-</td>
<td>6 (9.2)</td>
<td>6 (5.6)</td>
<td>-</td>
<td>6 (3.3)</td>
<td>6.5 (6.4)</td>
<td>Ru</td>
</tr>
<tr>
<td>Legacy†</td>
<td>85 (82.3)</td>
<td>-</td>
<td>10 (14.8)</td>
<td>1 (0.9)</td>
<td>-</td>
<td>2 (1.0)</td>
<td>1 (1.0)</td>
<td>Ru</td>
</tr>
</tbody>
</table>

* Compositions were provided by the manufacturers.
† Manufactured by J.F. Jelenko & Co., Armonk, NY
‡ Manufactured by Williams Dental Co., Div. Ivoclar North America, Amherst, NY.

Table 2.1—Compositions in Weight Percent (Atomic %) of the High-Palladium Alloys Studied†
<table>
<thead>
<tr>
<th>Element</th>
<th>Liberty (N=8)</th>
<th>Spartan Plus (N=6)</th>
</tr>
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<tbody>
<tr>
<td>Pd</td>
<td>76.4 ± 2.5 (72.6 ± 2.1)</td>
<td>80.8 ± 1.5 (75.1 ± 1.0)</td>
</tr>
<tr>
<td>Cu</td>
<td>7.6 ± 0.3 (12.0 ± 0.48)</td>
<td>8.3 ± 0.3 (13.0 ± 0.4)</td>
</tr>
<tr>
<td>Ga</td>
<td>4.9 ± 0.4 (7.0 ± 0.7)</td>
<td>7.0 ± 0.8 (10.0 ± 1.0)</td>
</tr>
<tr>
<td>Sn</td>
<td>5.1 ± 1.6 (4.4 ± 1.4)</td>
<td>-</td>
</tr>
<tr>
<td>Au</td>
<td>4.0 ± 1.8 (2.1 ± 0.9)</td>
<td>4.0 ± 1.8 (2.0 ± 1.0)</td>
</tr>
<tr>
<td>Ru</td>
<td>2.0 ± 0.8 (1.9 ± 0.8)</td>
<td>-</td>
</tr>
</tbody>
</table>

* Entries are mean value ± standard deviation.

Table 2.2—Standardless EDS Analyses in Weight Percent (Atomic %) for the Two Pd-Cu-Ga Alloys in the As-Cast Condition*

<table>
<thead>
<tr>
<th>Element</th>
<th>Protocol (N=8)</th>
<th>Legacy (N=8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>77.2 ± 1.5 (76.0 ± 2.3)</td>
<td>86.3 ± 1.6 (82.7 ± 1.3)</td>
</tr>
<tr>
<td>Ga</td>
<td>8.2 ± 1.9 (12.3 ± 2.7)</td>
<td>10.5 ± 0.2 (15.3 ± 0.3)</td>
</tr>
<tr>
<td>In</td>
<td>0.5 ± 0.6 (0.5 ± 0.6)</td>
<td>-</td>
</tr>
<tr>
<td>Au</td>
<td>6.1 ± 1.4 (3.3 ± 0.8)</td>
<td>2.6 ± 0.9 (1.4 ± 0.5)</td>
</tr>
<tr>
<td>Ag</td>
<td>5.4 ± 0.8 (5.2 ± 0.8)</td>
<td>0.1 ± 0.2 (0.1 ± 0.2)</td>
</tr>
<tr>
<td>Ru</td>
<td>2.6 ± 0.3 (2.7 ± 0.2)</td>
<td>0.6 ± 0.5 (0.6 ± 0.6)</td>
</tr>
</tbody>
</table>

* Entries are mean value ± standard deviation.

Table 2.3—Standardless EDS Analyses in Weight Percent (Atomic %) for the Two Pd-Ga Alloys in the As-Cast Condition*
Figure 2.1—Palladium-gallium phase diagram (Massalski, 1986).
Figure 2.2—Bright-field image of as-cast Spartan Plus without plasma cleaning.

Figure 2.3—Bright-field image of as-cast Spartan Plus after plasma cleaning.
Figure 2.4—Dark-field image of as-cast Liberty.
Figure 2.5—Bright-field image of as-cast Liberty, with 200 reflection excited.

Figure 2.6—SAED pattern of as-cast Liberty near the <001> zone axis, showing a row of 200 spots. Rotation calibration is counterclockwise 186° from this figure to Fig. 2.5.
Figure 2.7—Bright-field image of as-cast Liberty, with $11\overline{1}$ reflection excited.

Figure 2.8—SAED pattern of as-cast Liberty near the $<011>$ zone axis, showing a row of 111 spots. Rotation calibration is counterclockwise 186° from this figure to Fig. 2.7.
Figure 2.9—Bright-field image of as-cast Liberty with the $\overline{1}11$ reflection excited.

Figure 2.10—SAED pattern of as-cast Liberty near the $<011>$ zone axis, showing a row of 111 spots. Rotation calibration is counterclockwise 186° from this figure to Fig. 2.9
Figure 2.11—SAED pattern of as-cast Liberty for the <011> zone.

Figure 2.12—SAED pattern of as-cast Liberty for the <001> zone.
Figure 2.13—Bright-field image of Liberty annealed at 1,800°F.
Figure 2.14—Bright-field image of as-cast Spartan Plus, where the 200 reflection is excited. Note the absence of an overall band structure for the tweed morphology.

Figure 2.15—Bright-field image of a different representative region for as-cast Spartan Plus, exhibiting a band structure for the tweed morphology seen in Fig. 2.14.
Figure 2.16—Bright-field image of as-cast Spartan Plus, where the 11T reflection is excited.

Figure 2.17—Bright-field image of as-cast Spartan Plus, where the 11T reflection is excited.
Figure 2.18–Bright-field image of as-cast Spartan Plus, where the $1 \bar{1} 1$ reflection is excited. Note the similar appearance to Figure 2.16.

Figure 2.19–Bright-field image of as-cast Spartan Plus, where the $1 \bar{1} 1$ reflection is excited.
Figure 2.20—SAED pattern of as-cast Spartan Plus for the <011> zone.

Figure 2.21—SAED pattern of as-cast Spartan Plus for the <001> zone.
Figure 2.22–Dark-field image of as-cast Spartan Plus, using a \{011\} forbidden reflection in Fig. 2.21.

Figure 2.23–Bright-field image of Spartan Plus annealed at 1,800°F.
Figure 2.24—Bright-field image of as-cast Legacy, where the 200 reflection is excited.

Figure 2.25—Bright-field image of as-cast Legacy, where the $11 \overline{1}$ reflection is excited.
Figure 2.26—Bright-field image of as-cast Legacy, where the $1 \bar{1} 1$ reflection is excited.

Figure 2.27—Bright-field image of as-cast Legacy, showing a tweed structure without the overall band structure in Fig. 2.24.
Figure 2.28—SAED pattern of as-cast Legacy for the <001> zone.

Figure 2.29—Bright-field image of as-cast Protocol.
Figure 2.30—Bright-field image of heat-treated Protocol, where the 200 reflection has been excited. Note the absence of an overall band structure for the tweed ultrastructure.

Figure 2.31—Bright-field image of heat-treated Protocol, where the $\overline{1}11$ reflection has been excited.
Figure 2.32—Bright-field image of heat-treated Protocol, where the 11T reflection has been excited.

Figure 2.33—SAED pattern of as-cast Protocol for the <001> zone.
CHAPTER 3

ELECTROCHEMICAL BEHAVIOR
OF HIGH-PALLADIUM DENTAL ALLOYS

3.1 Introduction

As noted in the preceding chapter, the high-palladium dental casting alloys containing 75-80 wt. % palladium have been used extensively for metal-ceramic restorations, as well as for implant-supported prostheses (Stewart et al., 1992), since their introduction in the early 1980's (Carr and Brantley, 1991). These multiple uses are possible because of the excellent mechanical properties and much lower cost of the high-palladium alloys, compared to traditional gold-based alloys.

Corrosion resistance is a very important property for dental alloys, in addition to other properties such as strength, ductility and casting accuracy. Corrosion of dental alloys in the oral environment not only results in the deterioration of a restoration, but also involves a release of ions which is directly related to the biocompatibility of the alloys. With the widespread use of high-palladium alloys for metal-ceramic and all-metal restorations in many countries, especially in Europe, many adverse effects related to these alloys have been publicized lately.
The potentiostatic/potentiodynamic polarization test (Holland et al., 1986; Holland, 1990) is the major method commonly used to study the corrosion of dental alloys. However, this method is not generally accepted as being both applicable to and clinically relevant for every dental alloy. Several electrolytes have been used in the potentiostatic/potentiodynamic polarization test. The Fusayama solution (Fusayama et al., 1963) has been considered the artificial saliva in which the electrochemical behavior of dental alloys most closely resembles that in natural saliva (Meyer and Nally, 1975).

Despite the availability of the high-palladium dental alloys for over a decade, only a few studies on the in vitro corrosion of these alloys have been reported. Sumitra et al. (1983) conducted a corrosion study on high-palladium alloys shortly after their commercial introduction. Potentiodynamic polarization in a 1% NaCl solution revealed that a Pd-Co alloy and a Pd-Cu-Zn alloy had spontaneous passive behavior, while the three Pd-Cu alloys evaluated showed active-passive behavior. Active behavior for the latter was only observed at > +400 mV, followed by sharp passivation between +500 and +750 mV (SCE). Corrosion potentials for all the palladium-based alloys were close to the Pd/Pd(OH)$_2$ equilibrium potential of +260 mV. Variations in certain critical corrosion parameters observed were considered not to be associated with a grain refinement element or other alloying elements of gallium, indium and tin.

Paradiso (1984) systematically evaluated the effects of varying the amounts of the elements Zn, In, Sn and B on the corrosion resistance of the 79Pd-10Cu-9Ga (wt.%) alloy system in an artificial saliva. The 24-hour open-circuit potential (OCP) and the Tafel constant calculated from the slope of the initial linear portion on the anodic polarization
curve were obtained. The secondary alloying elements were found to have little effect on the corrosion parameters evaluated.

Lane et al. (1985) compared electrochemical properties of three high-palladium alloys (Athenium, Williams/Ivoclar; Option, Ney; and PTM-88, Jelenko) with a gold-based alloy (Olympia, Jelenko) in the as-cast condition, using an oxygenated 0.9% NaCl solution at 37°C. The corrosion current densities in the high-palladium alloys (0.017-0.065 mA/cm²), determined using the Tafel extrapolation, were similar to that of the gold-based alloy. Tarnishing was observed on the Option and Athenium alloys, but not on the other alloys evaluated.

Mezger et al. (1985) investigated the corrosion resistance of three Pd-Cu-Ga alloys in both the as-cast and simulated porcelain-fired conditions, using a dynamic polarization technique. Potentiodynamic hysteresis profiles were obtained from -900 mV to +900 mV (SCE) and in the reverse direction for three stagnant electrolytes exposed to air at room temperature: 0.9% and 0.09% saline solutions, and a modified Fusayama solution. Polarization resistance (R_p) was calculated from the anodic scan over a range of ±10 mV around the zero-current potential (ZCP). Values of ten-minute OCP for all the alloys and both conditions varied from +80 to +265 mV (SCE), and values of polarization resistance ranged from 9.0 to 42.1 kΩ-cm². The ZCP varied over a much larger range from -560 mV to 65 mV. All of the alloys showed immunity and/or spontaneously passive behavior up to +700 mV (SCE) in both the 0.09% NaCl solution and the artificial saliva. It was concluded that all three alloys had remarkable good saline corrosion resistance in the potential and chloride ion concentration range of the oral environment.
In a later study by Mezger et al. (1989), the in vitro corrosion behavior of eight Pd-Cu-Ga dental alloys in the simulated porcelain-firing condition were evaluated in a stagnant 0.9% saline solution and an artificial saliva at room temperature. The one-hour OCP was first measured, followed by an anodic potential scan between ±20 mV (SCE) around the OCP at a rate of 0.1 mV/sec to determine polarization resistance. A potentiodynamic scan from -1,000 mV to +1,000 mV (SCE) at a rate of 0.5 mV/sec was then performed. The results showed that the corrosion behavior of all the high-palladium alloys was very similar. The OCP, ZCP and corrosion current ($I_{corr}$) were equivalent among alloys within experimental accuracy. The ZCP was consistently lower than the OCP, and all alloys were immune or passive in both of the electrolytes to at least +400 mV potential. A current density peak at +600 mV in both the forward and reverse scans was observed with the 0.9% saline solution for all the alloys, while a peak in the forward scan was only seen with the artificial saliva. The results of this study indicated that the different microstructures and phase compositions of the high-palladium alloys did not greatly affect their corrosion behavior. The compositional variation among the alloys was too small to result in substantial electrochemical effects.

Goehlich and Marek (1990) examined corrosion behavior of Pd-14.8Cu and Pd-19.2Co (wt.%) binary alloys in a synthetic saliva. The 24-hour OCP was monitored in an aerated (air/10% CO$_2$) electrolyte. An anodic potentiodynamic scan was performed in deaerated (N$_2$-10% CO$_2$) solution from below the OCP to where the current density rose sharply at the end of the potential-independent region at a rate of 0.17 mV/sec. A region of current density almost independent of the potential was observed in the scan of both
alloys. Concentrations of Co, Cu and Pd in the electrolyte determined by atomic absorption spectrophotometry after potentiostatic or open-circuit exposures revealed that Co$^{2+}$ ions were always found at very low concentration, while the Cu$^{2+}$ ion concentration increased with both exposure length and the applied potential. No Pd was detected in the solution. X-ray photoelectron spectroscopic (XPS) analysis of the specimen surface after electrochemical testing showed that both Co and Cu were depleted compared to bulk concentrations. The near-surface Pd enrichment was more severe for the Pd-Cu alloy than for the Pd-Co alloy, and increased for Pd-Cu alloy with increasing potential and exposure time. The difference in the dissolution rates of Cu and Co from their respective alloys was attributed to differences in the diffusion rates of these elements toward the surface or to the formation of surface films which hinder dissolution.

Recently, Meyer and Reclaru (1995) conducted a study on the corrosion resistance of 44 noble dental casting alloys and pure metals, including three Pd-Cu-Ga alloys and one Pd-Ga alloy, using electrochemical methods with an artificial saliva derived from Fusayama solution. For each alloy, the 24-hour OCP in aerated solution was measured, followed by a linear polarization scan between -20 mV below the OCP and +20 mV (SCE) above the corrosion potential ($E_{\text{corr}}$) in deaerated solution to determined the $R_p$. Anodic potentiodynamic polarization scans were performed at rates of 0.03 mV/sec and 1 mV/sec from -500 mV up to +1500 mV (SCE) to measure the breakdown potential. For all the alloys studied, the high-palladium alloys showed the highest values of the OCP (100-248 mV), $E_{\text{CORR}}$ (55-227 mV) and breakdown potentials (1,285-1,370 mV).
The polarization resistance of the high-palladium alloys was ranked highest among the alloys for metal-ceramic restorations.

Although substantial research has been performed over the last decade to evaluate the corrosion resistance of the high-palladium alloys, the detailed relationships among the corrosion properties, microstructures and compositions for the commercial alloys are still not available. The objectives of this study were to characterize the in vitro corrosion behavior of five high-palladium alloys in both the as-cast and simulated porcelain-firing heat-treated conditions in 0.09% NaCl solution and Fusayama artificial saliva using the potentiodynamic polarization technique, and to examine the effect of in vitro corrosion on the alloy microstructures. The corrosion behavior of some of these alloy compositions has not previously been investigated.

3.2 Materials and Methods

Three Pd-Cu-Ga alloys and two Pd-Ga alloys were selected for this study. The metallurgical structures for four of these alloys (Liberty, Spartan Plus, Legacy and Protocol) have been investigated extensively by scanning electron microscopy and x-ray diffraction (Carr and Brantley, 1991; Brantley et al., 1993; Brantley et al., 1995a). The Freedom Plus alloy has been recently adopted for use in the clinics of the College of Dentistry, and its corrosion resistance was thus of considerable practical importance. The compositions and manufacturers of these alloys are listed in Table 3.1.

Cylinder-shaped alloy castings with 10 mm diameter and 6 mm thickness were prepared. Each wax pattern was sprued and invested individually with a carbon-free,
phosphate-bonded investment (Cera-Fina, Whip Mix Corp., Louisville, KY). A peak burnout temperature of 1,400°F (760°C) was chosen, based on recommendations from the alloy manufacturers, and burnout was accomplished using a dental furnace (Accu-Therm II 1000, J.F. Jelenko & Co., Armonk, NY). Each alloy was melted in an individual ceramic crucible with a conventional multiorifice gas-oxygen torch. Casting was performed in air with a broken-arm centrifugal casting machine (Kerr/Sybron, Romulus, MI), following standard dental laboratory procedures, and castings were bench-cooled in air. Two castings were prepared for each alloy. After devesting, each casting was embedded in epoxy resin and sectioned into two disks with approximately equal thickness, using a low-speed, water-cooled saw (Vari/Cut VC-50, Leco Corp., St. Joseph, MI) with a diamond-coated blade. Four disk-shaped specimens were thus available for each alloy. Each disk specimen was mounted individually in epoxy resin with the original cut surface exposed and polished with a standard sequence of metallographic abrasives through 0.05 μm Al₂O₃ slurry. Electrical contact to the disk specimen was established by threading a metal rod through the epoxy resin. After polishing, each disk specimen was ultrasonically cleaned in distilled water and ethanol for five minutes, respectively.

Corrosion measurements were made for both the as-cast and heat-treated conditions of each alloy. After the completion of corrosion measurements in the as-cast condition, each specimen was removed from the epoxy mounting and subjected to simulated porcelain-firing heat treatments. This heat treatment included both the initial oxidation step and the subsequent firing steps for the several standard layers of dental
porcelain. For the Spartan Plus and Protocol (Williams/Ivoclar) alloys, oxidation was performed at reduced atmospheric pressure (720 mm Hg), with a five-minute hold at the 1,850°F (1,010°C) peak temperature. The Liberty, Freedom Plus and Legacy (Jelenko) alloys were oxidized in air at the same peak temperature but without any hold. Heat treatment followed the full firing cycles for Vita VMK dental porcelain (Vident, Baldwin Park, CA) in a conventional dental porcelain furnace (Ultra-Mat CDF, Unitek/3M, Monrovia, CA), simulating the application of one opaque porcelain layer, two body porcelain layers and a glaze (Carr et al., 1993). Following recommended dental laboratory practice, the heat-treated specimens were subsequently bench cooled in air. A potentiostat (Model 273A Potentiostat/Galvanostat, EG & G Princeton Applied Research) controlled by a personal computer with dedicated software (Model 352/252 Soft Corr™ II Corrosion Measurement & Analysis Software, EG & G Princeton Applied Research, Princeton, NJ) was employed in this study. A platinum plate was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Deaerated and stagnant 0.09% NaCl solution, whose chlorine concentration is similar to that in human saliva (Mezger et al., 1985), and Fusayama artificial saliva (Fusayama et al., 1963) were used as the two electrolytes in this study. The composition of the Fusayama artificial saliva is listed in Table 3.2. Corrosion media were deaerated by bubbling nitrogen gas through the solution for two hours prior to and during the experiment. The corrosion medium was maintained at 37°C during the experiment.

Experimental procedures for each specimen consisted of two parts: (a) The specimen was first held at -1,000 mV (SCE) for two minutes in order to remove any
surface oxide films (Mezger et al., 1989). A cyclic polarization scan was then performed from -1,000 mV to +1,000 mV (SCE), and back to -1,000 mV (SCE) at 1 mV/sec with 100 μA as the selected current range. The zero-current potential (ZCP) and corrosion current ($I_{\text{corr}}$) of the specimen were determined from the cyclic polarization diagram. The few diagrams that could not be analyzed by the computer were instead analyzed using an extrapolation method. New corrosion medium was prepared for each specimen tested. In order to prevent the additional exposure of the specimen surface and possible crevice corrosion, the boundary between the specimen and the epoxy mounting was sealed by melted dental wax. The exposed surface area for the specimens was either 0.6362 cm$^2$ or 0.2826 cm$^2$ by using circular templates (to be described later). When the cyclic polarization scans for the four specimens of each alloy condition (as-cast or heat-treated) were completed, the average value of the ZCP was calculated from the four individual scans. The sealing wax was then removed from the specimen surface, and the specimen surfaces were repolished. (b) The second part of the experiment was the measurement of the twelve-hour open-circuit potential followed by linear polarization scans in the range ±30 mV of the determined average ZCP at 0.1 mV/sec. The polarization resistance ($R_p$) was determined for each specimen, using the computer software.

Statistical significance of the differences between the mean values of the electrochemical parameters measured was assessed by the Kruskal-Wallis test and the Mann-Whitney U test, using the SYSTAT 5.02 for Windows program (SYSTAT Inc., Evanston IL) with a selected significance level of $P < 0.05$. It was necessary to use these
nonparametric tests for statistical comparisons because of the substantial variation in measured corrosion parameters for specimens of the same alloy and test group.

Since the most common application of the high-palladium alloys is the metal-ceramic restoration, surfaces of representative heat-treated high-palladium alloy specimens after dynamic polarization were examined with an SEM. Specimen surfaces were repolished and cleaned, and both the deaerated 0.09% NaCl and Fusayama solution were used as the electrolytes. Each specimen was held at -1,000 mV (SCE) for two minutes followed by dynamic polarization from -1,000 mV to +1,000 mV at 1 mV/sec. The specimen was then retrieved and ultrasonically cleaned in distilled water for five minutes. Microstructures of the corroded specimens were examined with an SEM (JSM-820, JEOL Ltd., Tokyo, Japan) in both the secondary and backscattered electron image modes. Prior to observation, these specimen surfaces were sputter-coated with carbon to avoid electrical discharge during SEM observation.

3.3 Results

Casting defects (porosities) were observed with the optical microscope on the corrosion specimens used in this study, especially the Liberty and Spartan Plus specimens. The initial grinding and polishing of each specimen resulted in removal of the majority of these defects from the surface. However, on the final polished surface, some defects remained and the previously described circular templates were placed to minimize the defects in the exposed testing area on the specimen. The two disk
specimens that originated from the same cylindrical casting behaved very similarly for
the same test medium, compared to the two specimens from the other parent casting.

3.3.1 Corrosion Behavior of As-Cast High-Palladium Alloys

The change in average values of the OCP over a period of 12 hours (4.32x10^{4} sec)
for the five as-cast high-palladium alloys in deaerated 0.09% NaCl and Fusayama
solutions is shown in Figs. 3.1 and 3.2, respectively. Mean values and standard deviation
for the 12-hour OCP values are listed in Table 3.3. In both media the OCP stabilized
after 12 hours, although there was considerable fluctuation in the Fusayama solution for
time periods up to about 2x10^{4} sec. The average values of 12-hour OCP for the as-cast
alloys in 0.09% NaCl solution were 210 - 550 mV higher than those in Fusayama
solution. These differences were significant (P = 0.021) for all the alloys except Protocol
(P = 0.546). No significant differences were found between the mean values of 12-hour
OCP of the five as-cast alloys in each of the two media (P = 0.083).

Representative cyclic polarization diagrams for each as-cast alloy in both the
0.09% NaCl and Fusayama solutions are shown in Figs. 3.3-3.7. Similar cyclic
polarization diagrams were seen for both the Pd-Cu-Ga and Pd-Ga alloys. During the
cyclic polarization scan for all the alloys and the two test media, the shift from cathodic
to anodic currents occurred over a large range of potential rather than abruptly. Current
density reductions in the reverse anodic scan, compared to the forward anodic scan, were
observed for all the as-cast alloys in both media. A current density decrease was also
observed for the Liberty, Spartan Plus and Protocol alloys in the Fusayama solution, compared to the 0.09% NaCl solution.

Mean values and standard deviations of the ZCP, $I_{\text{CORR}}$, and $R_p$ for all the as-cast alloys are also listed in Table 3.3. No significant differences were found between the mean values of ZCP in the 0.09% NaCl solution for all the alloys using the Kruskal-Wallis test ($P > 0.05$). In the Fusayama solution, because of the lower values of standard deviation, significant differences were found in ZCP between the following pairs of alloys: Liberty and Protocol; Spartan Plus and Legacy; Spartan Plus and Protocol; Freedom Plus and Spartan Plus; Legacy and Protocol ($P = 0.021$). All the as-cast alloys showed significantly higher values of $I_{\text{CORR}}$ in the Fusayama solution compared to the 0.09% NaCl solution ($P = 0.021$). No significant differences ($P > 0.05$) were found between $I_{\text{CORR}}$ for all the as-cast alloys in each medium, using the Kruskal-Wallis test. Likewise, no significant differences were observed for $R_p$ of the as-cast alloys in Fusayama solution. Significant differences were found for $R_p$ between the other four as-cast alloys and Liberty in the 0.09% NaCl solution ($P = 0.021$), where the mean and standard deviation for this alloy had very large values.

For as-cast Liberty (Fig. 3.3) during the forward anodic scan in 0.09% NaCl solution, there was a current density peak above the ZCP at approximately -180 mV (SCE). Following this peak, the current density became almost independent of the potential for the remainder of the forward anodic scan, which is typical for a passive material. In the Fusayama solution, this peak on the forward anodic scan was smaller,
and the current density decreased approximately by half a decade with further increases in potential.

On the forward anodic scan of the cyclic polarization diagram for as-cast Freedom Plus in 0.09% NaCl solution (Fig. 3.4), there was a similar current density peak at about -180 mV (SCE), followed by decreasing current density with increasing potential. A second, smaller peak in current density was observed between 500 and 700 mV. The corresponding cyclic polarization diagram in Fusayama solution showed a similar pattern.

On the forward anodic scan for as-cast Spartan Plus in 0.09% NaCl solution (Fig. 3.5), there was again a current density peak near -200mV (SCE), with further active behavior again shown by a current density peak between +500 to +700 mV (SCE). This latter peak was absent in the Fusayama solution, and the current density for the forward anodic scan was less than that for the 0.09% NaCl solution.

The two Pd-Ga alloys, Legacy and Protocol, also showed similar active-passive behavior in 0.09% NaCl solution during the forward anodic scan, with a primary peak in current density near -200 mV (SCE) and a secondary peak between +600 mV and +900 mV (SCE) (Figs. 3.6 and 3.7). For the forward anodic scan in the Fusayama solution, the current density for Protocol was less than that in the 0.09% NaCl solution, whereas the secondary current density peak for Legacy near +700 mV (SCE) in the saline solution was absent.

3.3.2 Corrosion Behavior of Heat-Treated High-Palladium Alloys

Figures 3.8 and 3.9 show the change in average values of OCP over a 12-hour
period for the five alloys after porcelain-firing heat treatment in the 0.09% NaCl and Fusayama solutions, respectively. Again, a significant decrease (P = 0.021) of between 300-550 mV in the average 12-hour OCP was observed for all the alloys in Fusayama solution, compared to the value in 0.09% NaCl solution (Table 3.4). No significant differences were found in 12-hour OCP for all the heat-treated alloys in 0.09% NaCl solution (P = 0.329), but significant differences were found for OCP in Fusayama solution for the following alloy comparisons: Liberty, Spartan Plus and Protocol; Freedom Plus and Spartan Plus; Freedom Plus and Protocol; Spartan Plus and Legacy. No significant differences were found for 12-hour OCP of each alloy in the as-cast and heat-treated conditions for the same medium except for the Liberty alloy in Fusayama solution (Tables 3.3 and 4.3). Representative cyclic polarization diagrams for each alloy in both the 0.09% NaCl and Fusayama solutions are shown in Figs. 3.10 - 3.15.

Values of average OCP, ZCP and Rp for the heat-treated condition of all the alloys are listed in Table 3.4. From the Kruskal-Wallis test, no significant differences were found between the mean values of ZCP for all the alloys in the 0.09% NaCl solution (P = 0.131). However, with the Fusayama solution, significant differences were found in mean ZCP for the following alloy comparisons: Liberty and Freedom Plus; Liberty and Protocol; Spartan Plus and Protocol. No significant differences were found in ZCP between the two media for any alloy except Spartan Plus. Also, no significant differences were found in ZCP for each alloy in the as-cast and heat-treated conditions for the same medium, except for Spartan Plus in Fusayama solution. There was a significant increase of I_{CORR} in the Fusayama solution, compared to that in the 0.09% NaCl solution for the
heat-treated Liberty, Freedom Plus and Protocol alloys ($P = 0.021$). Significant
differences were also found for $I_{\text{CORR}}$ in 0.09% NaCl solution between all the alloys,
except for comparisons between Freedom Plus and Protocol, and between Spartan Plus
and Legacy. However, no significant differences were found in $I_{\text{CORR}}$ between all the
heat-treated alloys in Fusayama solution ($P = 0.101$). No significant differences were
found for $I_{\text{CORR}}$ of each alloy in the as-cast and heat-treated conditions in the same
medium, except for Spartan Plus and Legacy in 0.09% NaCl solution and Protocol in
Fusayama solution (Tables 3.3 and 3.4). Significantly higher values of $R_p$ were found for
all the heat-treated alloys in Fusayama solution compared to 0.09% NaCl solution, except
for Protocol ($P = 0.021$). Significant differences were also found for $R_p$ and the
following as-cast and heat-treated alloys and media: Liberty and Freedom Plus in 0.09%
NaCl solution; Spartan Plus in both media; Legacy in Fusayama solution.

Heat-treated Liberty showed active behavior in 0.09% NaCl solution for the
potential range of $0$ to $+400$ mV (SCE) (Fig. 3.10), which was not observed with as-cast
Liberty (Fig. 3.3); a current density peak at approximately $-200$ mV (SCE) was again
observed in the forward anodic scan. In Fusayama solution, the current density for the
forward anodic scan was less than that in the 0.09% NaCl solution and increased with
potential beyond $+500$ mV. It is evident from Fig. 3.10 that the current density reduction
in the reverse anodic scan was much smaller in the Fusayama solution than in the 0.09%
NaCl solution.

Heat-treated Freedom Plus (Fig. 3.11) exhibited passive behavior in 0.09% NaCl
solution, with current density becoming almost independent of potential increase above
approximately -100 mV (SCE) in the forward anodic scan. However, dramatic differences were found for this alloy in the Fusayama solution; current densities in the reverse anodic scan were much larger than those in the corresponding forward anodic scan between +1,000 and 0 mV (SCE), producing an anodic loop in the polarization diagram. This was the only alloy and condition that showed such behavior.

Heat-treated Spartan Plus (Fig. 3.12) showed a current density increase between +100 mV and +800 mV (SCE) for the forward anodic scan in 0.09% NaCl solution, as well as the peak near -200 mV seen in the as-cast alloy (Fig. 3.5). The potential range of this former activity was broader than that for the same alloy in as-cast condition. In the Fusayama solution, the current density in the forward anodic scan continued to increase with potential above the ZCP. The shape of the cyclic polarization diagram in Fusayama solution was similar to that of heat-treated Liberty (Fig. 3.10).

The cyclic polarization diagrams for the heat-treated Pd-Ga alloys, Legacy and Protocol (Figs. 3.13 and 3.14) in both the 0.09% NaCl and Fusayama solution were very similar to those for the as-cast alloys (Figs. 3.6 and 3.7).

3.3.3 SEM Examination of Heat-Treated High-Palladium Alloys After Dynamic Polarization

Casting defects, mainly porosities, were observed on all the heat-treated alloy specimens. Greater amounts of larger porosities with evidence of oxidation were observed on the heat-treated Liberty and Spartan Plus specimens. Microstructural
features were poorly revealed with the secondary electron image mode of the SEM on all the heat-treated alloy specimens corroded by dynamic polarization in both the 0.09% NaCl solution and Fusayama solutions. Under the backscattered compositional image mode, however, grain boundaries were partially observed on the heat-treated Liberty specimen, along with secondary grain boundary phases and some needle-shaped Ru-rich phases. Some of these Ru-rich structures were only observed partly above the surface. Grain boundary phases were also found on the surface of heat-treated Freedom Plus specimens. Dendritic microstructures with casting defects mainly in the interdendritic regions were observed for the heat-treated Spartan Plus specimen under backscattered compositional image mode. Specimens prepared in the two media showed similar appearances. For specimens of heat-treated Freedom Plus, Legacy and Protocol, small circular porosities with 1-3 µm diameter were observed on the specimen surfaces. The absence of oxidation layers surrounding these porosities indicated that these were pits produced during the dynamic polarization.

3.4 Discussion

The electrochemical nature of the oral environment has been characterized as having oxidation potentials ranging from -58 to +212 mV (SCE) (Ewers and Greener, 1985). The fact that the values of ZCP in general were 200-400 mV lower than the OCP in both the 0.09% NaCl and Fusayama solutions for all the high-palladium alloys in the as-cast and heat-treated conditions is probably due to the spontaneous passivation of the
high-palladium alloys either after polishing or upon direct immersion in these media (Mezger et al., 1985). In this study, the observed shift from cathodic to anodic current during cyclic polarization over a large potential range instead of a abrupt transition at a single potential can be attributed to inhomogeneous electrode surfaces and varying stability of the electrolyte redox potentials (Bessing et al., 1987). The presence of regions independent of the potential change during the anodic scans can be attributed to either passivity or surface enrichment of palladium, or a combination of both mechanisms (Goehlich and Marek, 1990). Stable passive film formation on all the alloy surfaces is indicated by the large reduction of current density in the reverse scan (hysteresis loop). Such passive films might provide resistance against pitting on these alloys (Mezger et al., 1989). The observed hysteresis loops also suggest that the surface changes that occurred on the alloys during the forward scan are irreversible (Sarkar et al., 1979). The lack of an anodic loop between the forward and reverse potentiodynamic polarization scans for all the alloys in this study, except for heat-treated Freedom Plus in the Fusayama solution, suggests that stable oxide films were formed on the alloy surfaces and that these alloys do not have the potential for crevice corrosion. Based on the compositions of the high-palladium alloys and recent x-ray diffraction studies of these alloys after oxidation heat treatment (Brantley et al., accepted for publication), it is expected that the oxide films formed on the specimen surfaces may consist of Ga₂O₃, In₂O₃, Cu₂O, and even CuGa₂O₄. The current density increase observed for these alloys above +400 mV (SCE) could be related to the Pd/PdCl₄²⁻ equilibrium potential of +380 mV (Mezger et al., 1989).
The much lower values of OCP observed for all the alloys and conditions in Fusayama solution compared to the 0.09% NaCl solution suggests that the former solution might be a more corrosive environment. The $I_{\text{CORR}}$ results for all the alloys also support this consideration, though the $R_p$ results were not conclusive.

It has been previously observed that the Liberty and Spartan Plus alloys undergo dramatic microstructural homogenization after porcelain-firing heat treatment (Carr et al., 1993; Brantley et al., 1993). For Liberty, the near-surface lamellar eutectic microstructures observed in the as-cast condition were almost completely eliminated after the heat treatment. Dendritic microstructures in as-cast Spartan Plus were replaced with a more homogeneous structure having additional new phases. Because of the rapid solidification of the alloys under dental casting conditions (Phillips, 1991), nonequilibrium microstructural phases, microsegregation and residual stress coexist in the as-cast alloy specimens.

It would be reasonable to expect improved corrosion resistance after heat treatment for these alloys because of composition homogenization and residual stress relief. However, the unanticipated results from this study suggest that the heat treatment actually somewhat reduced the corrosion resistance of these alloys in both of the in vitro testing media. For Liberty, the exposed surface for corrosion testing of the four specimens was originally in the middle of the starting cylindrical casting, which should contain much less lamellar eutectic constituent compared to the region near the surface (Carr and Brantley, 1991). The effect of the heat treatment on the eutectic constituent in the surface regions of the corrosion specimen might have been relatively minor, although
some reduction in microsegregation and residual stress is anticipated.

During the reverse cathodic scan between 0 and -600 mV, the current density became almost independent of the potential change for all the high-palladium alloys in both as-cast and heat-treated conditions, except the heat-treated Liberty. This indicates that the oxide films formed on the alloy surfaces during anodic portion of the scan undergo a reduction process and the oxide films formed were relatively thick.

The casting defects (principally porosity) observed on the surface of the corrosion specimens probably played an important role in the limited corrosion activity of the alloys. The observation that the two disk specimens originating from the same parent cylindrical casting of a given alloy behaved more similarly than the two disk specimens from the other cylindrical casting supports this explanation. The greater amounts of casting defects observed on the surfaces of both Liberty and Spartan Plus may explain the more active behavior of these two alloys during the cyclic polarization scan. Both external and internal oxidation have been observed for heat-treated high-palladium alloys (Suoninen and Herø, 1985; Carr et al., 1993; Brantley et al., 1993). However, despite the presence of casting defects on the surface, the heat-treated Liberty and Spartan Plus alloys still exhibited good corrosion resistance comparable to that reported for gold-based alloys (Meyer and Reclaru, 1995).

The small effects of heat treatment on the electrochemical behavior of these high-palladium alloys may therefore be somewhat obscured by casting defects. However, the correlation between microstructural homogeneity and corrosion behavior of dental alloys was previously found to be less than conclusive in a study on a low-gold dental
alloy (Holland et al., 1986), using potentiostatic and potentiodynamic polarization in an artificial saliva. This alloy, when prepared to yield a single-phase microstructure, experienced more corrosion than when the same alloy had a multiple-phase microstructure. However, no explanations were provided regarding the results in that study.

The casting defects on the specimen surfaces are assumed to account for the large variations in the electrochemical parameters measured, although some of these variations may simply be due to the highly sensitive nature of the in vitro corrosion experiment. Most of the previously reported corrosion studies of high-palladium alloys appear to have used only a single specimen, since mean values and standard deviations were not reported for the corrosion parameters.

For the heat-treated Pd-Cu-Ga alloy Freedom Plus, an anodic loop was observed for specimens tested in the Fusayama solution, while the behavior of this alloy in the 0.09% NaCl solution was not substantially changed compared to the as-cast condition. This suggests that there is a tendency for crevice corrosion of heat-treated Freedom Plus in the Fusayama solution. The much lower current density on the forward anodic scan for this alloy in Fusayama solution suggests that a thinner oxide film was formed on the surface, compared to the other high-palladium alloys evaluated. The deaerated environment may prevent the formation of a stable oxide film on the surface of Freedom Plus. The recommendation from the manufacturer (J.F. Jelenko & Co.) for firing dental porcelain on this alloy without any prior oxidation procedure also implies the distinctive oxidation behavior for this alloy. Previous examination of the microstructures of this
alloy in the as-cast and heat-treated conditions indicated that only minimal changes are caused by heat treatment.

The similar electrochemical behavior for the as-cast and heat-treated conditions of the two Pd-Ga alloys is consistent with the minimal microstructural changes observed in these alloys after simulated porcelain-firing heat treatment (Brantley et al., 1993).

3.5 Conclusions

The results from this in vitro corrosion study indicate that representative Pd-Cu-Ga and Pd-Ga dental alloys in both the as-cast and heat-treated conditions show either an active-passive transition or retain passivity under electrochemical conditions similar to the oral environment. The Pd-Cu-Ga alloys Liberty and Spartan Plus alloy became more active in the Fusayama solution after the porcelain-firing heat treatment. However, this change probably arises from the casting defects observed on the test specimens, which may experience internal oxidation during testing. Heat-treated Freedom Plus had an unstable oxide film to form on the surface during anodic polarization and appeared to have a tendency for crevice corrosion in the Fusayama solution.
<table>
<thead>
<tr>
<th>Alloy*</th>
<th>Pd</th>
<th>Cu</th>
<th>Ga</th>
<th>In</th>
<th>Sn</th>
<th>Au</th>
<th>Ag</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liberty†</td>
<td>76</td>
<td>10</td>
<td>5.5</td>
<td>-</td>
<td>6</td>
<td>2</td>
<td>-</td>
<td>Ru</td>
</tr>
<tr>
<td>Freedom Plus†</td>
<td>78</td>
<td>8</td>
<td>5</td>
<td>6</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>Ru</td>
</tr>
<tr>
<td>Spartan Plus‡</td>
<td>79</td>
<td>10</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Legacy‡</td>
<td>85</td>
<td>-</td>
<td>10</td>
<td>1</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>Ru</td>
</tr>
<tr>
<td>Protocol‡</td>
<td>75</td>
<td>-</td>
<td>6</td>
<td>6</td>
<td>-</td>
<td>6</td>
<td>6.5</td>
<td>Ru</td>
</tr>
</tbody>
</table>

*Compositions were provided by the manufacturers.
†Manufactured by J.F. Jelenko & Co., Armonk, NY.
‡Manufactured by Williams Dental Company, Division of Ivoclar North America, Amherst, NY.

Table 3.1—Compositions of the High-Palladium Alloys Selected for Corrosion Study (wt. %).
<table>
<thead>
<tr>
<th>Component</th>
<th>Amount in 500 ml (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$)</td>
<td>0.0008</td>
</tr>
<tr>
<td>Sodium sulfide ($\text{Na}_2\text{S}$)</td>
<td>0.0008</td>
</tr>
<tr>
<td>Mucin</td>
<td>2.0000</td>
</tr>
<tr>
<td>Urea ($\text{CH}_2\text{N}_2\text{O}$)</td>
<td>0.5000</td>
</tr>
<tr>
<td>Sodium phosphate dibasic ($\text{NaH}_2\text{P}_4$)</td>
<td>0.3000</td>
</tr>
<tr>
<td>Calcium chloride ($\text{CaCl}_2$)</td>
<td>0.3000</td>
</tr>
<tr>
<td>Potassium chloride ($\text{KCl}$)</td>
<td>0.2000</td>
</tr>
<tr>
<td>Sodium chloride ($\text{NaCl}$)</td>
<td>0.2000</td>
</tr>
</tbody>
</table>

Table 3.2—Composition of the Fusayama artificial saliva (Fusayama et al., 1963).
Table 3.3—Twelve-hour open-circuit potential (OCP), zero-current potential (ZCP), corrosion current ($I_{\text{CORR}}$) and polarization resistance ($R_p$) of the as-cast high-palladium alloys in deaerated 0.09% NaCl and Fusayama solutions.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Medium</th>
<th>OCP* (mV)</th>
<th>ZCP* (mV)</th>
<th>$I_{\text{CORR}}$ (μA/cm$^2$)</th>
<th>$R_p$* (kΩ·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liberty</td>
<td>0.09% NaCl</td>
<td>104 ± 124</td>
<td>-526 ± 26</td>
<td>0.84 ± 0.65</td>
<td>83.05 ± 141.46</td>
</tr>
<tr>
<td>Fusayama</td>
<td>-448 ± 21</td>
<td>-562 ± 25</td>
<td></td>
<td>13.06 ± 4.00</td>
<td>18.43 ± 7.22</td>
</tr>
<tr>
<td>Freedom Plus</td>
<td>0.09% NaCl</td>
<td>132 ± 140</td>
<td>-509 ± 94</td>
<td>0.43 ± 0.17</td>
<td>4.49 ± 3.07</td>
</tr>
<tr>
<td>Fusayama</td>
<td>-315 ± 143</td>
<td>-531 ± 12</td>
<td></td>
<td>12.2 ± 2.67</td>
<td>-†</td>
</tr>
<tr>
<td>Spartan Plus</td>
<td>0.09% NaCl</td>
<td>147 ± 81</td>
<td>-637 ± 109</td>
<td>1.14 ± 0.63</td>
<td>4.57 ± 2.21</td>
</tr>
<tr>
<td>Fusayama</td>
<td>-330 ± 77</td>
<td>-576 ± 7</td>
<td></td>
<td>12.62 ± 4.46</td>
<td>6.58 ± 2.67</td>
</tr>
<tr>
<td>Legacy</td>
<td>0.09% NaCl</td>
<td>80 ± 81</td>
<td>-471 ± 39</td>
<td>0.29 ± 0.23</td>
<td>5.77 ± 0.18</td>
</tr>
<tr>
<td>Fusayama</td>
<td>-310 ± 108</td>
<td>-545 ± 18</td>
<td></td>
<td>11.11 ± 4.89</td>
<td>6.81 ± 5.25</td>
</tr>
<tr>
<td>Protocol</td>
<td>0.09% NaCl</td>
<td>-34 ± 72</td>
<td>-445 ± 124</td>
<td>1.17 ± 1.72</td>
<td>5.64 ± 2.07</td>
</tr>
<tr>
<td>Fusayama</td>
<td>-176 ± 207</td>
<td>-507 ± 16</td>
<td></td>
<td>11.15 ± 1.24</td>
<td>6.89 ± 1.15</td>
</tr>
</tbody>
</table>

*Entries are mean ± standard deviation (N = 4).
†Not available from the experiment (see text).
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Medium</th>
<th>OCP* (mV)</th>
<th>ZCP* (mV)</th>
<th>$I_{\text{CORR}}$* (mA/cm²)</th>
<th>$R_p$* (kΩ·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liberty</td>
<td>0.09% NaCl</td>
<td>137 ± 50</td>
<td>-626 ± 85</td>
<td>2.12 ± 1.25</td>
<td>6.37 ± 3.37</td>
</tr>
<tr>
<td></td>
<td>Fusayama</td>
<td>-337 ± 45</td>
<td>-520 ± 28</td>
<td>15.93 ± 8.47</td>
<td>17.55 ± 4.63</td>
</tr>
<tr>
<td>Freedom Plus</td>
<td>0.09% NaCl</td>
<td>158 ± 24</td>
<td>-518 ± 114</td>
<td>0.44 ± 0.47</td>
<td>16.12 ± 8.53</td>
</tr>
<tr>
<td></td>
<td>Fusayama</td>
<td>-334 ± 20</td>
<td>-456 ± 41</td>
<td>7.60 ± 3.72</td>
<td>25.5 ± 10.91</td>
</tr>
<tr>
<td>Spartan Plus</td>
<td>0.09% NaCl</td>
<td>132 ± 128</td>
<td>-682 ± 63</td>
<td>13.63 ± 9.23</td>
<td>7.22 ± 0.72</td>
</tr>
<tr>
<td></td>
<td>Fusayama</td>
<td>-225 ± 55</td>
<td>-490 ± 17</td>
<td>11.34 ± 4.37</td>
<td>18.46 ± 3.03</td>
</tr>
<tr>
<td>Legacy</td>
<td>0.09% NaCl</td>
<td>130 ± 67</td>
<td>-567 ± 176</td>
<td>13.14 ± 11.98</td>
<td>9.50 ± 4.97</td>
</tr>
<tr>
<td></td>
<td>Fusayama</td>
<td>-351 ± 52</td>
<td>-465 ± 52</td>
<td>12.23 ± 6.88</td>
<td>31.58 ± 6.73</td>
</tr>
<tr>
<td>Protocol</td>
<td>0.09% NaCl</td>
<td>49 ± 85</td>
<td>-455 ± 176</td>
<td>0.42 ± 0.32</td>
<td>31.77 ± 35.49</td>
</tr>
<tr>
<td></td>
<td>Fusayama</td>
<td>-269 ± 13</td>
<td>-412 ± 24</td>
<td>4.27 ± 2.47</td>
<td>33.44 ± 14.73</td>
</tr>
</tbody>
</table>

*Entries are mean ± standard deviation (N = 4).

Table 3.4—Twelve-hour open-circuit potential (OCP), zero-current potential (ZCP), corrosion current ($I_{\text{CORR}}$) and polarization resistance of the heat-treated high-palladium alloys in deaerated 0.09% NaCl and Fusayama solutions.
Figure 3.1—Average open-circuit potential of as-cast high-palladium alloys in deaerated 0.09% NaCl solution.
Figure 3.2—Average open-circuit potential of as-cast high-palladium alloys in deaerated Fusayama solution.
Figure 3.3—Cyclic polarization diagram of as-cast Liberty.
Figure 3.4—Cyclic polarization diagram of as-cast Freedom Plus.
0.09% NaCl

Fusayama solution

Figure 3.5–Cyclic polarization diagram of as-cast Spartan Plus.
Figure 3.6—Cyclic polarization diagram of as-cast Legacy.
Figure 3.7—Cyclic polarization diagram of as-cast Protocol.
Figure 3.8–Average open-circuit potential of heat-treated high-palladium alloys in deaerated 0.09% NaCl solution.
Figure 3.9—Average open-circuit potential of heat-treated high-palladium alloys in deaerated Fusayama solution.
Figure 3.10—Cyclic polarization diagram of heat-treated Liberty.
Figure 3.11—Cyclic polarization diagram of heat-treated Freedom Plus.
Figure 3.12—Cyclic polarization diagram of heat-treated Spartan Plus.
Figure 3.13—Cyclic polarization diagram of heat-treated Legacy.
Figure 3.14—Cyclic polarization diagram of heat-treated Protocol.
CHAPTER 4

ON THE BIOCOMPATIBILITY OF HIGH-PALLADIUM ALLOYS

4.1 Introduction

In recent years the number of reported cases of allergic contact dermatitis caused by palladium alloys has increased, and a substantial portion of these reports arises from the much greater use of high-palladium alloys in dentistry. High-palladium alloys typically contain over 70 wt.% Pd, and are based upon the Pd-Cu-Ga or Pd-Ga systems. Because of their excellent mechanical properties, good corrosion resistance and much lower cost than traditional gold alloys, high-palladium alloys are in widespread clinical use for metal-ceramic restorations (Böning and Walter, 1990; Carr and Brantley, 1991) and implant-supported prostheses (Stewart et al., 1992). In addition, there have been numerous complaints from patients whose symptoms were believed to be due to psychophysical effects caused by palladium alloys.
4.2 Biocompatibility of Palladium and Palladium Compounds

Palladium and its alloys have been used extensively for a variety of industrial applications (Smith et al., 1978). Consideration of the biocompatibility of palladium would include its toxic, carcinogenic, and immunogenic effects in vivo. However, most of the information about the biocompatibility of palladium has been obtained from in vitro or animal studies. Estler (1992) has recently provided an excellent review of the toxicity of palladium. There are no reports of a toxic effect in humans from the exposure to palladium in industrial processes (Venugopal and Luckey, 1978). Human intake of palladium compounds by subcutaneous injection, topical application, or oral ingestion has not caused acute systemic effects (Smith et al., 1978). Palladium in colloidal Pd(OH)$_2$ form has been given therapeutically, but ineffectively, for the treatment of tuberculosis, gout and obesity (Browning, 1969).

When PdCl$_2$ was administered orally to rats, it was rapidly eliminated within 24 hours, mainly through the gastrointestinal tract; longer-term detectable quantities of palladium were only found in the kidneys and liver. Three days after administration, only 0.4% of the initial PdCl$_2$ dose was retained. Palladium chloride also has a slight diuretic activity in rats (Dodds et al., 1937), and intravenous injections of palladium hydroxide or palladium chloride are rapidly excreted in the urine (Browning, 1969).

In an in vitro study using chicken embryonic tissue explant and mouse fibroblast culture, no cytotoxic effects were found for pure palladium (Kawahara et al., 1968). An investigation of the cytotoxicity of dental alloys and their pure components, using mouse
fibroblasts and succinic dehydrogenase histochemistry assay, revealed that pure palladium (as well as pure gold) were in the least cytotoxic group of metals (Craig and Hanks, 1990).

Several studies have been published on the toxicity of palladium, in which principally the soluble salt PdCl$_2$ was administered to test animals. Substantial differences in the LD$_{50}$ of PdCl$_2$ were found for rats, ranging from 5 mg/kg body weight for intravenous, 70 to over 800 mg/kg body weight for intraperitoneal, and 200 to over 1200 mg/kg body weight for oral administration (Holbrook et al., 1975; Moore et al., 1975). Rapid intravenous injection of PdSO$_4$ to rats at 0.4mg/kg body weight resulted in an immediate cardiovascular effect of ventricular arrhythmia (Wiester, 1975). Injection of the Pd$^{2+}$ ions profoundly disturbed the electrical integrity of the ventricular myocardium, and both PdCl$_2$ and Pd(NO$_3$)$_2$ appeared to have similar effects. The mechanism of cardiovascular toxicity from Pd$^{2+}$ ions was attributed to deleterious effects on energy metabolism of tissues by inhibiting creatine kinase (Liu et al., 1979).

Inhibitory effects of Pd$^{2+}$ ions on enzymes have been observed both in vitro and in animal studies. At a concentration of 2 mmol, PdCl$_2$ was found to inhibit chymotrypsin and trypsin in vitro (Spikes and Hodgson, 1969). Another in vitro study indicated that Pd$^{2+}$ ions interfere with the synthesis of connective tissue macromolecules, collagen and sulfated proteoglycans by inhibiting prolyl hydroxylase, which is a key enzyme in collagen synthesis (Rapaka et al., 1976). A later in vitro study found that Pd$^{2+}$ ions in the concentration range of 0.16-20 mmol had significant inhibitory effects on several metabolically important enzymes, including creatine kinase, aldolase, succinate dehydrogenase, alkaline phosphatase, carbonic anhydrase and prolyl hydroxylase (Liu
et al., 1979). The results suggested that Pd$^{2+}$ ions may interfere with energy metabolism, acid-base and electrolyte equilibria, and bone metabolism. At a concentration of 0.3-0.6 mmol, PdCl$_2$ inhibited *in vitro* DNA synthesis in human thymocytes and peripheral lymphocytes (Nordlind, 1986).

Intraperitoneal injection of Pd(NO$_3$)$_2$ in rats over two days decreased the amount of hepatic microsomal protein (indicative of aminopyrine demethylase function) by one-third for doses of 56 and 113 µmol/kg body weight (Holbrook *et al.*, 1976). At 113 µmol/kg body weight, the hepatic microsomal contents of foreign body-metabolizing enzymes cytochrome P-450 was decreased by one-fifth. Intraperitoneal injection of Pd(NO$_3$)$_2$ at 14-56 µmol/kg body weight in rats affected DNA synthesis in the spleen, liver, kidney and testes by decreasing thymidine incorporation in tissues (Fisher *et al.*, 1975). The enzyme inhibition may be due to the interaction of Pd$^{2+}$ ions with sulfhydryl groups and/or the replacement of other metal ions by Pd$^{2+}$ ions in the active center of the enzyme (Spikes and Hodgson, 1969).

There are only a few published articles on the carcinogenic activity of palladium. When 5 ppm palladium chloride in drinking water was administered from weaning until natural death, growth rates of male and female mice were suppressed (Schroeder and Mitchener, 1971). Both the malignant tumor incidence and the life span of the male mice were increased. Most of the malignant tumors found were of the lymphoma-leukemia type, followed by adenocarcinoma or papillary adenocarcinoma of the lung. Based on these results, palladium was considered to have slight carcinogenic activity in mice.
It has been known for several decades that allergic effects are associated with palladium (Munro-Ashman et al., 1969). It was found with guinea pigs that a high percentage of the animals exposed to PdCl$_2$ reacted to various challenge concentrations of this salt (Wahlberg and Boman, 1990). PdCl$_2$ was considered as a grade III allergen, a more potent sensitizer than NiSO$_4$, in the guinea pig. Many studies have also indicated that palladium chloride is a common sensitizer for humans. The skin patch test has been a common method to test if a human individual is sensitized to a particular substance, such as PdCl$_2$ (Belsito, 1989).

Numerous reports of allergic contact dermatitis or mucositis due to palladium, palladium compounds and palladium alloys have been published (van Ketel and Niebber, 1981; Castelain and Castelain, 1987; Guerra et al., 1988; Camarasa et al., 1989; Downey, 1989; Rebandel and Rudzki, 1990; van Joost and Roesyanto-Mahadi, 1990; Camarasa and Serra-Baldrich, 1990; Camarasa et al., 1991; Hackel et al., 1991). The majority of these cases involved female patients who exhibited positive skin responses to both Pd$^{2+}$ and Ni$^{2+}$ ions. Individuals were generally not allergic to pure palladium, although a patch test might show a positive reaction to PdCl$_2$.

In a clinical study in Germany, patch tests were performed on 486 patients using a 1% PdCl$_2$ solution, in addition to standard allergens, and it was found that 36 patients were allergic to palladium (Augthun et al., 1990); 34 of these 36 patients were also allergic to nickel. Epicutaneous and epimucosal patch tests using pure palladium and a palladium alloy were performed on 18 of the 36 patients in this investigation. In a clinical study involving patch tests of 1,521 patients in four European countries, 42 patients (39 females
and 3 males) showed a positive reaction to PdCl$_2$ (Camarasa et al., 1991), and 39 patients were allergic to both palladium and nickel. It was suggested that palladium sensitizes through the skin as well as through the oral mucosa. In another clinical study involving patch testing of 1,307 patients with both PdCl$_2$ and NiSO$_4$ (de Fine Olivarius and Menne, 1992), 32 patients showed a positive reaction to PdCl$_2$; 29 of those individuals also exhibited a positive reaction to NiSO$_4$. Patch tests using metallic palladium discs were also performed on 470 of the subjects. Three patients showed a positive reaction to the palladium disc, but none was sensitive to PdCl$_2$ or NiSO$_4$. The individuals who showed a positive reaction to PdCl$_2$ could still tolerate skin contact with metallic palladium. In a subsequent study in Austria (Aberer et al., 1993), 1,382 eczema patients were patch-tested with PdCl$_2$, and 115 patients showed a positive reaction. There were 107 patients allergic to both nickel and palladium, while 8 patients reacted to palladium alone. The pattern of the palladium-positive patient population, in terms of age, sex, occupation and location of lesion was similar to that of nickel.

Many studies indicate that people who are allergic to PdCl$_2$ are usually not allergic to pure palladium in a patch test. In a clinical study with 17 subjects (van Loon et al., 1984), patch tests using pure palladium were performed on 12 patients at their buccal mucosa. No patients exhibited a positive response to pure palladium foil, even those with a positive reaction to PdCl$_2$ in their skin patch test. Similar results were also reported in another study where patch tests were performed on 12 patients (Todd and Burrows, 1992). These studies suggest that the Pd$^{2+}$ ion, rather than pure palladium, is the cause of sensitization and allergic reactions. Consequently, the results of solely PdCl$_2$ patch tests in
humans would not be expected to predict whether a person is allergic to palladium dental alloys.

In an animal study of the dermal irritancy of metal compounds (Campbell et al., 1975), PdCl$_2$ was considered non-irritating for intact skin but not for abraded skin without protection. However, lack of a standard preparation in palladium patch testing can be problematic, since use of a patch test with a nonstandard allergen can produce false positive reactions (Fowler, 1990). It is expected that with an increased understanding of the nature of allergic contact dermatitis, realistic alternative strategies for contact allergen identification can be developed that are superior to current methods (Kimber, 1989).

Individuals who show a positive reaction to palladium without a positive reaction to nickel are quite rare. Some recent investigations have indicated that the combined sensitization to both palladium and nickel was unlikely to arise from nickel contamination in the PdCl$_2$ patch test samples (Rebandel and Rudzki, 1990; Eedy et al., 1991). Rather, the similarity in the electronic structures of the palladium and nickel atoms has been suggested as the reason for their cross-sensitivity (Munro-Ashman et al., 1969; Rebandel and Rudzki, 1990). Although the origin for this combined sensitivity in some people is still unknown, the allergic history to nickel for a patient can still serve as a useful guide in the selection of a suitable dental alloy (Augthun et al., 1990). It has been observed that the oral mucosa are more resistant to sensitization compared to the skin (Fisher, 1974). When the skin is the surface originally sensitized, the mucosal membranes may or may not participate in the sensitization on a clinical level. Because of the differences between the skin and the oral
mucosa, different intraoral patch tests have been developed (Moffa et al., 1977; Axéll et al., 1986) to use both keratinized and non-keratinized oral mucosa as the sites of exposure.

4.3 Biocompatibility of High-Palladium Dental Alloys

In general, the biocompatibility of the high-palladium dental alloys should be dependent on the biological activity of the products from in vivo corrosion (Wataha et al., 1991). Research has shown that the microstructures of dental alloys may have a more important role than their compositions in the release of trace amounts of metal ions (Herø and Jørgensen, 1983; Wataha et al., 1991). As with pure palladium and palladium compounds, complete consideration of the biocompatibility of high-palladium alloys would include their toxic, carcinogenic, and immunogenic responses in vivo. No carcinogenic effects have been reported for high-palladium alloys in humans or animals. Current published literature suggests that trace amounts of palladium which might be released in vivo from the high-palladium alloys cannot cause psychophysical problems such as moodiness, listlessness, exhaustion and inability to work (Estler, 1992). However, many published case reports indicate that hypersensitivity to high-palladium alloys could be problematic in certain populations.

In the previously discussed in vitro study of the cytotoxicity of a wide variety of dental alloys and pure components using mouse fibroblasts and succinic dehydrogenase histochemistry (Craig and Hanks, 1990), two of the three high-palladium alloys tested were in the least cytotoxic group of metals along with pure gold and pure palladium, while one of the alloys was ranked as less cytotoxic but still considered acceptable. Although specific
commercial products were not identified in this study, elemental compositions of the alloys were provided. However, the microstructures of the palladium alloys were not shown, nor was any microscopic evidence presented of alloy attack by the cell culture medium or any data provided on the concentrations of ion species undergoing dissolution. In a very recently published study by the same group (Wataha et al., 1995), the cytotoxicity of a series of Pd-Cu model binary solid solution alloys (Subramanian and Laughlin, 1991) was investigated using similar methods. It was found that cytotoxicities of Pd-Cu alloys containing more than 70 wt.% Pd were minimal.

A recent article in the German press (Der Spiegel, 1993) indicated that large numbers of dental patients with palladium alloy crowns had experienced a variety of health problems, such as headaches, joint pains and feelings of exhaustion. In March 1993 a special commission under the auspices of the German Ministry of Health recommended that Pd-Cu based alloys no longer be used in dentistry (The Dentist's Weekly, 1993). Utilization of these palladium alloys in Germany had previously been widespread because of lower metal costs than for gold alloy restorations. This adverse experience has stimulated considerable recent interest in the biocompatibility of the high-palladium alloys.

At present there appears to be no article in the dental scientific literature which comprehensively reports the biocompatibility of palladium alloys. However, it is plausible that, when their microstructures are considered, the Pd-Cu-Ga alloys would be subject to in vivo corrosion and slow ion release. Figures 1 - 4 show that microstructures of two representative Pd-Cu-Ga alloys in the as-cast (bench-cooled) condition without any subsequent heat treatment contain a fine-scale eutectic structure consisting of the palladium
solid solution and a Pd$_2$Ga phase. This lamellar structure can appear as a constituent in a polycrystalline microstructure (Figs. 1 and 2) or as an interdendritic constituent (Figs. 3 and 4), depending upon whether the alloy composition does or does not, respectively, contain a grain-refining element which is typically ruthenium (Brantley et al., 1993).

While quantitative data have not been obtained, from the principles of electrochemical corrosion for dental alloys (Phillips, 1991) it is expected that in this eutectic constituent the Pd$_2$Ga phase would be anodic to the more noble palladium solid solution phase and thus subject to dissolution in the oral environment. The greater electrochemical activity of the Pd$_2$Ga phase (suggesting the potential for in vivo release of palladium and gallium ions) is consistent with the preferential attack of this phase compared to the palladium solid solution (eutectic phase and surrounding matrix phase) during chemical etching of the microstructures (Figs. 2 and 4). The previous discussions suggest the need for some concern about biocompatibility problems associated with palladium release from the Pd$_2$Ga phase. Wataha et al. (1994) recently found that gallium is moderately cytotoxic, from measurements of the succinic dehydrogenase activity of mouse fibroblast cells. Copper in gold alloys has been reported to cause lesions in the oral mucosa (Jobling, 1982), and Wataha et al. (1995) have noted the cytotoxicity of copper in their study of model Pd-Cu alloys. For the Pd-Cu-Ga alloys, copper is expected to be present in the Pd$_2$Ga phase (Brantley et al., 1993), the submicron face-centered tetragonal Pd$_2$Ga$_x$Cu$_{1-x}$ precipitates principally responsible for strengthening these alloys (Odén and Héra, 1986) and the palladium solid solution matrix (Brantley et al., 1993). However, highly important
information on the *in vivo* elution of palladium, copper and gallium from the Pd-Cu-Ga alloys is lacking.

The heat treatment that the Pd-Cu-Ga alloys receive during the porcelain firing cycles largely eliminates the eutectic microstructural constituent (Brantley *et al*., 1993; Carr *et al*., 1993) and should reduce the tendency of these alloys in metal-ceramic restorations to undergo dissolution *in vivo*. On the other hand, potential biocompatibility problems should be increased when Pd-Cu-Ga alloys are used in the as-cast condition without subsequent porcelain firing or other suitable heat treatment, such as typically occurs for all-metal restorations (inlays, crowns and onlays) and implant-supported prostheses.

The eutectic microstructural constituents principally form in the Pd-Cu-Ga alloys because of the effect of copper in shifting the binary Pd-Ga eutectic to alloys of lower gallium content (Cascone, 1984) and the rapid solidification conditions encountered during dental casting (Brantley *et al*., 1993). These near-surface eutectic constituents appear to be largely absent in as-cast Pd-Ga alloys containing indium, although small quantities of complex grain boundary precipitates (Carr and Brantley, 1991) and apparent grain boundary eutectic constituent (Brantley *et al*., 1995a) were observed in the bulk microstructures of two representative alloys, as well as substantial microsegregation (Brantley *et al*., 1993). Cascone (1984) has reported that the behavior of indium in shifting the Pd-Ga eutectic is similar to that for copper in the high-palladium alloys. While Pd-Ga alloys that do not contain substantial amounts of near-surface eutectic microstructural constituent might be expected to have superior *in vivo* corrosion resistance and greater biocompatibility than the Pd-Cu-Ga alloys, further research is necessary to verify this hypothesis. From the
preceding discussions, it would appear prudent to subject both the as-cast Pd-Cu-Ga (Brantley et al., 1995b) and Pd-Ga alloys to an appropriate elevated temperature heat treatment to eliminate any vestiges of eutectic microstructural constituent or microsegregation. Recent research has shown that the near-surface eutectic structure in as-cast fine-grained Pd-Cu-Ga alloys was no longer present after aging at room temperature for five years (Brantley et al., 1995b). Moreover, other recent research on palladium-based dental alloys not exhibiting the lamellar eutectic constituents shown in Figs 1 - 4 have shown that heat treatment of the alloys reduced the passivation range, as well as displaced the onset of passivation to more noble potentials (Manogaran et al., 1995; Vermilyea et al., 1995). This would be expected from the homogenization of the bulk microstructures of these alloys after heat treatment, which was reported previously (Vermilyea et al., 1994).

Although in vitro corrosion has been investigated for model Pd-Cu alloys (Goehlich and Marek, 1990) and for as-cast and heat-treated commercial high-palladium alloys (Mezger et al., 1985; Manogaran et al., 1995; Vermilyea et al., 1995), no published study appears to have examined the relationships between corrosion and microstructure, and provided data on the concentrations of ions released from commercial alloys during corrosion testing. For model Pd-Cu alloys and using atomic absorption spectroscopy, Goehlich and Marek (1990) detected the presence of copper ions but not palladium ions in the medium used for in vitro corrosion testing, whereas Wataha et al. (1991) detected both copper and palladium ions in the cell culture medium to which the alloys were exposed for evaluation of biocompatibility. Studies are underway in our laboratory to obtain this information for representative commercial Pd-Cu-Ga and Pd-Ga alloys of more complex
compositions and microstructures, which appears to be essential for evaluation of their biocompatibility.

4.4 Cellular Mechanisms for Contact Sensitivity to Palladium and Palladium Alloys

Contact sensitivity, clinically characterized in humans by eczematous reaction of the skin at the site of contact with the allergen, is a cell-mediated, delayed allergic reaction (Barnetson and Gawkrodger, 1993). The skin is an integral part of the human immune system. It not only provides sites for antigen entry and antigen-induced destruction, but also contains several kinds of cells that participate in both the induction and eliciting phases of the immune responses. In allergic contact dermatitis the immune response is predominantly an epidermal reaction, where the mononuclear cell infiltration is accompanied by edema of the epidermis with microvesicle formation. The oral mucosa and gingiva are also susceptible to immune hypersensitivity reactions, when in contact with materials that are allergenic. Contact sensitivity of the oral mucosa is termed contact mucositis (Craig, 1993).

Haptens are lipid-soluble, small molecules with one or more reactive groups, and are normally not antigenic. These molecules must penetrate the intact stratum corneum and attach to normal body proteins to become antigenic (Abbas et al., 1994). Most haptens are extremely electrophilic and conjugate to proteins via covalent bonding. It has been suggested that metal ions can behave like haptens and form complexes with carrier proteins through chelating reactions that result in conformational changes of the protein (Dupuis and Benezra, 1982).
4.4.1 Inductive Phase of Contact Dermatitis

The primary immune response to a contact sensitizer has two distinguishable portions: the inductive phase and the eliciting phase (Polak, 1980). The process of sensitization (inductive phase) takes about 10 to 14 days in humans (Barnetson and Gawkrodger, 1993). The antigen recognition starts with antigen processing by the antigen-presenting cells (APC), followed by antigen-bearing APC migration through the lymph vessels to the draining lymph node and antigen presentation to the antigen-specific T cells. The APC are a special group of accessory cells that are required for the initiation of antigen-dependent T lymphocyte activation and proliferation (Cruz and Bergstresser, 1990). The Langerhans cells, which are a normal component of the skin, are the major APC in the immune system of the skin (Kalish, 1991; Abbas et al., 1994), and it has been observed that there is same percentage of Langerhans cells in the buccal mucosa as in the skin (Cruchley et al., 1987). Major histocompatibility (MHC) class II glycoproteins, processed antigens, cell adhesion molecules and co-stimulators of growth are four sets of surface molecules expressed on the APC that are crucial for effective antigen presentation (Harding et al., 1988). Several other cells of non-bone marrow origin, e.g., keratinocytes, fibroblasts and endothelial cells in the skin, may also be induced to express MHC class II molecules and function as antigen-presenting cells, but their antigen-presenting capacity is limited compared to that of Langerhans cells (Geppert and Lipsky, 1989).

Keratinocytes may play an important role in the development of allergic contact dermatitis since they are the major source of cytokines in the epidermis (Kupper, 1990). For instance, large amounts of interleukin-1α (IL-1α) are produced and stored in normal
resting keratinocytes and are released following cell damage (Hauser et al., 1986). IL-1 is known to participate in the activation of T lymphocytes, and is chemotactic for both T cells and neutrophils. Moreover, IL-1 can activate neutrophils, eosinophils, fibroblasts and endothelial cells, and plays an important role in both inflammatory and immune responses in the microenvironment of the skin (Kupper, 1988). In addition to the production of IL-1, keratinocytes also express high affinity IL-1 receptors, which indicates that IL-1 has the capacity of inducing autocrine effects on keratinocytes. IL-1 could activate keratinocytes that synthesize additional cytokines which may be involved in the inflammatory process in allergic contact dermatitis via different mechanisms (Kupper, 1989).

Antigen processing is a modification of an antigen protein molecule from a non-MHC to an MHC-binding form (Cruz and Bergstresser, 1990). The Langerhans cells begin antigen processing by taking up the antigens via endocytosis. Processed antigen fragments are bound to MHC class II molecules and form antigen-MHC (Ag-MHC) complexes which are then transported back to and expressed on the membranes of the Langerhans cell surfaces, to be recognized by T lymphocytes and subsequently activate the cells.

The CD4+ T cells are sensitized by antigen-bearing Langerhans cells at both the skin site of hapten application (peripheral sensitization) and the draining lymph node (central sensitization) (Polak, 1980). It is observed that the Langerhans cells are transformed into dendritic cells as they migrate out of the epidermis into lymphoid organs, where they can present processed antigens efficiently to the antigen-specific T cell clones (Cruz and Bergstresser, 1990). Within 24 hours of antigen application on the skin, antigen-bearing
Langerhans cells migrate to the local lymph nodes. The engagement of the antigen-MHC class II complex on the Langerhans cell surface with the (TCR)-CD3 complex receptor on the CD4+ T cell is primarily responsible for initiating T cell activation. In response, the activated T cells express new surface molecules, secrete lymphokines, proliferate and differentiate.

In lymph nodes, antigen-specific T cells are sensitized in the paracortical area by the migrated Langerhans cells, transformed into immunoblasts, and further differentiated into two different subpopulations: effector or memory cells (Polak, 1980). Memory T cells recirculate between the lymphoid organs and the blood vessels, and store the information of the previous contact with the antigen in the body. Upon a new contact with the same antigen associated with APC at the site of allergen contact, they are able to proliferate and differentiate into a new progeny of sensitized lymphocytes repeating the cycle of inexperienced antigen-specific T cells in an accelerated manner. The effector T cells leave the lymph nodes and enter the lymph and blood circulatory systems. They traverse the capillary endothelium and migrate to the antigen contact area. These cells induce inflammatory response in the site of allergen contact by activating more antigen-specific and non-antigen-specific T cells and other inflammatory cells to infiltrate the area, thereby resulting in allergic contact dermatitis.

4.4.2 Differences Between Skin and Oral Mucosa in Sensitization

The much lower prevalence of contact allergy for the oral mucosa compared to the skin follows from the basic environmental, histological and anatomical differences for the
two tissues (Jobling, 1982; Spiechowicz et al., 1984). The saliva dilutes any antigen present and aids in washing it away; therefore the intensity and duration of exposure for the oral mucosa are decreased. There may be fewer protein conjugates in the oral mucosa than in the skin due to the relative absence of the stratum corneum region (horny layer) where these protein conjugates are hypothesized to reside. The appendages of the skin facilitate antigen absorption. An antigen can penetrate the thin membrane of a hair follicle or the ducts of sweat or sebaceous glands and enter the blood stream. Additionally, the keratinized layer of the skin consists of loose layers of keratotic material and presents weak resistance to penetration, contrary to expectation (Jobling, 1882). This layer is well-developed in the masticatory mucosa (hard palate and gingiva), which in addition has a moderate vascular supply (Ten Kate, 1989). Salivary glycoprotein films that form on mucosal surfaces may act as diffusion barriers (Glantz et al., 1981). Moreover, the vascular system in the skin is different from that of the oral mucosa. In the skin there is an extensive lymphatic network which arises in the papillary layer as blind loops, the walls of which have large pores through which particulate matter enters the system (Nicoll and Cortese, 1972).

4.4 Eliciting Phase of Contact Dermatitis

The eliciting phase of contact sensitivity is defined as a sequence of events which occurs upon application of the specific hapten to a skin area of a hypersensitive individual (Polak, 1980). The initial steps in the eliciting phase are identical to those in the inductive phase. The hapten penetrates the skin and binds to the carrier protein to form the same
hapten-protein conjugate. Memory T cells that formed in the induction phase circulate in the blood and come into contact with the antigen present at the site of hapten application, thereby becoming activated T cells. A series of biological events is initiated by this contact, which results in a local inflammatory reaction. This reaction peaks in 24 to 48 hours after the challenge with the hapten and slowly dissolves over the next few days.

Based upon the understanding of the antigen-recognition process by T lymphocytes at the lymph nodes, the lymphocyte transformation test (LTT) has been used as an in vitro correlate of contact sensitivity in animals and humans (Polak, 1980; Barinetson and Gawkrodger, 1993). However, this test is only applicable for T memory cells. The events in the draining lymph nodes during sensitization can be demonstrated in vitro by the LTT, in which lymphocytes from the spleen, lymph nodes or blood are incubated with or without a specific antigen and pulsed with $^3$H-thymidine at the end of the incubation period. In the presence of the antigen, lymphocytes from hypersensitive individuals undergo transformation into blast cells and exhibit increased DNA synthesis, but the lymphocytes from normal individuals do not. The LTT has proved to be reliable and reproducible when used in animals sensitized with a hapten-carrier conjugate prepared in vitro, but the results were less satisfactory when used in animals sensitized with an unconjugated hapten, e.g., metal ions. This is probably due to the differences between the carriers involved in the sensitization in vitro and those for the elicitation in vivo (Polak, 1980). In a study of palladium contact dermatitis (Camarasa et al., 1991), LTTs were performed on four female patients who showed allergic reactions to both PdCl$_2$ and NiSO$_4$ in their patch tests. The in vitro LTT test with PdCl$_2$ could not confirm the patch test results, while good correlation
was found for Ni\textsuperscript{2+} ion hypersensitivity. In animal studies, a local lymph node assay, where the lymph node cell proliferate was measured \textit{in situ} following the intravenous injection of \textsuperscript{3}H-thymidine after the application of skin allergens to the animal, has been utilized in investigation of allergic sensitization (Kimber, 1989).

The mechanism underlying the migration of the activated T cells is not clear. However, the evidence that signs of epidermal injury and intercellular adhesion molecule-1 (ICAM-1) expression on keratinocytes prior to T cell infiltration to the lesion in poison ivy contact dermatitis (GrifGths and Nickolo, 1989) suggests that the allergen of contact dermatitis may directly, or indirectly through cytokines released by Langerhans cells, induce the release of preformed IL-1\textalpha{} from keratinocytes. It has been shown that Ni\textsuperscript{2+}, which is a common allergen in contact dermatitis, can induce ICAM-1 expression in human keratinocytes (Gueniche \textit{et al}., 1994).

Animal studies have shown that less than 1\% of the T cells in a lesion of allergic contact dermatitis are specific for the relevant antigen (McCluskey \textit{et al}., 1963). Cytokines released by activated T cells can regulate the expression of adhesion molecules on capillary endothelial cells and keratinocytes to facilitate the migration of antigen-specific and non-specific lymphocytes and inflammatory cells to the site of the allergen. These cytokines also induce the gene expression of chemotactic and pro-inflammatory cytokines in keratinocytes and fibroblasts, which then attract and activate more leukocytes and amplify the inflammatory response. Non-antigen-specific T cells and other leukocytes infiltrate into the lesion through interaction with adhesion molecules and the chemotactic

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gradient. The infiltrated cells may release inflammatory factors or be activated at the site of the lesion by contacting the APC and antigen.

The local inflammatory reaction begins to dissolve after 48 to 72 hours, and this behavior may be mediated by several mechanisms. Inhibition of IL-1 production by prostaglandin E produced by macrophages and keratinocytes, binding of T cells to activated keratinocytes and degradation of the hapten-protein conjugate may all contribute to the dissolution (Barnetson and Gawkrodger, 1993).

Many factors determine whether a substance is an allergen to an individual subject. For example, if the chemical species cannot bind to a host protein, it will not be recognized by the Langerhans cell. Alternatively, if the MHC-II molecule of a host does not recognize the hapten-carrier complex, then the series of responses cannot be initiated. There is evidence that reduced Langerhans cell density by ultraviolet (UV-B) light or topical use of steroids decreases the ability of a hapten to induce contact sensitization (Toews et al., 1980; Ashworth et al., 1988). The ability of an allergen to induce the expression of MHC-II on APC or of an adhesion molecule on capillary endothelial cells may also be crucial to the induction of contact dermatitis.

Although it has been well documented that the majority of the allergic contact dermatitis patients are female, the mechanism has not been elucidated. The effects of estrogen on the cytokine production of epithelial cells might relate to this observation (Tabibzadeh et al., 1990). Additionally, the lack of correlation between results from dermal hypersensitivity tests and intraoral hypersensitivity makes identification of intraoral allergens very difficult with the use of conventional dermatological patch testing.
4.5 Conclusion

It can be seen that the relevant effector cells and control mechanisms of allergic contact dermatitis are still not fully understood in general, and minimal scientific information relating to detailed effects of palladium, palladium compounds and palladium alloys is available. Currently, much of the knowledge regarding the mechanisms of contact dermatitis is obtained through animal studies using rodents. It should be realized, however, that there are major differences between the skin immune systems of rodents and humans. Therefore, results obtained in rodents cannot be easily applied to humans (Bos et al., 1989). The foregoing are important areas of oral biology research that are needed to achieve fundamental understanding of the possible relationships between high-palladium dental alloys and contact dermatitis. The preceding discussions suggest future experiments to investigate this matter at the cellular level.
Figure 4.1—SEM photomicrograph (secondary electron image) of the dendritic microstructure of the as-cast Pd-Cu-Ga alloy Spartan. This complex microstructure has been previously described (Brantley et al., 1993). Bar = 10 μm.

Figure 4.2—Higher magnification SEM photomicrograph (SEI image) of the fine-scale interdendritic eutectic constituent in as-cast Spartan (Brantley et al., 1993). The more heavily etched, thin, dark lamellae are the Pd$_2$Ga phase, whereas the thicker, light-appearing lamellae are the palladium solid solution. Bar = 1 μm.
Figure 4.3—SEM photomicrograph (SEI image) of the fine-grained microstructure of the as-cast Pd-Cu-Ga alloy Liberty, illustrating the near-surface eutectic constituent (Brantley et al., 1993). The specimen surface is located beyond the top edge of the photomicrograph. Bar = 10 µm.

Figure 4.4—Higher-magnification SEM photomicrograph (SEI image) of the eutectic constituent in as-cast Liberty (Brantley et al., 1993). As with the very similar eutectic structure in Fig. 2, this two-phase constituent would be expected to undergo some in vivo dissolution relative to the palladium solid solution grains. Bar = 1 µm.
CHAPTER 5

CONCLUSIONS

In this study, TEM was employed to investigate the ultrastructure of four representative commercial high-palladium dental alloys in both the as-cast and simulated porcelain-firing heat-treated conditions. It was expected that the ultrastructural differences would provide answers to the substantial differences in hardness and strength previously observed for the Pd-Cu-Ga and Pd-Ga alloys. However, the results indicated that a tweed ultrastructural (space between striations ~ 20 nm) associated with shear strain on the \{110\} planes in the \langle110\rangle directions of the fcc lattice was the common feature for both the Pd-Cu-Ga and Pd-Ga alloys. An overall band structure (band width ~ 100 nm) was observed to be associated with the tweed structure in both Pd-Cu-Gg alloys and Pd-Ga alloys. The persistence of the tweed ultrastructure in the specimens of the two Pd-Cu-Ga alloys annealed at 1,800°F and subsequently quenched in ice water indicated that the formation of this structure occurs by a rapid martensitic transformation. The transformation from the palladium solid solution into two fct structures may involve only small atomic movements, based on a previously proposed fcc-fct transformation. The formation of a
tweed ultrastructure in these alloys may be associated with the minimization of strain energy arising from the transformation of the fcc palladium solid solution into the two fct phases. The \{100\} and \{110\} forbidden reflections observed on the \langle001\rangle zone of all the high-palladium alloys studied suggested that the fct peritectoid phases are also ordered. The prominent bands observed in the ultrastructures were considered to be antiphase boundaries separating ordered domains of different orientation. It is expected that these very fine-scale tweed structures may undergo coarsening under clinical condition, and the compositional variations in such a coarsened structure might result in galvanic corrosion in the oral environment. However, this transformation may require an extended period of time at mouth temperature.

Potentiostatic/potentiodynamic polarization tests were performed to evaluate the corrosion resistance of five representative commercial high-palladium alloys in both the as-cast and simulated porcelain-firing heat-treated conditions, using two deaerated stagnant electrolytes: 0.09% NaCl and the Fusayama solutions. The deaerated Fusayama solution was considered a more corrosive environment, compared to the 0.09% NaCl solution, based on the results from this study. It was found that the Pd-Cu-Ga and Pd-Ga alloys exhibited similar electrochemical behavior. The somewhat active behavior on the two heat-treated Pd-Cu-Ga alloys, Liberty and Spartan Plus, was attributed to casting defects (principally porosity) in the testing specimens. Heat-treated Freedom Plus had an unstable oxide film to form on the surface during anodic polarization and appeared to have a tendency for crevice corrosion in the Fusayama solution. It was concluded from this \textit{in vitro} study that high-palladium alloys in both the as-cast and heat-treated conditions show either an
active-passive transition or retain passivity under electrochemical conditions similar to the oral environment.

Many adverse effects related to high-palladium alloys have been publicized lately with the widespread use of these alloys for metal-ceramic and all-metal restorations in many countries, especially in Europe. In this literature review study, a systematic summary of published information regarding the biocompatibility of palladium and some palladium compounds was provided, and the current literature on the biocompatibility of high-palladium dental alloys was discussed with emphasis on certain metallurgical and microstructural factors which may have important roles in vivo. Recent research on the immune system responses to foreign substances was also reviewed to provide fundamental information about the complex cellular mechanisms for the hypersensitivity to these alloys.
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