Microstructural Features and Corrosion Behaviour of a New Solder Ag-Au-Cu-Pd-Ti Alloy

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A new solder Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy was obtained and characterized. Internal microstructure for casted alloy consists in a dentrite Ag-based solid solution and fine mixture of an eutectic and a compound. Also, small pores were observed. The alloy presented an electrochemical behaviour of passive, stable, resistant metal, belonging to the “Stable” category in corrosion classification. Open circuit potentials (monitored for 1000 h) are placed in the immunity domains of Ag, Au, Cu and Pd and in the passive domain of Ti, characterizing this stable state. Open circuit potential gradients have very low values meaning that galvanic or local corrosion cannot be generated.

Keywords: Ag-Au-Cu-Pd-Ti alloy; dental alloy; corrosion; open circuit potential; polarisation curves

An ideal soldering or welding alloy used in dentistry must have some characteristics as follows: high fluidity for an easy flow in melted state; mechanical characteristics compatible with bonded material; high resistance to corrosion and colour changes.

Certain dental prostheses are made by two or more component parts, being necessary to bond together by soldering or welding at a temperature above 425°C; this is realized using special soldering alloys. Generally, the soldering alloys can be divided in two groups, namely soft and hard soldering alloys [1-3].

The soft soldering alloys include so called plumber-type alloys (eutectic-type Sn-Pb alloys) with lower melting temperature, usually below 260°C. However, because of their poor corrosion resistance these soldering alloys cannot be used in stomatology.

The hard soldering alloys have higher melting temperature, higher mechanical strength and hardness. In stomatology are used two types of hard soldering alloys:
- Au-based alloys, usually used in soldering bridges, crowns, etc [4-6];
- Ag-based alloys, usually used in orthodontic applications [7-11].

Au-based alloys, used in stomatology, contain Au, Ag and Cu and also small quantities of Sn, Zn and Pb which can influence the melting temperature [12-14]. These alloys may also contain different chemical elements in order to influence their physico-mechanical and functional characteristics. The chemical composition of Au-based alloys varies according to specific manufacturer. Usually, the Au content is situated between 45 – 81%, Ag content is between 8 – 30% and Cu content between 7 – 20%. Lower solidus temperatures can be obtained for Au-Cu-Ag-Pd and Au-Ag-Pd-In alloys, between 865 – 875°C.

Ag-based alloys are used both in stomatology and other industrial applications [14]. Mainly, Ag-based alloys are used when it is necessary to bond or weld together parts made by stainless steel. For these alloys, the resistance at colour changes is lower in comparison with Au-based alloys. Concerning mechanical properties, one can observe that both Ag-based alloys and Au-based alloys have almost similar behaviour. Usually, Ag-based alloys contain 10 – 80% Ag, 15 – 30% Cu and 4 – 35% Zn. Other chemical elements, such as Cd, Sn and Pb, can be added in order to control the melting temperature and mechanical characteristics. The melting temperatures for these alloys are situated between 620 – 700°C.

In order to bond or weld alloys that contain titanium [15-18], some particular alloys with melting points close to titanium alloys are necessary; also, these bonding alloys have to present favorable mechanical (hardness, elasticity modulus, elongation, bending resistance), anticorrosive and adhesion properties.

Solder alloys for dentistry have to resist to the aggressivity of the oral fluids that contain [19-29] many ions (Na+, K+, Fe2+, Ca2+, Cl-, Br-, OH-, PO4 3-, HCO3 -), aminoacids, proteins, vitamins, etc. at a variable pH from 3 to 9 value. For instance, a pH = 2 – 3 appears in traumatic tissues [30] as well as due to the non-uniformities in saliva composition and pH along the dental work [31-36]. In case of infections, the pH increases till to 9 value [37], whereas after a meal or drink, the pH has the value 5. The normal saliva has pH = 7.4 – 8.

The aim of the work is to present data concerning synthesis and structural features for a new solder Ag-Au-Cu-Pd-Ti alloy and its corrosion resistance in Carter-Brugirard artificial saliva un-doped and doped with fluoride ions at different pH values, simulating various functional conditions.

Experimental part
The alloy was prepared in an EMA-TEC-LEYBOLD HERAEUS electrical induction melting furnace type EMA-

<table>
<thead>
<tr>
<th>Table 1: CHEMICAL COMPOSITION OF PREPARED ALLOY</th>
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<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>---------</td>
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<tr>
<td>Concentration (wt%)</td>
</tr>
</tbody>
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MFAS 40, under normal atmosphere. The synthesis was performed in two steps. In the first step a Pd-Ti pre-alloy was obtained which supplied the concentration of Pd and Ti in the final alloy. In the second step the Pd-Ti pre-alloy was melted together with Ag, Au and Cu. After melting the alloy was casted in a cylindrical graphite die.

The obtained composition for the final alloy is presented in Table 1.

Microstructural futures were investigated using an electron scanning microscope TESCAN Vega II – XMU equipped with a BSE detector.

For electrochemical experiments, the paralelipipical electrodes were polished with metallographic paper of different granulations, fixed in a Steri-Makrides hold system, rinsed with distilled water, degreased in boiling benzene and dried.

All electrochemical measurements were carried out in the nondoped and fluoride ion doped saliva:
- artificial Carter-Brugirard saliva of $pH = 2.46$ and $pH = 5.4$ (both obtained by HCl addition), $pH = 7.89$ (normal $pH$), $pH = 8.96$ (obtained by KOH addition); the Carter-Brugirard saliva composition is (g/L): NaCl – 0.7; KH$_2$PO$_4$ – 0.26; KSCN – 0.33; Na$_2$HPO$_4$ – 0.19; urea – 0.13; NaHCO$_3$ – 1.5;
- artificial doped Carter-Brugirard saliva (containing 0.05M NaF like in the products of oral hygiene) of $pH = 2.54$ and $pH = 5.52$ (both obtained by HCl addition), $pH = 8.21$ (normal $pH$), $pH = 8.81$ (obtained by KOH addition).

In all experiments the temperature was kept at 37°C ± 1°C.

The following electrochemical techniques were used: cyclic potentiodynamic and linear polarization, monitoring of the open circuit potentials as well as of the corresponding open circuit potential gradients.

Potentiodynamic polarization was performed starting from −0.5V to +1.2V with a scan rate of 2mV/sec using a Voltalab 80 equipment with a Voltamaster 4 program for corrosion data analysis. The main electrochemical parameters were determined: $E_{corr}$ – corrosion potential like zero current potential; $E_p$ – passivation potential; $E_b$ – breakdown (pitting) potential when the current density increases sharply; $E_p$ – pitting protection potential at which the current density on the negative sweep equals the passive current density; $E_T$ – transpassive potential; $E_{corr}$ – potential range of passivation; $E_{b}$ – $E_{pp}$ difference, representing the pitting corrosion resistance (low values mean that the pitt repassivation takes place very easy and quickly); $E_{corr}$ – $E_{pr}$ difference, that characterizes tendency to pitting corrosion (high values represent a reduced tendency); $i_{corr}$ – passive current density. In the opposite case, the reverse curve presents lower currents than the direct curve, it results a very stable passive state. If the reverse curve shows higher currents than the direct curve, pitting corrosion exists.

The linear polarization was applied for ±200 mV around the open circuit potential and corrosion current density, $i_{corr}$ was obtained; then, the corrosion rates, $V_{corr}$ were calculated.

The monitoring of the open circuit potential, $E_{corr}$ (in saliva. A Hewlett-Packard instrument was used.

The open circuit potential gradients that could appear due to the non-uniformity of either saliva, $pH$, $\Delta E_{corr} (pH)$, or composition, $\Delta E_{corr} (c)$, were simulated, calculated and monitored for 1000 hours. Values of the following differences were discussed:

\[
\Delta E_{corr} (pH) = E_{corr}^{pH+2.46} - E_{corr}^{pH+5.4}
\]
\[
\Delta E_{corr} (pH) = E_{corr}^{pH+2.46} - E_{corr}^{pH+7.75}
\]
\[
\Delta E_{corr} (pH) = E_{corr}^{pH+5.54} - E_{corr}^{pH+7.75}
\]
\[
\Delta E_{corr} (pH) = E_{corr}^{NaF+0.52} - E_{corr}^{NaF+0.82}
\]
\[
\Delta E_{corr} (pH) = E_{corr}^{pH+7.75} - E_{corr}^{pH+8.21}
\]

Results and discussion

Microstructural properties

As shown in figure 1 one can observe a general dendrite microstructural aspect of Ag-Au-Cu-Pd-Ti alloy. From these micrographs four structural features can be identified: Ag solid solution (1); pores (2); probable eutectic phases (3); probable compounds (4).

Because Ag can form solid solutions with almost all other alloying elements, it is necessary to make EDX and/or WDX investigations in order to identify the specific formed eutectic phases. Also, owing to dendrite segregation the locally specific chemical compositions are favourable to form specific compounds such as: TiAg; Au; Pd; AuPd; TiPd; TiCu; these compounds can also be identified by EDX and/or WDX investigations.

Concerning mechanical properties of the casted Ag-Au-Cu-Pd-Ti alloy, we mention that good results were obtained, meaning that this solder alloy can be used in dentistry.

Corrosion behaviour evidenced from polarization curves

In Carter-Brugirard saliva of $pH = 2.5$, the cyclic polarization curves (fig. 2) show a behaviour of passive metal for Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy. The corrosion potential, $E_{corr}$ (table 2) has noble values placed in the same immunity and passive domains of the constituent elements. The potential domain of passivation, $\Delta E_{corr}$ in this medium is placed in the same immunity and passive domains of the constituent elements. The potential domain of passivation, $\Delta E_{corr}$ is large, around 1.2 V, being very favourable for a good resistance to corrosion. The passive current density in the interest potential domain (0.1 V ÷ +0.5 V) for oral environment is relatively low (3.9 mA/cm$^2$, respectively 6.1 mA/cm$^2$), denoting a relative good corrosion resistance.

In Carter-Brugirard saliva of $pH = 5.4$ some changes appear in the behaviour of the Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy because the corrosion potentials in doped saliva have little more negative values than in $pH = 2.5$ (table 2). Of course, in Pourbaix diagrams, Ag, Au, Cu and Pd are still placed in the immunity state and Ti in the passive state. Cyclic polarisation curves (fig. 3) revealed the same passive behaviour with relative low current densities of passivation, characterizing a relative good resistance to corrosion both for un-doped and doped Carter-Brugirard salivas.

In Carter-Brugirard saliva of $pH = 8$, this saliva being a normal saliva that frequently exists in oral cavity, the Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy presented also behaviour of a passive metal (fig. 4) although the corrosion potentials in fluoride ions containing saliva are most electropositive. However, the positions in Pourbaix diagrams remain in the immunity domains of Ag, Au, Cu and Pd and in the passivity domain of Ti (table 2). The passive current densities are relative low in these cases. Consequently, the alloy is stable, resistant in un-doped Carter-Brugirard saliva.
We mention that in Carter-Brugirard saliva doped with 0.05M NaF, the pitting corrosion was registered; the breakdown potential, \( E_b \), has an electropositive value (+0.79 V), a value that cannot be reached in oral cavity [39-41]. The pitting protection potential, pit repassivation potential \( E_{pp} \) (under its value no pit can be initiated) presents a favourable value of +0.69 V, that also cannot be reached in oral fluid (table 2). Moreover, \( E_b - E_{pp} \) difference, representing the pitting corrosion resistance, has a low value, meaning that the pit repassivation takes place in a very narrow potential range, very easily and very quickly. Regarding the tendency to pitting corrosion, the value of \( |E_{corr} - E_b| \) difference is high, showing a very reduced tendency to pitting corrosion. Thus, we consider that the Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy cannot develop pitting corrosion in Carter-Brugirard saliva doped with 0.05M NaF, at \( p\text{H} \approx 8 \).

In Carter-Brugirard saliva of \( p\text{H} \approx 9 \), an alkaline medium that can accidentally appear in the oral cavity, the same behaviour of passive metal (fig. 5) results due to the more electronegative corrosion potentials. The positions in Pourbaix diagrams, in the same immunity domains of Ag, Au, Cu and Pd and the passivity domain of Ti (table 2) lead to relative reduced current densities of passivation.

The pitting corrosion appeared both in un-doped and doped alkaline Carter-Brugirard saliva only at very electropositive values of +0.95 V and +0.84 V, respectively, but these values cannot be reached in the oral biofluid [40,41]. All other pitting parameters (table 2) have favourable values; pitting protection potential \( E_{pp} \), has very electropositive values (+0.8 V and +0.78 V, respectively); the pitting corrosion resistance is high and the tendency to pitting corrosion is low, showing that it is not possible to appear this type of local corrosion, even in extreme functional conditions of alkaline \( p\text{H} \).
From linear polarisation (Tafel) curves it resulted low corrosion rates in "Stable" category of corrosion classification and low ion release (table 3). The case of nondoped saliva at $pH \approx 2.5$ corresponds to "Very Stable" type (VS symbolized). In fluoride ion doped saliva, the ion releases have higher values than in un-doped saliva due to aggressiveness of this medium.

Taking into account that, the Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy is used in store teeth for soldering and welding in very little narrow and hidden zones, but in contact with saliva, this alloy can be considered very good as solder alloy in dentistry.

**Corrosion behaviour from the monitoring of the open circuit potentials**

The open circuit potentials in the un-doped Carter-Brugirard salivas of $pH = 2.46$, 5.4 and 7.89 (fig. 6) became more electronegative in the first 300 – 400 exposure hours, due to a slow corrosion processes of the constituent phases (solid solutions or compounds). In a prolonged exposure, they tended to more electropositive values.

The presence of the fluoride ion in saliva generated more active values of the open circuit potentials at $pH \approx 5.4$ (fig. 7) and $pH = 8$ (fig. 8) due to its higher aggressiveness. However, all values of $E_{oc}$ are placed in the immunity domains of Ag, Au, Cu and Pd and in the passive domain of Ti, characterizing a stable, resistant state of investigated alloy.

Also, no local corrosion was observed for 1000 exposure hours.

From monitoring of the open circuit potential gradients in some moments during 1000 exposure hours in un-doped saliva, (table 4) it resulted very low values of these gradients (from 0.004 V to 0.241 V), under the limit of 0.6 – 0.7 V. This

<table>
<thead>
<tr>
<th>$pH$</th>
<th>$i_{cor}$ ($\mu A/cm^2$)</th>
<th>$v_{cor}$ (mm/ann)</th>
<th>Category</th>
<th>Ion release (ng/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\approx 2.5$</td>
<td>0.22</td>
<td>72.6</td>
<td>VS</td>
<td>7376</td>
</tr>
<tr>
<td>$\approx 2.5 + NaF$</td>
<td>2.71</td>
<td>89.18</td>
<td>S</td>
<td>9060</td>
</tr>
<tr>
<td>$\approx 5.4$</td>
<td>2.26</td>
<td>74.31</td>
<td>S</td>
<td>7550</td>
</tr>
<tr>
<td>$\approx 5.4 + NaF$</td>
<td>2.72</td>
<td>89.55</td>
<td>S</td>
<td>9908</td>
</tr>
<tr>
<td>$\approx 8$</td>
<td>0.37</td>
<td>12.08</td>
<td>S</td>
<td>1227</td>
</tr>
<tr>
<td>$\approx 8 + NaF$</td>
<td>2.79</td>
<td>91.54</td>
<td>S</td>
<td>9300</td>
</tr>
<tr>
<td>$\approx 9$</td>
<td>1.53</td>
<td>50.18</td>
<td>S</td>
<td>5998</td>
</tr>
<tr>
<td>$\approx 9 + NaF$</td>
<td>2.42</td>
<td>79.67</td>
<td>S</td>
<td>8094</td>
</tr>
</tbody>
</table>

VS – Very Stable; S – Stable

![Fig. 6. Values of open circuit potentials for Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy in un-doped Carter-Brugirard saliva of different $pH$ values](image)

![Fig. 7. Comparison of open circuit potentials for Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy in un-doped and fluoride ion doped (with 0.05M NaF) Carter-Brugirard saliva of $pH = 5.4$](image)
leads to the conclusion that either galvanic or local corrosion cannot be generated [42-44].

Conclusions

The microstructure of new prepared Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti solder alloy consists in a large dendrite Ag solid solution, in interdendritic spaces other two constituents were observed: an eutectic and a compound; also, fine pores were observed inside microstructure.

The alloy presented an electrochemical behaviour of passive and stable metal in Carter-Brugirard saliva both for undoped and doped with 0.05M NaF, at different pH values simulating extreme functional conditions.

Low corrosion rates lead to framing this alloy in “Stable” category.

The open circuit potentials (monitored for 1000 h) are placed in the immunity domains of Ag, Au, Cu and Pd and in the passive domain of Ti.

The open circuit potential gradients have very low values showing that a galvanic or local corrosion cannot be generated.

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References


Fig. 8. Comparison of open circuit potentials for Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti alloy in undoped and fluoride ion doped (with 0.05M NaF) Carter-Brugirard saliva of: pH = 8

Table 4

OPEN CIRCUIT POTENTIAL GRADIENTS FOR Ag-8.8Au-7.6Cu-7.4Pd-1.3Ti ALLOY IN CARTER- BRUGIRARD SALIVA, LA 37°C

<table>
<thead>
<tr>
<th>Gradient (mV)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔEaux(pH)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>+0.051</td>
</tr>
<tr>
<td>ΔEaux(pH)</td>
<td>+0.065</td>
</tr>
<tr>
<td>ΔEaux(pH)</td>
<td>+0.015</td>
</tr>
<tr>
<td>ΔEaux(pH)</td>
<td>+0.004</td>
</tr>
<tr>
<td>ΔEaux(c)</td>
<td>+0.060</td>
</tr>
<tr>
<td>ΔEaux(c)</td>
<td>-0.010</td>
</tr>
</tbody>
</table>

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