Characterization of the interface of two dental palladium alloys cast on a prefabricated implant gold cylinder

Vasilis K. Vergos, Triantafillos D. Papadopoulos *

Department of Biomaterials, Dental School, National and Kapodistrian University of Athens, Thivon 211527, Athens, Greece

A R T I C L E   I N F O
Article history:
Received 4 August 2008
Received in revised form 1 December 2008
Accepted 13 December 2008
Available online 24 December 2008

Keywords:
Dental alloys
Microstructure
Corrosion
Metallography
Scanning electron microscopy (SEM)

A B S T R A C T

The interface between two dental alloys (Pd–Cu–Ga, Pd–Ga) cast-to a prefabricated gold cylinder in two thicknesses (1, 2 mm) was investigated. Specimens were observed in optical and scanning electron microscopes. Line scan microanalysis by EDS was performed and polarization curves were taken. Gold cylinders shape was preserved. Characteristic elongated grains were detected at the gold cylinder alloy. The boundaries between the cylinder and the cast-to alloys were distinct. The 2 mm thick Pd–Ga alloy cast to the gold cylinder revealed high porosity at the interface, while the rest of the subgroups showed no or negligible porosity. Line scan analysis revealed the gradual diffusion of the main elements of each alloy in the structure of the gold cylinder and vice-versa in a 3–5 µm zone. Corrosion behaviour was estimated by cyclic polarization tests in 1 M lactic acid. The polarization curves showed negative hysteresis. In the reverse anodic scan the current density was less than that for the forward scan. This fact confirms that all the tested materials are not susceptible to corrosion in 1 M lactic acid.

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1. Introduction

In order to fabricate the prosthetic superstructures on osseo-integrated dental implants an alloy (cast-to alloy) is cast on a prefabricated implant gold cylinder (gold cylinder). In this technique the machined wrought structure of the gold cylinder is incorporated in the cast framework, providing precise fitting of the prosthetic superstructure on the implant fixtures. Additionally, precise fitting, gold cylinders offer better mechanical properties to the prosthetic superstructures.

To achieve a complete incorporation between the wrought microstructure of the gold cylinder and the cast-to alloy, it is critical to avoid microstructural changes during laboratory procedures. A crucial factor is the alloy casting temperature, which must be 80–100 °C lower than gold cylinder’s melting temperature [2,3]. Strict evidences of a successful union between the two alloys (cast-to and gold alloy) are preservation of the wrought gold alloy microstructure, controlled elemental diffusion, absence of porosity in the alloy mass and their interface, lack of interfacial reaction regions and well-defined boundaries between cast-to alloy and gold cylinder [4,5].

In the early 1980s high-palladium alloys were introduced in the dental field as an alternative to gold alloys for the fabrication of implant superstructures [6,7]. Alloys containing more than 75%wt palladium are cost-effective and posses good mechanical properties. Two types are available: The Pd–Cu–Ga alloy (1st generation) and the Pd–Ga alloy (2nd generation). They also contain other elements (Au, Pt, Ag, Sn, Ir, In, Ru) in lower concentrations. Because of their complex microstructures, these alloys are more technique sensitive [8,9]. The Pd–Cu–Ga alloy exhibits well-defined grain structure, which contains eutectic or lamellar dendritic constituents. The Pd–Ga alloy exhibits grains with a Pd-rich matrix boundary with fine scale precipitates, without eutectic reaction regions. Despite the absence of Cu, which is responsible for their lower mechanical properties, these alloys are acceptable for clinical use. [10,11].

It has been reported in the literature that thick castings have different microstructure compared to thin castings of the same alloy system [8]. The amounts of eutectic constituents in Pd–Cu–Ga are greater in thin sections or in near-surface portions of a casting. This has been attributed to the different rate of heat flow during solidification between the casting and the much cooler investment [8]. It is known that changes in microstructure lead to changes in mechanical and chemical properties [1,5]. A well documented microstructural change is due to the high affinity between Pd and C contained in some dental investments and crucibles. [12,13]. This interaction between microstructure and different thicknesses of implant superstructures has not been clarified. It would be interesting to investigate possible effects of the use of various cast-to alloys types of different thickness.

Many researchers have underlined the negative effect of corrosion on the clinical performance of the prosthetic superstructures of osseo-integrated dental implants. [14,15]. Especially palladium ion release because of corrosion may be related to biocompatibility,
while composition and structure influence the corrosion resistance of these alloys. In a Pd–Ga alloy increased surface oxidation was observed [16].

The aim of the present study was to characterize the interface between two cast alloys (Pd–Cu–Ga, Pd–Ga) in combination with a prefabricated gold cylinder, when two different cast thicknesses were used, as well as to examine the corrosion behavior of the different interfaces.

The Null hypothesis of the study was that the thickness and/or the type of the cast alloy do not affect the quality of the union between the prefabricated wrought gold cylinder and the cast-to alloy. High corrosion resistance is not expected for all the examined combinations.

2. Materials and methods

Two high-palladium dental alloys, one Pd–Cu–Ga (Mentor P) and the other Pd–Ga alloy (IPSD.SIGN84), were selected as cast-to alloys. A high-gold alloy (IPSD.SIGN98) was also used as control. These alloys were cast-to on the same type of the cast alloy. High corrosion resistance is not expected for all the examined combinations.

For the fabrication of the specimens 12 gold cylinders were waxed using an appropriate hard inlay casting wax (Inlay Wax, Whip Mix Corp, Ky, USA) peripheral-

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Materials tested.</td>
</tr>
<tr>
<td>Commercial name</td>
</tr>
<tr>
<td>Mentor P</td>
</tr>
<tr>
<td>IPSd.SIGN84</td>
</tr>
<tr>
<td>IPSd.SIGN98</td>
</tr>
<tr>
<td>MW-GPC10</td>
</tr>
</tbody>
</table>

Table 2 Composition of the cast-to alloys and the prefabricated gold cylinder (wt%).

<table>
<thead>
<tr>
<th>Elements</th>
<th>MW-GPC10</th>
<th>MENTOR P</th>
<th>IPS d.SIGN84</th>
<th>IPS d.SIGN98</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>60.0</td>
<td>1.4</td>
<td>9.0</td>
<td>85.9</td>
</tr>
<tr>
<td>Platinum</td>
<td>19.0</td>
<td>–</td>
<td>–</td>
<td>12.1</td>
</tr>
<tr>
<td>Silver</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>–</td>
</tr>
<tr>
<td>Palladium</td>
<td>20.0</td>
<td>78.5</td>
<td>75.2</td>
<td>–</td>
</tr>
<tr>
<td>Copper</td>
<td>–</td>
<td>11.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tin</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.5</td>
</tr>
<tr>
<td>Iridium</td>
<td>Balanced</td>
<td>0.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Indium</td>
<td>–</td>
<td>–</td>
<td>6.5</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Gallium</td>
<td>–</td>
<td>8.5</td>
<td>6.0</td>
<td>–</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>–</td>
<td>–</td>
<td>&lt;1.0</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 1. Specimen prepared for optical and scanning electron microscopy.

while composition and structure influence the corrosion resistance of these alloys. In a Pd–Ga alloy increased surface oxidation was observed [16].

and invested in a carbon-free phosphate-bonded investment material (Bellavest T, Bego BGW&Co, Bremen, Germany). Casting followed the manufacturer’s instructions, by melting the alloys in individual ceramic crucibles, using a multiflame gas-oxygen torch and a standard broken-arm centrifugal casting machine (Minitarg, Ugin, Seyssins, France). Each of the three types of alloys mentioned above was used for the production of four castings.

The castings were divested, air-abraded with aluminum oxide particles (50 µm) and embedded in transparent auto-polymerizing epoxy resin (Durafix-2, Struers, Copenhagen, Denmark). After resin polymerization the specimens were sectioned with a diamond disk at low speed under water-cooling, using a microtome (Macro- tome II, Metals Research, Cambridge, UK). Sectioning was performed in a direction parallel to the long axis of the gold cylinder (Fig. 1), followed by grinding with Sic papers under continuous water-cooling up to 2000 grit and polishing with 0.01 µm alumina powders in a grinding-polishing machine (ECOMET III, Buehler, Evanston, IL, USA). The specimens were then cleaned for 10 min in an ultrasonic-bath (Vitasonic II, Vita Zahnfabrik, Bad Sackheim, Germany), using an 70% aqueous ethanol solution and air-dried.

Half of the sectioned specimens were observed in an optical microscope (Eclipse 200, Nikon, Kogaku, Japan) at 10× and 20× magnifications. To reveal the as-cast microstructures, specimens were chemically etched in aqua regia solutions (hydrochloric and nitric acids). Etching times and solution concentrations were adjusted properly for each alloy. The preservation of the cylinder shape, the maintenance of the alloy microstructure, the existence of distinct boundaries between alloys, the absence of oxide layer formation and the possible presence of pores within the interfaces were evaluated.

The other half of the specimens were observed in a scanning electron microscope (Quanta 200, FEI, Hillsboro, Oregon, USA). Line scans, in standard lines across the interface cylinder-cast alloy were received to study changes of element concentrations.
concentrations and possible abrupt diffusion of elements. Microanalysis was made by an Energy-Dispersive X-Ray Spectrometer (EDS, CDU, Saphire EDAX Int, Mawhaw, NJ, USA) with an extra thin beryllium window on secondary electron images (SEI) in high magnifications. Quantitative non standard analysis with ZAF-correction method was applied. The elements studied were palladium, gallium, gold, platinum, silver, copper, tin, iridium, indium and ruthenium.

One representative specimen of every subgroup was prepared for corrosion tests. The specimens were ground until the sprue of the casting was revealed in purpose to make them conductive. Then the upper surface, including the two alloys and their interface, was polished with SiC papers up to 1000 grit, cleaned for 10 min in an ultrasonic bath with distilled water and left to dry. Cyclic polarization measurements were made with a potentiostat (Versa Stat II, EG&G Instruments, Princeton, TN, USA) to evaluate the corrosion behaviour of the tested alloys. The apparatus and the polarization cell conformed to ASTM G5-94 standards. An Ag–AgCl electrode was used as a reference and the platinum plate as an auxiliary counter electrode. A solution of 1 M lactic acid was the irrigating solution, which was heated to 37 °C until the end of the tests. Then, the specimens were placed in the polarization cell for 1 h before initiating polarization. Polarization curves were obtained with a potential scan rate of 5 mV/min.

3. Results

The interface quality observed in the optical microscope revealed that the shape of all the specimens was preserved. Moreover, characteristic microstructure with elongated grains along the longitudinal axis was detected at the cylinder alloy (Fig. 2). The interfaces between the cylinder and the cast-to alloys were distinct in all specimens (Fig. 3). The specimens of subgroup B2 (2 mm thick Pd–Ga alloy cast-to on the gold cylinder) revealed high porosity at the interface, while the rest of the subgroups showed

![Fig. 2](image1.png)

**Fig. 2.** Cross-section of a 1 mm Pd–Cu–Ga cast-to the gold cylinder specimen (subgroup A1) in magnification 10× in optical microscope. A close contact without pores and voids between the two materials was obtained.

![Fig. 3](image2.png)

**Fig. 3.** Cross-section of a 2 mm Pd–Cu–Ga cast-to the gold cylinder specimen (subgroup A2) in magnification 10× in optical microscope. A close contact without pores and voids between the two alloys was obtained.

![Fig. 4](image3.png)

**Fig. 4.** Cross-section of a 2 mm Pd–Ga cast-to the gold cylinder specimen (subgroup B2) in magnification 10× in optical microscope. Extensive porosity between the two alloys was revealed.

![Fig. 5](image4.png)

**Fig. 5.** (a) Line scan image of a 2 mm Pd–Cu–Ga cast-to the gold cylinder specimen (subgroup A2). A gradual decrease of the concentrations of elements is revealed within a 3–4 μm diffusion zone. Randomly located solely medium size pores are present and (b) line scan image of a 2 mm Pd–Ga cast-to the gold cylinder specimen (subgroup B2). A gradual decrease of the concentrations of elements is revealed within a about 4 μm diffusion zone. Medium size pores are present, accompanied by small-sized pores spread all over the diffusion zone.
Fig. 6. (a), (b), (c) Typical cyclic polarization curves from a Pd–Cu–Ga (a), Pd–Ga (b) and a gold alloy (c) specimens immersed in 1 M lactic acid. It can be observed that all the polarization curves showed negative hysteresis, as in the reverse anodic scan the current density was less than that for the forward scan.

4. Discussion

According to the results of the present study, the hypothesis was verified because all groups presented an acceptable behavior, independently of the type of the alloy or the thickness of the specimens used. The hypothesis was not verified only for subgroup B2 (2 mm thick Pd–Ga alloy cast-to on the gold cylinder). Concerning corrosion resistance, the hypothesis was not verified because all examined combinations presented high corrosion resistance.

Carr and Brantley [5] recorded an acceptable metal to metal union with maintenance of cylinder microstructure up to the interface, absence of interfacial reaction regions and lack of porosity created by volatilization of components from Pd alloys during the casting process. Based on the cast interface criteria as proposed by Carr and Brantley [4], the preservation of the cylinder shape, the maintenance of the alloy microstructure, the existence of distinct boundaries between alloys and the possible formation of pores within the interfaces were also recorded in the present study. The extended voids present in subgroup B2 specimens can be attributed to the poor castability of the Pd–Ga binary alloy in combination with the lower heat flow due to the higher thickness of the specimen (2 mm). Carr and Brantley [8] have already reported that the rate of heat flow from the solidifying alloy into the cool investment may play an important role in the microstructure quality of the castings.
Indeed the higher melting temperature of Pd–Ga alloy compared to the other cast-to alloys used, created a higher temperature difference between the solidifying castings and the much cooler investment material. Gilson et al. [17] had early (1965) observed the negative influence of the increasing thickness of the castings in the quality of the union of different dental alloys. This might lead to inferior clinical performance of the implant superstructure.

In the present study the anodic scan revealed gradual elemental concentrations from the bulk mass of the gold cylinder to the bulky mass of the cast-to alloy for both Pd alloys. Diffusion of multiphase alloy systems is complex. It is affected from the lattice type, the melting point of the participating elements and their atomic radius. Better diffusion is observed in the case of same lattice type, while atoms with a lower melting point and similar atomic radius possess a higher diffusion coefficient \((D)\) [18]. In the present study the atomic radius of the participating elements are similar (about 4 Å) and their lattice type is face centered cubic (fcc). Ga possess a low melting point of 296 °C resulting in a better diffusion.

In an elemental spot analysis [5] in seven regions across the interface between the bulk of a gold cylinder (SGC 30) to the bulk of a cast-to Pd–Ga alloy (IS 85), at a total distance of 40 μm, it was found that Ga diffused approximately 14 μm across the interface from the alloy into the cylinder and Pt diffused similarly from the cylinder into the cast alloy. Also in another study [4] the inter-diffusion of Au and Pd over an approximately 20 μm region across the interface between a gold cylinder (DCA 072) and a Pd–Ga alloy (IS 85) exhibited metal to metal bonding. The concentrations of Au and Pd appeared to decrease more gradually over a distance of approximately 10 μm at the interface between the cast-to alloy and the cylinder. The authors reported no apparent differences in the microstructures of thick versus thin sections of castings alloys.

According to the results of the present study, the cyclic polarization curves exhibit negative hysteresis, given that in the reverse anodic scan the current density is lower than that for the forward scan. This fact confirms that all the tested materials are not susceptible to corrosion in 1 M lactic acid. Moreover, although a passive region is observed in the polarization curves concerning the Pd–Ga and Au alloys, a passive region is not present for the Pd–Cu–Ga alloy, as the potential continuously increases following current increase. This fact is probably due to the presence of copper, which deteriorates the corrosion behaviour [19].

5. Conclusions

Under the limitations of the present study the following conclusions can be derived:

There is no significant influence of the type of the cast-to alloys on the cylinder shape, the alloy microstructure, the existence of distinct boundaries between alloys, the absence of oxide layer formation and the presence of pores within the interfaces.

Also the thickness of the cast-to made alloys did not influence significantly the above parameters. The only exception was for the 2 mm thickness Pd–Ga alloy which revealed high porosity at the interface and abrupt elemental transition.

The alloys Pd–Cu–Ga, Pd–Ga and Au are not susceptible to corrosion in 1 M lactic acid.

Acknowledgements

We thank MIS Company for supporting part of the project and Metallurgists Mrs Darabara M. and Spiros Zinelis for helping us in metallurgical analysis and corrosion tests, respectively.

References