Laser weld: microstructure and corrosion study of Ag–Pd–Au–Cu alloy of the dental application

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Abstract

The laser welding process was introduced into dentistry by the end of the 1980s, resulting on a great impulse to that area with the development of cheaper and smaller equipment, using simpler technique. This allowed greater use of that process on the confection of prostheses compared to the brazing process since the heat source for that process is a concentrated light beam of high power, which minimizes distortion problems on the prosthetic pieces. Ag–Pd–Au–Cu alloy used on the confection of dental implant prostheses was observed before and after subjection to the laser welding process. The microstructure was analyzed with the use of optic microscopy and the corrosion resistance was studied by the traditional electrochemical techniques and by electrochemical impedance, under environmental conditions simulating the aggressiveness found in the mouth cavity. A structural change was detected on the weld area, which presented a refined microstructure deriving from the high-speed cooling. The base metal out of the weld area presented a fusion coarse microstructure. The electrochemical essays showed differences on the potentiodynamic polarization behavior in both weld and metal base areas, indicating superior corrosion resistance in the weld area. The impedance spectra were characterized by capacitive distorted components, presenting linear impedance in the low frequencies area.

Keywords: Ag–Pd–Au–Cu; Laser; Corrosion; Dental alloys

1. Introduction

In search for alternative metal alloys for odontological purposes, some researchers have applied the AgPd alloy to substitute the gold alloys, trying to reduce costs and to improve mechanical properties and corrosion resistance [1–4]. Due to some difficulty in obtaining adaptation in prosthetic pieces, mainly the larger ones such as metallic structures molten into one piece, called cast monoblocks, the use of welding is necessary since this technique accepts the work with segments of the prosthesis, which makes possible a balanced force distribution and the best suitable adaptation, occurring in an accurate passive way [4,5].

The process of laser welding produces a coherent, monochromatic, concentrated light beam of high power, and it has been applied to substitute the brazing in odontological prostheses welding.

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great impulse to the area with the development of cheaper and smaller equipment due to its advantages and wide application, which made possible to use welding in a wide variety of metals and prosthetic pieces [6].

The use of electrochemical techniques in the corrosion study is important for the understanding of its performance, biocompatibility and biofunctionality, when clinically applied, for these are constantly exposed to aggressive environments.

This research observes Ag–Pd–Au–Cu alloy microstructure behavior and the material’s resistance to corrosion under environmental conditions simulating the aggressiveness found in the mouth cavity, when used on dental implant prostheses before and after subjected to the laser welding process.

2. Experimental

Table 1 presents the mineral composition of the studied material, using Wave Dispersive Spectroscopy—WDS. The cylindrical test specimens, with 0.27-cm diameter and 1.0-cm length, have been subjected to the welding process on butt joints [7]. The welding machine, Dentaurum DL 20002S, used for the laser welding, uses a crystal Nd:YAG as source of laser, and the beam power was approximately 6.08 kW in 14 ms, originating a welding energy of approximately 85.12 J. The test specimens were manually placed in the chamber, with shield atmosphere of argon, and spots of lap welding, in approximately 2/3 of the surfaces, were applied in the whole section of the joint, with 60% of beam penetration.

A precise disc model 15 HC DIAMOND was used to obtain the test specimens of Ag–Pd–Au–Cu alloy with area comprehending only the welding area, and an ISOMET 1000-BUEHLER machine was used to separate the base metal from the welding area after the laser process. The exposed geometric areas of the welding cord and of the base metal were 0.057 cm². The metallographic analysis of the exposed surface of the base metal and the welding area was done with optic microscopy, after polish with emery cloth from 180 to 1000 mesh, alumina with granulation 1 and 0.3 μm and nitro-muriatic acid application [8]. The work electrodes were prepared from the test specimens used on the metallographic analysis. Measures of open circuit potential versus time were used in the electrochemical essays, as well as potentiodynamic polarization and electrochemical impedance. An electrochemical cell containing NaCl 0.15 mol l⁻¹ (0.9%) airy solution with three electrodes was also used, with the saturated calomel electrode (SCE) as reference system and a graffiti cylinder as auxiliary electrode.

Electrochemical measures of corrosion were done with a potentiometer Solartron SI1287. Potentiodynamic polarization curves were observed at 0.001 V s⁻¹ immediately. Impedance measures were done with the analyzer of frequency response, Solartron 1255, connected to an electrochemical interface, Solartron 1287, and an amplitude of 10 mV was applied to a frequency channel that varied from 100 kHz to 6 MHz, obtaining five points for each frequency decade, controlled by the software Zplot [9]. The software Zview [10] was responsible for the adjustments.

3. Results and discussion

Fig. 1 presents a coarse biphasic fusion microstructure in the base metal area. Fig. 2 illustrates a refined dendritical microstructure in the laser weld area, deriving from the high speedy cooling imposed by the laser weld because of a located fusion process, followed by a quick cooling during the welding, which does not allow the microstructure to return to its initial biphasic structure.

Fig. 3 shows the open circuit potential versus time curves for the base metal and laser weld areas of the Ag–Pd–Au–Cu alloy. The stabilization of the potential was observed 3 h after immersion for both areas, and the laser weld presented a stabilization potential 50 mV higher. Some AgPd alloy researchers have observed that, usually, an alloy open circuit potential increases with the increase of the noble metals concentration [1].

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<th>Au</th>
<th>Ag</th>
<th>Pd</th>
<th>Cu</th>
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<tr>
<td>wt.%</td>
<td>1.25 ± 0.57</td>
<td>64.78 ± 4.35</td>
<td>24.80 ± 2.16</td>
<td>9.16 ± 1.80</td>
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The polarization curves on Fig. 4 present differences on the anodic behavior, with the occurrence of an area corresponding to the first transpassive region close to +0.07 V (SCE) on the laser weld. The numbers obtained for the corrosion potentials, $E_{\text{cor}}$, indicate that the laser weld area presents higher corrosion resistance.

The impedance responses originated in the open circuit potential, obtained in the steady state for the base metal area, present the occurrence of one distorted semicircle at high frequencies (Fig. 5). The equivalent electrical circuit model better adjustable to the characteristics of the resulting spectrum is composed of a parallel association of $R_{TC}$ and CPE, which represents the electrochemical behavior of the interface in the high frequencies area, including only one charge transfer process. In the low frequencies areas, the spectrum is controlled by the occurrence of a straight line, and a new $R_p$ and CPE$_p$ composition was used to represent the formation of a permeable nature interface since this dispersion, observed during the frequency variation, may have been originated from the formation of pits on the surface, thus confirmed by the optic microscopy analysis after the corrosion essays (not showed) and by the significant decrease on the polarization resistance number from around 10 kΩ cm$^2$ to 100 Ω cm$^2$ (Table 2). According to the correspondent impedance diagrams obtained with the Bode format, fair concordance between the experimental and calculated numbers is observed.
The use of one CPE to substitute the double electrical layer is due to a correction of the distortions caused by the uniformity in the current distribution caused by the geometry of the electrode surface [11–13]. A diffusion process represented by a straight line on the complex plane and by the distortion degree, $\alpha \approx 0.5$ (Table 2), is observed at low frequencies.

The laser welded joint area presented two distorted semicircles within the studied frequency channel (Fig. 6). For that reason, an equivalent electrical circuit model with two series RC terms was proposed. On the laser weld, $R_{p2}$ was considerably higher than $R_{p1}$ (Table 3), with the occurrence of a passive nature layer, formed from the corrosion products themselves.

Fig. 6 also presents the corresponding Bode formats. According to the variation of the phase angle

<table>
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<th>Table 2</th>
<th>Fitting of impedance spectra for AgPdCuAu alloy, base metal</th>
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<tr>
<td>$R_d$ (Ω cm$^2$)</td>
<td>$R_{TC}$ (kΩ cm$^2$)</td>
</tr>
<tr>
<td>6.29</td>
<td>11.2</td>
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</table>
versus frequency, the first maximum point is observed close to 20°. Lemaitre et al. [14] have observed that a phase angle of 22.5°, half of 45° (free diffusion of the species in solution), may indicate diffusion due to some specific type of pore, which can be taken into account in this case because of this alloy’s permeable nature.

### 4. Conclusions

The weld area presented refined microstructure, deriving from the high speedy cooling, while the base metal out of the weld area showed a fusion coarse microstructure.

The Ag–Pd–Au–Cu alloy presented high corrosion resistance both for the base metal and for the laser weld areas. AgCl probably forms the passiveness films occurring in both circumstances.

In general, all the areas studied presented linear impedance response at low frequencies, including a non-uniform diffusion.

The Ag–Pd–Au–Cu laser alloy impedance responses were adjusted by an equivalent electrical
circuit model involving two series RC terms with \( R_{p2} \gg R_{p1} \) and the \( R_p \) numbers varied from 10 to \( 10^3 \) \( \Omega \) cm\(^2\).

On the base metal area of the Ag–Pd–Au–Cu alloy, the impedance responses at low frequencies were interpreted from a model that considers the occurrence of a pore layer.

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**References**